# PLATINUM GROUP METAL COMPLEXES OF PYRIDYL- AND ANILINYLDIPHOSPHINE LIGANDS 

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#### Abstract

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#### Abstract

This thesis describes the synthesis, structure, solution behaviour, reactivity and catalytic properties of a collection of platinum metal complexes coordinated by pyridyl- or anilinyldiphosphine ligands; the ligands have the general formula $\operatorname{Ar}_{2} \mathrm{P}(\mathrm{Z}) \mathrm{PAr}_{2}$ (for $\mathrm{Ar}=$ $o-\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{NMe}_{2}, \mathrm{Z}=\mathrm{CH}_{2}$ (dmapm), $\left(\mathrm{CH}_{2}\right)_{2}$ (dmape), cyclic- $\mathrm{C}_{5} \mathrm{H}_{8}$ (dmapcp); for $\mathrm{Ar}=o$-py, $\mathrm{Z}=\left(\mathrm{CH}_{2}\right)_{2}$ (dpype), cyclic- $\mathrm{C}_{5} \mathrm{H}_{8}($ dpypcp $) ;$ py $=$ pyridyl $)$.  dmapm  dmape  dmapcp  dpype  dpypcp


The ligands are made in 33-55 \% yield by the low temperature reaction of $\mathrm{Cl}_{2} \mathrm{P}(\mathrm{Z}) \mathrm{PCl}_{2}$ in $\mathrm{Et}_{2} \mathrm{O}$ with 4 equiv. of 2-lithiopyridine or 2-lithio- $N, N$-dimethylaniline generated in situ from the appropriate 2 -bromoarene and ${ }^{n} \mathrm{BuLi}$. Dmape and dmapcp are characterised crystallographically.

The number of C -atoms in the "bridge" connecting the P -atoms in an anilinyldiphosphine ligand determines the coordination mode with $\mathrm{M}^{\mathrm{II}}$ halides ( $\mathrm{M}=\mathrm{Pd}$, $\mathrm{Pt}):$ dmapcp gives solely $\left[\mathrm{MX}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{X}$; dmape establishes in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ the equilibrium $\mathrm{MX}_{2}\left(P, P^{\prime}\right.$-dmape $) \rightleftharpoons\left[\mathrm{MX}\left(P, P^{\prime}, N\right.\right.$-dmapcp) $] \mathrm{X}(\mathrm{I})$ (for $\mathrm{M}=\mathrm{Pd}$ and $\mathrm{X}=$ $\mathrm{Cl}, \Delta \mathrm{H}^{\circ}=-11 \pm 7 \mathrm{~kJ} \mathrm{~mol}^{-1}, \Delta \mathrm{~S}^{\circ}=-60 \pm 20 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$; for $\mathrm{M}=\mathrm{Pt}$ and $\mathrm{X}=\mathrm{Cl}, \Delta \mathrm{H}^{\circ}=-$ $\left.19 \pm 4 \mathrm{~kJ} \mathrm{~mol}^{-1}, \Delta \mathrm{~S}^{\circ}=-100 \pm 30 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}\right)$; dmapm gives $\mathrm{PdX}_{2}\left(P, P^{\prime}-\mathrm{dmapm}\right) \rightleftharpoons$ $\mathrm{PdX}_{2}\left(P, N\right.$-dmapm) (II) (for $\mathrm{X}=\mathrm{Cl}, \Delta \mathrm{H}^{\circ}=-5.5 \pm 0.5 \mathrm{~kJ} \mathrm{~mol}^{-1}, \Delta \mathrm{~S}^{\circ}=-10 \pm 1 \mathrm{~J} \mathrm{~K}^{-1}$ $\mathrm{mol}^{-1}$ ), and solely $\mathrm{PtX}_{2}\left(P, P^{\prime}-\mathrm{dmapm}\right) . \mathrm{PtCl}_{2}\left(P, P^{\prime}-\right.$ dmape $),\left[\mathrm{PtCl}\left(P, P^{\prime}, N-\mathrm{dmapcp}\right)\right] \mathrm{Cl}$ and $\mathrm{PdCl}_{2}(P, N$-dmapm) are characterised crystallographically. The 4-membered ring strain associated with the last complex is $c a .32 \mathrm{~kJ} \mathrm{~mol}^{-1} .\left[\mathrm{MCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl}$ complexes are formed stereoselectively, and exhibit slow exchange of coordinated and free anilinyl N -atoms.


I

II
(In I-VIII, Ar $=o-\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{NMe}_{2}$ )

The $\mathrm{PdCl}_{2}$ (dmape) system reacts with KOH followed by $\mathrm{KPF}_{6}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{H}_{2} \mathrm{O}$ to form $[\mathrm{PdCl}(\mathrm{dmapeO})]_{2}\left[\mathrm{PF}_{6}\right]_{2}$ (III) which is structurally characterised and possesses a PdPd separation of $4.873 \AA$.

In reactions of $\mathrm{PdX}_{2}$ (diolefin) (diolefin $=\operatorname{cod}$, nbd) with dmapcp and dmapm, long-lived, presumed trigonal bipyramidal intermediates are formed in which the coordinated olefin has undergone nucleophilic attack by either the P - (IV) or the N -atom (V) of the anilinyldiphosphine ligand.


III


IV


V
$\mathrm{PdCl}_{2}\left(P, N\right.$-dmapm) reacts with peroxides and with sulphur to form $\mathrm{PdCl}_{2}(P, N-$ dmapmO) and $[\mathrm{PdCl}(P, N, S$-dmapmS $)] \mathrm{Cl}$ (VI), respectively, and with trans$\mathrm{PdCl}_{2}(\mathrm{PhCN})_{2}, \mathrm{~K}_{2} \mathrm{PtCl}_{4}$ and $1 / 2\left[\mathrm{Rh}(\mu-\mathrm{Cl})(\mathrm{CO})_{2}\right]_{2}$ to form the phosphine-bridged bimetallic complexes $\mathrm{PdCl}_{2} \mathrm{M}(\mathrm{X})(\mathrm{Y})(\mathrm{dmapm})(\mathrm{VII})(\mathrm{M}=\mathrm{Pd}, \mathrm{X}=\mathrm{Y}=\mathrm{Cl} ; \mathrm{M}=\mathrm{Pt}, \mathrm{X}=\mathrm{Y}$ $=\mathrm{Cl} ; \mathrm{M}=\mathrm{Rh}, \mathrm{X}=\mathrm{Cl}, \mathrm{Y}=\mathrm{CO}$, respectively). The $\mathrm{Pd}_{2}$ and PtPd bimetallic complexes catalyse effectively the Heck coupling of iodobenzene and styrene under air in DMF/ $\mathrm{H}_{2} \mathrm{O}$ solution to give predominantly trans-stilbene; the catalyst precursor eventually
decomposes by phosphine oxidation and via an equilibrium-controlled splitting into monometallic species. A generally applicable index of cooperativity for polymetallic catalysts is proposed.

Conproportionation of $\mathrm{PdCl}_{2}\left(P, N\right.$-dmapm) and $\mathrm{Pd}_{2}(\mathrm{dba})_{3}$ gives the metal-metal bonded complex $\mathrm{Pd}_{2} \mathrm{Cl}_{2}$ (dmapm) (VIII, $\mathrm{M}=\mathrm{Pd}$ ) which is structurally characterised and possesses a very short ( $2.527 \AA$ ) Pd - Pd bond. The mixed-metal analogue (VIII, $\mathrm{M}=\mathrm{Pt}$ ) is made by reducing $\mathrm{PtPdCl}_{4}(\mathrm{dmapm})$ with ethanolic KOH . These complexes react with CO and diethylacetylene dicarboxylate to give bridged species which are stable in the $\mathrm{Pd}_{2}$ case, but disproportionate in the PtPd case to Pd metal and $\mathrm{PtCl}_{2}\left(P, P^{\prime}-\mathrm{dmapm}\right)$.


VI


VII


VIII

The pyridyldiphosphine ligands $\mathrm{P}-\mathrm{P}$ react with $\mathrm{M}^{\mathrm{II}}$ halo precursors to give exclusively the $P, P^{\prime}$-bonded species $\mathrm{MX}_{2}(\mathrm{P}-\mathrm{P})$ and $\left[\mathrm{M}(\mathrm{P}-\mathrm{P})_{2}\right] \mathrm{X}_{2}$, depending on the M to $\mathrm{P}-\mathrm{P}$ ratio. Unlike the anilinyldiphosphines which do not react, $1: 1$ combinations of $\mathrm{P}-\mathrm{P}$ and $\mathrm{M}\left(\mathrm{PPh}_{3}\right)_{4}$ give $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}(\mathrm{P}-\mathrm{P})$ and $\mathrm{Pd}(\mathrm{P}-\mathrm{P})_{2}$; these complexes react with the electron deficient olefins dimethyl- and diethylmaleate and the corresponding fumarates to form $\operatorname{Pt}\left(\eta^{2}\right.$-olefin) $(\mathrm{P}-\mathrm{P})$ (which do not catalyse olefin isomerisation), and with $\mathrm{CDCl}_{3}$ to form $\left[\mathrm{PtCl}\left(\mathrm{PPh}_{3}\right)(\mathrm{P}-\mathrm{P})\right]^{+} . \mathrm{Pt}\left(\eta^{2}\right.$-dimethylfumarate) $($ dpypcp $)$ is structurally characterised.

Several water-soluble complexes are assayed as catalyst precursors for the homogeneous, aqueous-phase hydration of maleic acid to form malic acid; the most active compound, $[\mathrm{PdCl}(P, N, S$-dmapmS $)] \mathrm{Cl}$, gives only 8 turnovers in 24 h at $100^{\circ} \mathrm{C}$.

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## List of Abbreviations and Symbols

| Anal. | Analysis |
| :---: | :---: |
| aq. | Aqueous |
| Ar | Aromatic, aryl |
| av. | Average |
| $\mathrm{BDDP}_{\mathrm{DS}}$ | 1,3-Bis(diphenylphosphino)propane disulphonate |
| BINAP | 2,2'-bis(diphenylphosphino)-1,1'-dinaphthyl |
| BINAPO | 2,2'-bis(diphenylphosphino)-1,1'-dinaphthyl monooxide |
| bipy | 2,2'-Bipyridine |
| BPMO | Bis(phosphine)monooxide |
| br | Broad |
| ${ }^{n} \mathrm{Bu}$ | Normal-butyl |
| Calcd | Calculated |
| cod | 1,5-cyclooctadiene |
| COSY | Correlation NMR spectroscopy |
| Cp | Cyclopentadienyl |
| Cp* | Pentamethylcyclopentadienyl |
| Cy | Cyclohexyl |
| d | Doublet |
| dba | Dibenzylidene acetone ( $\mathrm{PhCH}=\mathrm{CHC}(\mathrm{O}$ ) $\mathrm{CH}=\mathrm{CHPh}$ ) |
| dcp | Dicyclopentadiene |
| dcype | 1,2-bis(dicyclohexylphosphino)ethane ( $\left.\mathrm{Cy}_{2} \mathrm{P}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{PCy}_{2}\right)$ |
| dd | Doublet of doublets |
| DEAD | Diethylacetylene dicarboxylate ( $\mathrm{EtOC}(\mathrm{O}) \mathrm{C} \equiv \mathrm{CC}(\mathrm{O}) \mathrm{OEt})$ |
| def | Diethylfumarate ( $E$-EtOC(O) $\mathrm{CH}=\mathrm{CHC}(\mathrm{O}) \mathrm{OEt}$ ) |
| dem | Diethylmaleate ( $Z-\mathrm{MeOC}(\mathrm{O}) \mathrm{CH}=\mathrm{CHC}(\mathrm{O}) \mathrm{OMe})$ |
| demOH | Diethylmalate ( $\left.\mathrm{EtOC}(\mathrm{O}) \mathrm{CH}_{2} \mathrm{CH}(\mathrm{OH}) \mathrm{C}(\mathrm{O}) \mathrm{OEt}\right)$ |
| depm | 1,1-bis(diethylphosphino)methane ( $\mathrm{Et}_{2} \mathrm{PCH}_{2} \mathrm{PEt}_{2}$ ) |
| dil. | Dilute |
| DIOP | 4,5-bis((diphenylphosphino)methyl)-2,2-dimethyl-1,3-dioxolane |
| DMAD | Dimethylacetylene dicarboxylate ( $\mathrm{MeOC}(\mathrm{O}) \mathrm{C} \equiv \mathrm{CC}(\mathrm{O}) \mathrm{OMe})$ |
| dmapcp | 1,2-bis(di(o- $\mathrm{N}, \mathrm{N}$-dimethylanilinyl)phosphino)cyclopentane |
| dmape | 1,2-bis(di(o-N,N-dimethylanilinyl)phosphino)ethane |
| dmapm | 1,1-bis(di(o- $N, N$-dimethylanilinyl)phosphino)methane |
| dmapmO | 1,1-bis(di(o- $N, N$-dimethylanilinyl) phosphino)methane monooxide |
| dmf | Dimethylfumarate ( $E$-MeOC(O)CH=CHC(O)OMe) |


| DMF | Dimethylformamide |
| :---: | :---: |
| dmm | Dimethylmaleate ( $Z$ - $\mathrm{MeOC}(\mathrm{O}) \mathrm{CH}=\mathrm{CHC}(\mathrm{O}) \mathrm{OMe})$ |
| dmpb | 1,2-bis(dimethylphosphino)benzene ( $\mathrm{Me}_{2} \mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{4}\right) \mathrm{PMe}_{2}$ ) |
| dmpe | 1,2-bis(dimethylphosphino)ethane ( $\mathrm{Me}_{2} \mathrm{P}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{PMe}_{2}$ ) |
| dmphen | 2,9-dimethyl-1,10-phenanthroline |
| dmpm | 1,1-bis(dimethylphosphino)methane ( $\mathrm{Me}_{2} \mathrm{PCH}_{2} \mathrm{PMe}_{2}$ ) |
| DMSO | Dimethyl sulphoxide ( $\mathrm{Me}_{2} \mathrm{~S}=\mathrm{O}$ ) |
| dppb | 1,4-bis(diphenylphosphino)butane ( $\left.\mathrm{Ph}_{2} \mathrm{P}\left(\mathrm{CH}_{2}\right)_{4} \mathrm{PPh}_{2}\right)$ |
| dppep | 1,2-bis(diphenylphosphino)cyclopentane ( $\mathrm{Ph}_{2} \mathrm{PCH}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CHPPh}_{2}$ ) |
| dppe | 1,2-bis(diphenylphosphino)ethane ( $\mathrm{Ph}_{2} \mathrm{P}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{PPh}_{2}$ ) |
| dppm | 1,1-bis(diphenylphosphino)methane ( $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{PPh}_{2}$ ) |
| dppp | 1,3-bis(diphenylphosphino)propane ( $\mathrm{Ph}_{2} \mathrm{P}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{PPh}_{2}$ ) |
| dрурср | 1,2-bis(di-o-pyridylphosphino)cyclopentane ( $\mathrm{py}_{2} \mathrm{PCH}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CHPpy}_{2}$ ) |
| dрypcp( O$)_{2}$ | 1,2-bis(di-o-pyridylphosphino)cyclopentane dioxide ( $\mathrm{py}_{2} \mathrm{P}(\mathrm{O}) \mathrm{CH}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CHP}(\mathrm{O}) \mathrm{py}_{2}$ ) |
| dpype | 1,2-bis(di-o-pyridylphosphino)ethane ( $\left.\mathrm{py}_{2} \mathrm{P}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{Ppy}_{2}\right)$ |
| dpype(O) 2 | 1,2-bis(di-o-pyridylphosphino)ethane dioxide ( $\left.\mathrm{py}_{2} \mathrm{P}(\mathrm{O})\left(\mathrm{CH}_{2}\right)_{2} \mathrm{P}(\mathrm{O}) \mathrm{py}_{2}\right)$ |
| dpypm | 1,1-bis(di-o-pyridylphosphino)methane ( $\mathrm{py}_{2} \mathrm{PCH}_{2} \mathrm{Ppy}_{2}$ ) |
| e.e. | Enantiomeric excess |
| eq. | Equation |
| equiv. | Equivalent(s) |
| Et | Ethyl |
| EXSY | Exchange NMR spectroscopy |
| fa | Fumaric acid ( $\left.E-\mathrm{HO}_{2} \mathrm{CCH}=\mathrm{CHCO}_{2} \mathrm{H}\right)$ |
| FID | Flame ionisation detector |
| GC | Gas chromatography |
| HEMA | 2-hydroxethyl methacrylate |
| HETCOR | Heteronuclear correlation NMR spectroscopy |
| H.P. | High purity |
| HT | Head-to-tail |
| hxd | 1,5-hexadiene |
| i.d. | Internal diameter |
| $J$ | Coupling constant (Hz) |
| IR | Infra-red |
| m | Multiplet |
| ma | Maleic acid ( $2-\mathrm{HO}_{2} \mathrm{CCH}=\mathrm{CHCO}_{2} \mathrm{H}$ ) |
| Me | Methyl |
| mol | Mole |
| Hmtpo | 4,7-H-5-methyl-7-oxo[1,2,4]triazolo[1,5a]pyrimidine |
| nbd | Norbornadiene |
| NMR | Nuclear magnetic resonance |
| NOE | Nuclear Overhauser effect |
| OAc | Acetate, acetato |
| $\mathrm{OPN}_{2}$ | Di(o-pyridyl)phenylphoshine oxide ( $\mathrm{Ph}(\mathrm{py})_{2} \mathrm{P}=\mathrm{O}$ ) |
| $\mathrm{O}^{\prime} \mathrm{Bu}$ | Tertiary-butoxide |
| OTf | Trifluoromethanesulphonate, triflate ( $\mathrm{CF}_{3} \mathrm{SO}_{3}{ }^{-}$) |
| ox | Oxalate, oxalato ( $\mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-}$ ) |
| p | Pseudo- (e.g., pd = pseudo-doublet) |
| p. | Page |
| Ph | Phenyl |
| phen | 1,10-phenanthroline |
| PMA | Diphenyl-o- $\mathrm{N}, \mathrm{N}$-dimethylanilinylphosphine, $\mathrm{Ph}_{2} \mathrm{P}-\mathrm{o}-\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{NMe}_{2}$ |
| $\mathrm{PN}_{1}$ | Diphenyl-o-pyridylphosphine ( $\mathrm{Ph}_{2} \mathrm{Ppy}$ ) |
| $\mathrm{PN}_{2}$ | Di-o-pyridylphenylphosphine ( $\mathrm{PhPpy}_{2}$ ) |
| $\mathrm{PN}_{3}$ | Tri(o-pyridyl)phosphine |
| ppm | Parts per million |
| py | Pyridyl |


| q | Quartet |
| :--- | :--- |
| quin | 2-quinaldinate, 2-quinaldinato |
| Ref. | Reference |
| ROMP | Ring-opening metathesis polymerisation |
| R/RP | Ruhrchemie/Rhône-Poulenc |
| RVBM | Resonating valence-bond theory of metals |
| s | Singlet |
| sh | Shoulder |
| SHOP | Shell higher olefin polymerisation |
| spt | Septet |
| $t$ | Triplet |
| THF | Tetrahydrofuran |
| TOF | Turnover frequency (mol product per mol catalyst per unit time) |
| TON | Turnover number (mol product per mol catalyst) |
| TPA | 1,3,5-triaza-7-phosphaadamantane |
| TPPMS | Triphenylphosphine monosulphonate |
| TPPTS | Triphenylphosphine trisulphonate |
| tw | This work |
| UV-vis | Ultraviolet-visible |
| vol. | Volume |
| WGS | Water-gas shift |
| $\delta$ | Chemical shift (ppm) |
| $\varepsilon$ | Extinction coefficient (L mol ${ }^{-1} \mathrm{~cm}^{-1}$ ) |
| $\eta$ | Hapticity |
| $\kappa$ | Ligating atom |
| $\lambda$ | Wavelength (nm) |
| $\Lambda_{M}$ | Molar conductivity (ohm ${ }^{-1} \mathrm{~mol}^{-1} \mathrm{~cm}^{2}$ ) |
| $\mu$ | Bridging coordination mode |
| $v$ | Wavenumber (cm ${ }^{-1}$ ) |
| [] | Concentration |
| $\}$ | Broad-band decoupled |

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## 1 General Introduction

### 1.1 Evolutionary Trends in Homogeneous Catalysis

The case of hydrogenation serves to illustrate a general trend in the evolution of homogeneous catalysis. ${ }^{1,2}$ The first kinetically detailed report of a homogeneous catalytic hydrogenation by a platinum metal complex is due to Halpern and coworkers. ${ }^{3}$ In this system, aqueous solutions of chlororuthenate(II) were active for the hydrogenation of maleic, fumaric and acrylic acids at hydrogen pressures of up to 1 atm and at temperatures of $65-90^{\circ} \mathrm{C}$. Olefins not bearing carboxylate groups were not hydrogenated. Two years later, in 1963, Cramer et al. from Du Pont reported that a Pt-Sn complex in methanol solution was the first effective catalyst for the room temperature reduction of ethylene at 1 atm hydrogen pressure. 4

In 1965, Ru-phosphine complexes were introduced by Wilkinson et al. who reported that $\mathrm{RuCl}_{2}\left(\mathrm{PPh}_{3}\right)_{n}(n=3,4)$ reacted with hydrogen at room temperature in ethanol/benzene to give $\mathrm{RuCl}(\mathrm{H})\left(\mathrm{PPh}_{3}\right)_{3}$ which was an extremely active catalyst for the reduction of olefins and acetylenes. ${ }^{5}$ Likewise, Pt-Sn complexes containing phosphines were investigated: a wide range of olefins could be reduced by $\mathrm{PtCl}_{2}\left(\mathrm{PPh}_{3}\right)_{2} / \mathrm{SnCl}_{2}$ in benzene/methanol under 40 atm of hydrogen at $90-105^{\circ} \mathrm{C} .6-9$

Also in 1965, what is now his eponymous catalyst, $\mathrm{RhCl}\left(\mathrm{PPh}_{3}\right)_{3}$, was reported by Wilkinson; ${ }^{10,11}$ its catalytic activity was discovered simultaneously and independently by Coffey. ${ }^{12}$ This complex, which is capable of effecting the reduction of a wide range internal and terminal olefins in benzene solution at $25^{\circ} \mathrm{C}$ under 1 atm of hydrogen pressure, ${ }^{13-15}$ has been the focus of intensive study and is now accepted as the prototypical hydrogenation catalyst.

In other reactions, as in hydrogenations, phosphine ligands came to be introduced. The Ruhrchemie hydroformylation process which is based on $\mathrm{Co}(\mathrm{H})(\mathrm{CO})_{4}$ was discovered by Roelen in 1938. ${ }^{16}$ The system has since been modified by the addition of trialkylphosphine. In the process developed by Shell, ${ }^{17}$ the active catalyst, $\mathrm{Co}(\mathrm{H})\left(\mathrm{PBu}_{3}\right)(\mathrm{CO})_{3},{ }^{18}$ is less active for hydroformylation than the phosphine-free
compound, but gives higher selectivity for the linear aldehyde. In addition, the same catalyst can be used to hydrogenate the aldehyde so that long chain linear alcohols can be produced in a single reactor from terminal olefins. Because $\mathrm{Co}(\mathrm{H})\left(\mathrm{PBu}_{3}\right)(\mathrm{CO})_{3}$ is more stable than $\mathrm{Co}(\mathrm{H})(\mathrm{CO})_{4}$, significantly lower pressure can be employed (100 vs. 200300 atm of $\mathrm{H}_{2} / \mathrm{CO}$ ) and because of the enhanced stability and lower volatility of the catalyst, product-catalyst separation can be achieved by simple distillation.

In addition, to the improved catalyst activity, selectivity and stability that were often achieved by the incorporation of phosphine ligands, this development greatly advanced the solution characterisation of the complexes by facilitating their study by ${ }^{31} \mathrm{P}$ NMR spectroscopy. But the evolution of catalysts from simple salts to metal-phosphine complexes also had a secondary effect: because of the water-insolubility of phosphines, water and hydrophilic liquids were gradually eliminated as solvents for homogeneous catalytic reactions. In the examples of homogeneous hydrogenation presented here, the astute reader will recognise the progression in solvent polarity from water to methanol to benzene/ethanol and finally to benzene.

The impetus to reinstate water as a solvent for homogeneous catalytic reactions is derived from two sources: the need for a cheap, environmentally benign solvent and the need for facile product-catalyst separation. So strong have been these motivations that catalytic hydrogenation has now come full circle. Tóth et al. have developed a Rh catalyst based on an ammonium phosphine ligand which is capable of effecting the asymmetric hydrogenation of cinnamic acid derivatives with high efficiency and excellent enantioselectivity in water solution. ${ }^{19}$ With the publication of dedicated books, ${ }^{20}$ journal issues ${ }^{21}$ and numerous review articles, ${ }^{22-24}$ catalysis in water has made an impressive return to the research spotlight.

### 1.2 Product-Catalyst Separation

The problem of product-catalyst separation has been addressed most successfully by the development of biphasic catalysis. In this approach, the goal has been to combine the advantages of homogeneous catalysis, ${ }^{25,26}$ i.e., enhanced activity and selectivity, ease of characterisation and tailoring of the catalyst, and relatively mild operating conditions,
with the primary advantage of heterogeneous catalysis, i.e., ease of product-catalyst separation. In this sense, the active catalyst is "trapped" in or on a solid or liquid support which can be removed from the products once the reaction is complete by a simple physical process such as filtration or decanting.

The "heterogenisation" of a homogeneous catalyst sees its most simple application in a system consisting in two immiscible liquid phases. The approach was first enunciated in the academic literature in 1973 by Manassen ${ }^{27}$ who wrote, "The use of two immiscible liquid phases, one containing the catalyst and the other containing the substrate, must be considered. The two phases can be separated by conventional means and a high degree of dispersion can be obtained through emulsification. This ease of separation may be particularly useful in situations where frequent catalyst regeneration or reactivation is required."

The benefits of this approach over other types of immobilization are that even though the catalyst is heterogeneous, i.e., in a different phase from the reactants and products, the catalysis is homogeneous, i.e., goes via a discernible catalyst cycle which gives rise to reproducible reaction kinetics and which consists of molecular intermediates which are dispersed uniformly within the medium and are accessible to study by spectroscopy. ${ }^{28}$ Other means of immobilizing an intrinsically homogeneous catalyst, e.g., by attaching it to a solid polymer or other scaffold, ${ }^{29}$ are more problematic because stresses on the bond between metal and support lead over time to leaching of the metal.

The first commercial application of liquid-liquid biphasic catalysis was the Shell Higher Olefin Polymerisation (SHOP) process due to Keim. ${ }^{30,31}$ In this system, ethylene is polymerised to give $\mathrm{C}_{4}-\mathrm{C}_{20} \alpha$-olefins at $80-120^{\circ} \mathrm{C}$ and $70-140$ bar. The catalyst is generated from $\mathrm{Ni}(\operatorname{cod})_{2}$ and $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{COOH}$ dissolved in 1,4-butanediol. The products, which are apolar and less dense than the solvent, are removed by decanting.

Sheldon, in a 1992 article entitled "Organic Synthesis - Past, Present and Future," took the idea of Manassen one step further by saying that, "If a solvent is needed, it should preferably be water ... the development of water-soluble catalysts that work in a two phase system could be the answer in some cases." ${ }^{32}$

Biphasic catalysis in which one of the phases is water forms the basis of the Ruhrchemie/Rhône-Poulenc (R/RP) oxo process, ${ }^{33}$ which converts propylene to $n$ -
butyraldehyde on a scale of $3 \times 10^{5}$ metric tons per annum. ${ }^{34}$ In this process, an aqueous solution containing Rh and the sodium salt of tris( $m$-sulphonatophenyl)phosphine, also known as triphenylphosphinetrisulphonate or TPPTS, is used as the catalyst (the active species is $\left.\left[\mathrm{Rh}(\mathrm{H})(\mathrm{CO})(\text { TPPTS })_{3}\right]^{9-}\right)$. The product and catalyst are once again separated by decanting: olefin and aldehyde are only sparingly soluble in the aqueous phase, and the catalyst is completely insoluble in the organic fraction. A simplified schematic of the R/RP oxo process reactor design is shown in Figure 1.1.


Figure 1.1 Schematic representing the application of the biphasic catalysis principle to industrial reactor design (adapted from ref. 28). The system illustrated here is very similar to that used in the $\mathrm{R} / \mathrm{RP}$ oxo process.

Prior to the 1980s, the field of homogeneous catalysis was almost exclusively confined to the use of organic solvents, with the exception of the Wacker process for the oxidation of olefins. The primary reasons for this were the insolubility of the catalysts in water and their chemical reactivity with it. Water was seen as detrimental, and extensive precautions were taken to exclude it even though it had been recognised in some cases to be beneficial, e.g., in solubilising Co catalyst precursors in the hydroformylation processes of BASF ${ }^{35}$ and Ruhrchemie. ${ }^{36,37}$ Also, the addition of aqueous sodium formate
was found by Ruhrchemie to increase the overall yield by cleaving the initially-formed formic esters which hampered hydroformylation reactions. 38

The tremendous success of the $\mathrm{R} / \mathrm{RP}$ process is in large part due to the pioneering academic research of Kuntz who began investigating biphasic hydroformylation while at Rhône-Poulenc. ${ }^{33}$ His breakthrough can be attributed to a combination of three factors: the use of Rh as the catalytic centre instead of Co , the modification of the Rh -catalyst with phosphine ligands, and the choice of water as the catalyst-immobilizing phase. ${ }^{28}$ This last choice was based on the unique physiochemical properties of water and its fulfilment of several criteria posited by chemical engineers: it is a nearly ubiquitous substance which is cheaply available in large volumes of reasonable purity; it is odourless and colourless which makes detection of impurities easy; it is not flammable or combustible making it safe for scaled-up reactors; it is polar which makes it easy to separate from non-polar organic solvents, reactants and products from which it also (typically) differs in density; it has a high thermal conductivity, specific heat capacity and enthalpy of evaporation making it ideal as a solvent as well as a temperature control substance; and, finally, it is non-toxic and environmentally safe.

### 1.3 Water-soluble Phosphine Ligands

The R/RP process constitutes an excellent example demonstrating the possibility for combination of the advantageous properties of metal-phosphine complexes with those of homogeneous catalysis in water. The prerequisite for this type of combination is a library of water-soluble phosphine ligands which can be used to solubilise and stabilise metal centres. In general, phosphine ligands can be made water-soluble by the incorporation of polar groups such as sulphonate, carboxylate, ammonium, pyridinium, phosphonium or hydroxyl. ${ }^{24}$ The selection of ligands given in Chart 1.1 is not intended to be comprehensive, but rather is meant to convey an impression of the types and variety of water-soluble phosphines which have been investigated to date. (Where the ligands have names that are in common use in the literature, they are given; otherwise, they are denoted by numbers.)

## Chart 1.1



TPPMS ${ }^{39,40}$


TPPTS 3 3,41,42

$\operatorname{BDPP}_{\mathrm{Ds}}{ }^{43}$


TPA ${ }^{45}$

$2^{46}$


347


650
$5^{49}$


### 1.4 Aqueous Phase Homogeneous Catalysis

Following the success of the R/RP oxo process in 1984, aqueous phase homogeneous catalysis has received renewed attention. The potential for transferring a wide variety of catalytic reactions from organic solvents into water is the subject of ongoing research and, as mentioned previously, has been reviewed on a number of occasions. ${ }^{22-24}$ Table 1.1 illustrates the general applicability of homogeneous, aqueous phase catalysis to organic synthesis by giving a selection of the reactions which can be carried out either in water or in water-organic solvent biphasic mixtures, and the metal-ligand combinations which catalyse them.

Table 1.1. A selection of reactions catalysed by metal-phosphine complexes dissolved in water.

| Reaction type | Example reaction and metal/ligand combination ${ }^{\text {a }}$ | Ref. |
| :---: | :---: | :---: |
| Hydroformylation | Rh/TPPTS | 33 |
| Hydrogenation | $\mathbf{C}=\mathbf{C}$ | 53 |
|  | $\mathrm{Rh} / 2$ |  |
|  | $\mathbf{C}=\mathbf{O}$ | 54-57 |
|  | Ru/TPPMS, Ru/TPA <br> (by hydrogen transfer from sodium formate) |  |
|  | $\mathrm{C}=\mathrm{N}$ | $\begin{aligned} & 43,58, \\ & 59 \end{aligned}$ |



Table 1.1 (cont.)

| Reaction type | Example reaction and metal/ligand combination ${ }^{\text {a }}$ | Ref. |
| :--- | :--- | :--- |
| Polymerisation | ROMP | 47,67 |


$\mathrm{Ru} / \mathbf{3} / 4$
Ethylene/CO copolymerisation

$\mathrm{Pd} / 1$
${ }^{\text {a }}$ Throughout this thesis, * designates a chiral carbon centre.

### 1.5 Other Considerations

The hydrophobic effect, which plays a critical rôle in the folding of proteins, in the formation and stabilisation of membranes and micelles, and in molecular recognition events such as those between antibody and antigen, substrate and enzyme, and receptor and hormone, also contributes significantly to organic reactions conducted in water. For example, Breslow's discovery of the dramatic acceleration of the Diels-Alder reaction in aqueous solution has been attributed to hydrophobic packing of the reagents. ${ }^{71,72}$ This has been postulated by Lubineau to be due to the high cohesive energy of water $\left(2.3 \mathrm{~kJ} \mathrm{~mL}^{-1}\right)$ which necessitates that every kinetically-controlled reaction between two non-polar molecules for which $\Delta V^{\ddagger}$ is negative must be accelerated in water. ${ }^{73}$

In addition to the hydrophobic effect, rate enhancement in water is brought about by stabilisation of polar transition states, especially when one of the reagents is a hydrogen-bond donor or acceptor. Monte-Carlo simulations of Diels-Alder reactions involving methyl vinylketone as the dienophile reveal significant polarisation of the $\mathrm{C}=\mathrm{O}$ bond in the transition state, and consequently enhanced hydrogen-bonding. This makes a contribution to the rate enhancement equal to that of the hydrophobic effect. ${ }^{74}$

Another important factor influencing the reactivity of substances dissolved in water is pH . As an illustrative example of this point, Scheme 1.1 shows the equilibrium reactions of the dichloro-bridged diruthenium compound $\left[\mathrm{RuCl}_{2}(\mathrm{TPPMS})_{2}\right]_{2}$ with $\mathrm{H}_{2}$ in the presence and absence of added TPPMS.

## Scheme 1.1

$$
\begin{gathered}
{\left[\mathrm{RuCl}_{2}(\mathrm{TPPMS})_{2}\right]_{2}+2 \mathrm{H}_{2} \rightleftharpoons\left[\mathrm{Ru}(\mathrm{H}) \mathrm{Cl}(\mathrm{TPPMS})_{2}\right]_{2}+2 \mathrm{H}^{+}+2 \mathrm{Cl}^{-}} \\
{\left[\mathrm{RuCl}_{2}(\mathrm{TPPMS})_{2}\right]_{2}+2 \mathrm{H}_{2}+2 \mathrm{TPPMS} \rightleftharpoons 2 \mathrm{Ru}(\mathrm{H}) \mathrm{Cl}(\mathrm{TPPMS})_{3}+2 \mathrm{H}^{+}+2 \mathrm{Cl}^{-}} \\
{\left[\mathrm{RuCl}_{2}(\mathrm{TPPMS})_{2}\right]_{2}+4 \mathrm{H}_{2}+4 \mathrm{TPPMS} \rightleftharpoons 2 \mathrm{Ru}(\mathrm{H})_{2}(\mathrm{TPPMS})_{4}+4 \mathrm{H}^{+}+4 \mathrm{Cl}^{-}}
\end{gathered}
$$

Obviously, the position of these equilibria and therefore the rate of Ru /TPPMS-catalysed olefin hydrogenations, for example, will be crucially dependent upon pH . It has been determined by Joó et al. that below pH 3 , the major species in solution is $\mathrm{Ru}(\mathrm{H}) \mathrm{Cl}(\mathrm{TPPMS})_{3}$, whereas $\mathrm{Ru}(\mathrm{H})_{2}(\mathrm{TPPMS})_{4}$ dominates in neutral and basic solutions; at $\mathrm{pH} 3-7$, a mixture of hydrides is present. ${ }^{75}$ The implication of these findings is that kinetic data are valid only within a narrow pH range; differences in pH , therefore, may account for apparent contradictions in the literature. Since the active catalyst for olefinic hydrogenation is the monohydride " $\mathrm{Ru}(\mathrm{H}) \mathrm{Cl}(\mathrm{TPPMS})_{2}{ }^{" 76}$ while for aldehyde groups it is the dihydride $\mathrm{Ru}(\mathrm{H})_{2}(\mathrm{TPPMS})_{4},{ }^{77,78}$ the rate and product distribution of $\mathrm{H}_{2}$ reductions of unsaturated aldehydes like prenal (2-methylpropen-2-al) are especially sensitive to pH. ${ }^{78,79}$

### 1.6 Atom Economy

In a 1991 article in Science, Trost laid out the concept of atom economy, i.e., the maximisation of the mass of atoms in the reactants which is incorporated into the desired product. ${ }^{80}$ Two reactions can be compared: $\mathrm{A}+\mathrm{B} \rightarrow \mathrm{C}+\mathrm{D}$, and $\mathrm{A}+\mathrm{B} \rightarrow \mathrm{C}$. The first type can be very wasteful indeed, as is the case in the Wittig reaction where the unwanted product, D , is triphenylphosphine oxide which has a molecular weight of $285 \mathrm{~g} \mathrm{~mol}^{-1}$ and usually dwarfs that of the desired olefinic product, C (Scheme 1.2). For example, when
the aldehyde is benzaldehyde, this reaction has an atom economy of only $28 \%$, and can be better regarded as a synthesis of $\mathrm{OPPh}_{3}$ (atom economy $=75 \%$ ).

## Scheme 1.2

$$
\mathrm{RCHO}+\mathrm{Ph}_{3} \mathrm{P}=\mathrm{CH}_{2} \rightarrow \mathrm{RCH}=\mathrm{CH}_{2}+\mathrm{OPPh}_{3}
$$

In the case of the addition reaction, $\mathrm{A}+\mathrm{B} \rightarrow \mathrm{C}$, all of the atoms in the reactants are incorporated into the product. This is the definition of a zero-waste process. As the chemical industry faces ever more stringent environmental regulations, the more it will be pressured to devise synthetic strategies of this type.

Sheldon expands the concept of atom economy to consider not only the amount of waste resulting from a reaction, but also its nature. ${ }^{32}$ In addition, he takes into account not only the reactants and products, but also the volume and nature of solvent(s). If possible, he asserts, solvents should not be used at all but, when necessary, the solvent should preferably be water.

The aqueous phase catalytic hydration of olefins (Scheme 1.3) takes these concepts to their highest level: the solvent is environmentally benign, and is a reactant in an addition, zero-waste reaction. So appealing is this result that the anti-Markovnikov addition of water to terminal olefins to produce linear alcohols has been cited as one of the ten remaining challenges for homogeneous catalysis. ${ }^{81}$ In principle, prochiral olefins could also be asymmetrically hydrated to give optically pure alcohols.

## Scheme 1.3

$$
\mathrm{RCH}=\mathrm{CH}_{2}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{RCH}_{2} \mathrm{CH}_{2}(\mathrm{OH}) \text { and/or } \mathrm{RC} * \mathrm{H}(\mathrm{OH}) \mathrm{CH}_{3}
$$

### 1.7 Scope of this Thesis

This thesis is founded on the study of platinum metal complexes of two nitrogencontaining families of chelating diphosphine ligands. The first family is characterised by having $o$ - $N, N$-dimethylanilinyl rings appended to each of the P -atoms, and the second by
having o-pyridyl substituents in the same positions. All of the ligands and their monikers are given in Chart 1.2. Prior to the beginning of this study in September 1996, the pyridyldiphosphine dpype had been reported by this group, ${ }^{82}$ and the other ligands, with the exception of dmapm which is new in this work, had been isolated in impure form by a previous postdoctoral fellow, Martin Smith, but had not yet been reported in the open literature.

## Chart 1.2

## Anilinyldiphosphine Ligands


dmapm

dmape

dmapcp

## Pyridyldiphosphine Ligands



The main objectives of this work were to uncover good synthetic strategies for each ligand family and their corresponding platinum metal complexes, to study the solution behaviour of the complexes, which hopefully would show enhanced water-
solubility, and to use these as catalysts in aqueous or mixed aqueous/organic homogeneous reactions with the primary goal being the hydration of olefins.

The anilinyldiphosphine ligands and $\mathrm{M}^{\mathrm{II}}(\mathrm{M}=\mathrm{Pt}, \mathrm{Pd})$ complexes of dmape and dmapcp are discussed in Chapter 2. Chapter 3 investigates $M^{I I}$ and $M_{2}{ }^{I}$ complexes of dmapm, and discusses the use of homo- and heterobimetallic complexes bridged by dmapm as catalysts for the Heck reaction in a water/organic medium. Chapter 4 summarises the coordination chemistry of the pyridyldiphosphine ligands with $\mathrm{M}^{0 / I I}$ precursors and some reactions of the complexes. Finally, Chapter 5 presents a summary of the results for the attempted catalytic hydration of maleic acid in water.

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## 2 Anilinyldiphosphine Ligands and Pt and Pd Complexes

### 2.1 Introduction

The following chapter deals with the three tetraanilinyldiphosphine ligands shown in Chart 2.1 and a selection of their $\mathrm{Pt}^{\mathrm{II}}$ and $\mathrm{Pd}^{\mathrm{II}}$ complexes. The ligands fall into a general class whose members incorporate at least 2 tertiary P -atoms and at least 1 amine N -atom. As these have not yet been discussed as a collective in the literature (although a significant body of work exists), the following paragraphs will provide a brief overview of the known types, their metal complexes and uses in catalysis.

## Chart 2.1


dmapm

dmape

dmapcp

Whereas the synthesis of dmapm is covered in this chapter (Section 2.9.1.1) as is a discussion of the organometallic intermediates which result from its reaction with $\mathrm{PdCl}_{2}(\mathrm{cod})$ (Section 2.5.8), a detailed investigation of its complexes and their use in catalysis appears in Chapter 3.

### 2.1.1 Philosophical approach

Over the last 25 years, amine functional groups have been incorporated into diphosphine ligands with a view to surmounting the most problematic aspect of homogeneous
catalysis: separation of the catalyst from the product. The most successful approach to solving this problem has been to "heterogenise" the homogeneous catalyst either by its incorporation into an insoluble polymer, or by solubilising it in a solvent (such as $\mathrm{H}_{2} \mathrm{O}$ ) with which the reactants and products are only very slightly miscible, or by extracting it post-reaction with a solvent (such as aqueous acid) in which the product does not dissolve, etc. All of these approaches have been investigated with varying degrees of success.

Prior to the 1990 pioneering work of Tóth et al.,,$^{1-5}$ amine N -atoms in diphosphine ligands were viewed as functional groups either for incorporation of the ligands into polymers (Achiwa, ${ }^{6}$ Stille and coworkers; ${ }^{7}$ Section 2.1.2.1), or for the subsequent introduction of water-solubilising sulphonate moieties (Whitesides and coworkers; ${ }^{8}$ Section 2.1.2.2) and not as potential water-solubilising sites themselves (via quaternisation).

Since 1990, however, most of the work using this ligand class has been with a view to water-solubilisation of metal complexes for use in aqueous catalysis via protonation or alkylation of the N -atoms. The N -atoms are typically distant from the P centres and are not involved in coordination in the complexes. For example, in all of the ligands made by Tóth et al. (see p. 23), the N -atoms are incorporated as $p-\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{NMe}_{2}$ substituents which prohibits their coordination to the same metal centre bound by the P atoms. No reports of this type of ligand in a bridging mode have appeared.

The ligands presented in this and the following chapter (Chart 2.1) are different from those of Tóth et al. in that they bear ortho- as opposed to para-anilinyl substituents on their P -atoms. This makes the N -atoms available for coordination to the same metal centre as the P -atoms, and in some cases renders complexes water-soluble by displacing halide from the coordination sphere.

Because the N -atoms are positioned for coordination, and because of the different affinities of group 10 metals for P ("soft") and N ("hard"), complexes of the $o$ anilinyldiphosphine ligands exhibit fluxional behaviour in organic solution, i.e., the ligands are "hemilabile".

### 2.1.2 A brief literature survey

By far the majority of the research into diphosphine ligands bearing amine groups has been directed towards the search for hydrogenation catalysts, although some work has also focussed on hydroformylations. Without exception, the catalysts that have appeared in the literature to date have been complexes of $\mathrm{Rh}^{1}$ and $\mathrm{Ru}^{\mathrm{II}}$.

### 2.1.2.1 Polymer-attached optically-active diphosphine ligands

The first group of ligands to combine 2 or more tertiary P -atoms and at least 1 amine N atom is derived from prolene and is due to Achiwa. ${ }^{9}$ Representatives of this group are illustrated in Chart $2.2(\mathbf{1 - 4})$. In these ligands, the N -atom serves as an attachment point for groups such as $-\mathrm{C}(\mathrm{O}) \mathrm{CH}=\mathrm{CH}_{2}$ which facilitate the incorporation of the diphosphine into polymers. The goal of this approach was to heterogenise the catalyst.

Stille's group has successfully copolymerised both the $S, S$ and $R, R$ enantiomers of 3 with 2-hydroxyethyl methacrylate (HEMA) to give polymer 5 (Chart 2.3), and $N, N$ dimethylacrylamide (polymer not shown) by free-radical initiators using ethylene dimethacrylate as a crosslinking agent. ${ }^{7}$ These workers used $\mathrm{Rh}^{1}$ complexes of these polymers in the asymmetric hydrogenation of dehydroaminoacids with e.e.s as high as $91 \%$.

## Chart 2.2

 $R=H$

(2)

(3)

(4)

In a similar fashion, Achiwa has copolymerised $S, S-4$ with HEMA in the presence of azobisisobutylnitrile. ${ }^{6}$ Subsequent reaction of this polymer with $[\mathrm{Rh}(\mu-\mathrm{Cl})(\operatorname{cod})]_{2}$ generated an insoluble catalyst for the hydrogenation of itaconic acid with e.e.s up to $82 \%$, and ( $Z$ )-2-acetamidocinnamic acid with optical yields of $70 \%$.

In order to facilitate product catalyst separation by using two immiscible liquid phases, Malmström and Andersson have generated the water-soluble polymer 6 (Chart
2.3) by acylation of $S, S-1$ with poly(acrylic acid) in the presence of dicyclohexylcarbodiimide, followed by neutralisation with $\mathrm{NaHCO}_{3} .{ }^{10}$ Reaction of this with $\left[\mathrm{Rh}(\mathrm{nbd})_{2}\right]\left[\mathrm{CF}_{3} \mathrm{SO}_{3}\right]$ gave a polymeric water-soluble catalyst which was employed in the asymmetric hydrogenation of ( $Z$ )-2-acetamidocinnamic acid with e.e.s of up to 93 \%.

## Chart 2.3


(5)

(6)

Ligand 2 has also been successfully employed in the homogeneous asymmetric hydrogenation of itaconic acid and $\alpha$-acylamino acrylic acid and its derivatives. Ojima et al. have found that the stereoselectivity of the reaction catalysed by $[\mathrm{Rh}(\operatorname{cod})(2)]\left[\mathrm{ClO}_{4}\right]$ is sensitive to $\mathrm{H}_{2}$ pressure, the presence or absence of base $\left(\mathrm{NE}_{3}\right)$, and the temperature. ${ }^{11}$

Lemaire and coworkers have synthesised a 6,6 methylamine-substituted BINAP in 5 steps starting from $S$-binol ( 7 in Scheme 2.1). ${ }^{12}$ This ligand has been copolymerised with 2,6 -tolylene disocyanate to give $\mathbf{8}$. Reaction of $\mathbf{8}$ with either of $\left[\mathrm{RuCl}_{2}\left(\mathrm{C}_{6} \mathrm{H}_{6}\right)\right]_{2}$ or
$\mathrm{Ru}(\mathrm{cod})(2-\mathrm{Me}-\mathrm{allyl})_{2}$ gave catalysts whose exact composition was not determined but which were effective for the asymmetric hydrogenation of $\beta$-ketoesters with e.e.s consistently $c a .99 \%$; the catalyst can be recovered by simple filtration as the polymer is insoluble in MeOH in which the reactions are conducted, and there is negligible loss of activity over 4 cycles.

## Scheme 2.1


(8)

### 2.1.2.2 Water-solubilisation via incorporation of sulphonate groups

The use of a secondary amine incorporated in a diphosphine ligand as a site for the subsequent introduction of sulphonate groups was initiated by Whitesides's group. ${ }^{8}$ This work was based on bis(2-diphenylphosphinoethyl)amine (9, Chart 2.4). The general method for sulphonate group introduction involved the coupling of the amine and an acid chloride acid anhydride (trimellitic (10) or tricarballylic (11)) followed by opening of the acid anhydride with sodium taurinate $\left(\mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{SO}_{3} \mathrm{Na}\right)$ to give 12, for example. Reaction of the sulphonated ligands with $[\mathrm{Rh}(\mu-\mathrm{Cl})(\mathrm{nbd})]_{2}$ in the presence of AgOTf generated catalysts (which remain uncharacterised) for the aqueous phase hydrogenation of unsaturated acids. The highest TOF was $>200 \mathrm{~h}^{-1}$, recorded for the hydrogenation of $\mathrm{CH}_{2}=\mathrm{C}(\mathrm{NHAc}) \mathrm{CO}_{2} \mathrm{H}$ by $\mathbf{1 2} \cdot \mathrm{Rh}$.

## Chart 2.4


$R=\begin{gathered}H \\ (9)\end{gathered}$
(9)

(10)


(11)
(12)

### 2.1.2.3 Water-solubilisation via quaternisation

Although water-solubilisation of phosphine ligands and their corresponding complexes by the introduction of charge via alkylation of amine groups had been accomplished earlier (e.g., in the 1982-3 work of Baird et al. on $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{CH}_{2} \mathrm{NMe}_{3}{ }^{+}$and its $\mathrm{Fe}^{0}, \mathrm{Mo}^{0}{ }^{13}$ and $\mathrm{Rh}^{1}$ complexes ${ }^{14}$ ), it was not until 1990 that such an approach had been applied to diphosphine ligands, and more specifically to chiral diphosphine ligands for use in aqueous phase, asymmetric catalysis.

Tóth et al. reported the synthesis of a range of chiral diphosphine ligands bearing $p-\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{NMe}_{2}$ substituents on the P -atoms (Chart 2.5, 13-15, 17). ${ }^{1-4}$ These workers have shown that $\mathrm{Rh}^{1}$ complexes of the ligands can be used as asymmetric hydrogenation catalysts in water once the N -atoms have been quaternised either via protonation with aq. $\mathrm{HBF}_{4}$ or by alkylation with $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{OBF}_{4}$. The $[(\mathbf{1 5}) \mathrm{Rh}(\mathrm{nbd})]\left[\mathrm{BF}_{4}\right]$ and $[(16) \mathrm{Rh}(\mathrm{nbd})]\left[\mathrm{BF}_{4}\right]$ complexes could also be immobilized on Nafion and other cation exchange resins according to Scheme 2.2; the modified resins could be used for the asymmetric hydrogenation of dehydroaminoacid derivatives with e.e.s up to $76 \%$ and could be recycled 6 times with minimal loss of catalytic activity. ${ }^{5}$

Scheme 2.2

$$
\text { (Nafion) }-\mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{SO}_{3} \mathrm{H}+[\mathbf{1 5} \cdot \mathrm{Rh}]\left[\mathrm{BF}_{4}\right] \rightarrow\left[(\mathrm{Nafion})-\mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{SO}_{3}\right][\mathbf{1 5} \cdot \mathrm{Rh}]+\mathrm{HBF}_{4}
$$

Following their report of 8, Lemaire's group demonstrated that 7 (Scheme 2.1) can be protonated at the N -atoms with $\mathrm{HBr} .{ }^{15}$ Reaction of the ammonium salt with either of $\left[\mathrm{RuCl}_{2}\left(\mathrm{C}_{6} \mathrm{H}_{6}\right)\right]_{2}$ or $\mathrm{Ru}(\mathrm{cod})(2-\mathrm{Me}-\mathrm{allyl})_{2}$ gave a catalyst, again uncharacterised, which was water-soluble and effective for the biphasic reduction of ethylacetoacetate with good enantioselectivity. The catalyst could be recycled once the water-soluble alcohol product had been extracted with pentane. The recycled catalyst showed minimal loss of activity, but did suffer a loss of enantioselectivity by the $3^{\text {rd }}$ cycle.

Ligand 13 was reported by Mirabelli et al. in 1987, and a derived $\mathrm{Au}^{1}$ complex was assayed for antitumor activity. ${ }^{16}$ However, no synthetic or characterisation data for these compounds were included in the publication. Ligand 17 is covered by a Hoechst patent. ${ }^{17}$

## Chart 2.5


(13)

(16)

(14)

(17)

(15)

(18)

Nagel and Kinzel were the first to report ligand 20 (Chart 2.6) and its Rh complex $[\operatorname{Rh}(\operatorname{cod})(\mathbf{2 0})]\left[\mathrm{BF}_{4}\right] .{ }^{18}$ Treatment of the complex with $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{OBF}_{4}$ resulted in the methylation of the N -atom to give the water-soluble complex $[\mathrm{Rh}(\operatorname{cod})(\mathrm{Me}-20)]\left[\mathrm{BF}_{4}\right]_{2}$
which was employed in the asymmetric hydrogenation of $\alpha$-acylaminocinnamic acid in $\mathrm{H}_{2} \mathrm{O}$ to give ( S )- N -acetylphenylalanine with $90 \%$ e.e..

## Chart 2.6


$\mathrm{R}=\mathrm{H}, \mathrm{Me}$
(19) (20)

### 2.1.2.4 Post-reaction separation by aqueous acid extraction

Van Leeuwen and coworkers have synthesised a number of $p-\mathrm{Et}_{2} \mathrm{NCH}_{2} \mathrm{C}_{6} \mathrm{H}_{4}$-substituted diphosphine ligands (Chart 2.7). ${ }^{19,20}$ These N-containing analogues of bisbi (21), POP (22) and xantphos (23) have large bite angles that allow them to occupy equatorial sites in the trigonal bipyramidal Rh-hydride complex which is the crucial intermediate in the hydroformylation catalytic cycle. This geometry leads to higher proportions of the $n$ aldehyde product than does that in which the P -atoms of the smaller bite angle ligands are constrained to chelate in the apical and equatorial positions. ${ }^{21}$

## Chart 2.7


(21)

(22)


The Rh catalysts with ligands $\mathbf{2 1 - 2 3}$ in the hydroformylation of oct-1-ene in toluene solution behaved similarly to their phenyl analogues, giving almost identical
activity and linear:branched aldehyde product ratios. In addition, the catalysts could be almost quantitatively recovered using aqueous acid, but re-extraction after neutralisation by fresh toluene for subsequent catalytic runs was only partially successful and the recycled catalysts had residual activities ranging between $51-86 \%$. ${ }^{19,20}$

### 2.1.2.5 Miscellaneous ligand

In a study of the hemilabile nature of phosphine ligands containing amine groups, Andrieu et al. have synthesised compound 24 (Chart 2.8) by treatment of 2 equiv. of $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{CH}(\mathrm{Ph}) \mathrm{NH}(\mathrm{Ph})$ with oxalylchloride. ${ }^{22}$ Although the ligand is well characterised, these researchers do not report any of its metal complexes.

## Chart 2.8


(24)

### 2.2 Scope

This chapter describes the syntheses (Sections 2.9.1) and structures (Sections 2.3.3) of alkyl-bridged anilinyldiphosphine ligands of the general formula (o$\left.\mathrm{Me}_{2} \mathrm{NC}_{6} \mathrm{H}_{4}\right)_{2} \mathrm{P}(\mathrm{X}) \mathrm{P}\left(o-\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{NMe}_{2}\right)_{2}\left(\mathrm{X}=\mathrm{CH}_{2}\right.$ (dmapm), $\left(\mathrm{CH}_{2}\right)_{2}$ (dmape), cyclic-C5 $\mathrm{H}_{8}$ (dmapcp); Chart 2.1) and investigates their coordination chemistry with $\mathrm{Pt}^{\mathrm{II}}$ and $\mathrm{Pd}^{\mathrm{II}}$. The syntheses of the complexes are given in Section 2.9.2, and ORTEP representations of the molecular structures of $\left[\mathrm{PtCl}\left(P, P^{\prime}, N \text {-dmapcp }\right)\right]^{+}$(Figure 2.4), $\mathrm{PtCl}_{2}\left(P, P^{\prime}-\mathrm{dmape}\right)$ (Figure $2.10)$ and $[\mathrm{PdCl}(\mathrm{dmapeO})]_{2}{ }^{2+}$ (Figure 2.16) are presented.

The behaviour of a selection of the complexes dissolved in chlorinated solvents is investigated: thermodynamic parameters for the equilibrium between $P, P^{\prime}-$ and $P, P^{\prime}, N$ -
bound dmape are evaluated for $\mathrm{MCl}_{2}$ (dmape) $(\mathrm{M}=\mathrm{Pd}, \mathrm{Pt})$ (Section 2.4.2.1); exchange of free and coordinated anilinyl N -atoms is demonstrated for $\left[\mathrm{MCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl}$ and a mechanism for the stereoselective formation of these compounds is presented (Section 2.4.1).

The possible structure(s) of organometallic intermediates which result from the reaction of dmapcp (Section 2.5) and dmapm (Section 2.5.8) with $\operatorname{PdX} X_{2}$ (diolefin) $(X=$ halide; diolefin $=\operatorname{cod}, \operatorname{nbd})$ en route to the formation of the expected metal-ligand complexes are discussed, and the reaction of $\mathrm{PdCl}_{2}$ (dmape) with KOH to form a bis(phosphine) monooxide (BPMO) complex (Section 2.6.1), as well as with other bases and $\mathrm{Pd}^{0}$ to give metal-metal bonded species (Section 2.6.2), is investigated.

### 2.3 The 2-Anilinyldiphosphine Ligands

### 2.3.1 Historical

A family of 2 -anilinyldiphosphine ligands of formula $\left(o-\mathrm{NMe}_{2} \mathrm{C}_{6} \mathrm{H}_{4}\right)_{2} \mathrm{P}(\mathrm{X}) \mathrm{P}(o-$ $\left.\mathrm{NMe}_{2} \mathrm{C}_{6} \mathrm{H}_{4}\right)_{2}\left(\mathrm{X}=\mathrm{CH}_{2}\right.$ (dmapm), $\left(\mathrm{CH}_{2}\right)_{2}$ (dmape), cyclic- $\mathrm{C}_{5} \mathrm{H}_{8}$ (dmapcp); Chart 2.1) was synthesised during the course of this work. The ligand family was initially conceived by Dr. Martin Smith, a postdoctoral fellow in the James laboratory during 1992-3, as a variation on the $p$-anilinyldiphosphine compounds which had been made previously by Tóth et al. ${ }^{1-4} \mathrm{He}$ attempted to make dmape and dmapcp, but was not able to isolate them pure. A subsequent postdoctoral fellow, Dr. Patric Meessen (1998-9), made subtle modifications to the syntheses which resulted in the isolation of pure dmape and dmapcp. This author, using the procedure developed by Meessen, was the first to make dmapm.

### 2.3.2 Synthesis

Sulphonated phosphines, like TPPTS, are typically made by the direct action of oleum on the corresponding neutral ligand; sulphonation occurs exclusively in the meta position. ${ }^{23}$ Because of the oxidising effects of the oleum, a significant proportion of the phosphine is converted to phosphine oxide which complicates the purification process, and the harsh reaction conditions preclude modification of ligands like DIOP which bear sensitive (in this case, acetal) functional groups. ${ }^{24}$ A solution to the former problem involves reduction of the phosphine oxide by trichlorosilane following conversion of the
sulphonates to sulphonic esters; hydrolysis of the esters then regenerates the watersoluble ligand. ${ }^{25}$ An important procedure by Herrmann et al. allows direct sulphonation of arylphosphines without oxidation of the P-atom. ${ }^{26}$ Here, the sulphonating reagent is the superacidic mixture of orthoboric and anhydrous sulphuric acid. Because free $\mathrm{SO}_{3}$ is absent and because the P -atom is protected by protonation, oxidation is eliminated.

As an alternate approach, sulphonate groups can be introduced during the synthesis of the aryl phosphine according to Scheme 2.3.27

## Scheme 2.3



In a similar manner, the water-soluble soluble phosphines $\mathrm{Ar}_{3-n} \mathrm{P}\left(m-\mathrm{SO}_{3}-\mathrm{C}_{6} \mathrm{H}_{4}\right)_{n}(n=1-3$; $\mathrm{Ar}=\mathrm{Ph}, 2-\mathrm{py}, 3-\mathrm{py}$ ) can be made by the reaction of $p$-fluorobenzenesulphonate with $\mathrm{PH}_{3}$ or primary or secondary phosphines in the "superbasic" medium KOH/DMSO. ${ }^{28}$ The last two approaches offer the significant advantages of eliminating phosphorus oxidation and giving freedom over the position of the substituent on the ring.

The synthesis of the anilinyldiphosphine ligands (Sections 2.9.1.1-2.9.1.3) is similar to that shown in Scheme 2.3 in that it involves coupling of a substituted arene with a phosphine, although in this case the alkali metal attends the aryl group. The procedure is the same in principle as that used for the synthesis of the pyridyldiphosphine ligands (Section 4.3.1). It involves a low-temperature, two-step, one-pot procedure in which $N, N$-dimethyl-2-lithioaniline is first generated by the reaction of ${ }^{n} \mathrm{BuLi}$ with $N, N$ -dimethyl-2-bromoaniline, and then this is exposed to 0.25 mol equiv. of the appropriate chlorodiphosphine (see Scheme 2.4 for an example). The ligand is removed from the reaction mixture by dissolution in dil. aq. HCl and purified after neutralisation by recrystallisation from boiling EtOH. The procedure results in an analytically pure, phosphine oxide-free product.

Scheme 2.4


### 2.3.3 Structures

Single crystals of dmape and dmapcp suitable for X-ray diffraction analysis were isolated by Meessen from $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solutions onto which EtOH had been layered; the structures are reported in this thesis because of their relevance to this work and because they have not yet appeared in the literature. The former compound crystallised with 2 independent molecules in the unit cell. One of these contained an inversion centre and is represented as an ORTEP in Figure 2.1. The other is essentially the same but does not contain an inversion centre. The ORTEP representation of dmapcp is given in Figure 2.2, and selected bond lengths and angles for the two ligands appear in Table 2.1 and Table 2.2, respectively.


Figure 2.1 ORTEP representation of the centrosymmetric crystallographic form of dmape ( $50 \%$ ellipsoids). H-atoms are omitted for clarity.

Table 2.1 Selected bond distances $(\AA)$ and angles $\left({ }^{\circ}\right)$ for dmape with estimated standard deviations given in parentheses.

| $\mathrm{C}(35)-\mathrm{C}\left(35^{*}\right)$ | $1.538(4)$ | $\mathrm{P}(3)-\mathrm{C}(35)$ | $1.849(2)$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{P}(3)-\mathrm{C}(36)$ | $1.844(2)$ | $\mathrm{P}(3)-\mathrm{C}(44)$ | $1.837(2)$ |
| $\mathrm{N}(5)-\mathrm{C}(37)$ | $1.426(2)$ | $\mathrm{N}(5)-\mathrm{C}(42)$ | $1.466(3)$ |
| $\mathrm{N}(5)-\mathrm{C}(43)$ | $1.461(3)$ |  |  |
| $\mathrm{C}\left(35^{*}\right)-\mathrm{C}(35)-\mathrm{P}(3)$ | $110.7(2)$ | $\mathrm{C}(35)-\mathrm{P}(3)-\mathrm{C}(36)$ | $96.62(9)$ |
| $\mathrm{C}(35)-\mathrm{P}(3)-\mathrm{C}(44)$ | $101.99(8)$ | $\mathrm{C}(36)-\mathrm{P}(3)-\mathrm{C}(44)$ | $101.42(8)$ |
| $\mathrm{C}(37)-\mathrm{N}(5)-\mathrm{C}(42)$ | $115.2(2)$ | $\mathrm{C}(37)-\mathrm{N}(5)-\mathrm{C}(43)$ | $115.6(2)$ |
| $\mathrm{C}(42)-\mathrm{N}(5)-\mathrm{C}(43)$ | $111.2(2)$ |  |  |



Figure 2.2 ORTEP representation of dmapcp (50 \% ellipsoids). H-atoms are omitted for clarity.

Table 2.2 Selected bond distances $(\AA)$ and angles $\left({ }^{\circ}\right)$ for dmapcp with estimated standard deviations given in parentheses.

| $\mathrm{C}(1)-\mathrm{P}(1)$ | $1.882(2)$ | $\mathrm{C}(2)-\mathrm{P}(2)$ | $1.879(2)$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{C}(1)-\mathrm{C}(2)$ | $1.537(3)$ | $\mathrm{P}(1)-\mathrm{C}(6)$ | $1.852(2)$ |
| $\mathrm{P}(2)-\mathrm{C}(22)$ | $1.831(2)$ | $\mathrm{N}(1)-\mathrm{C}(7)$ | $1.441(3)$ |
| $\mathrm{N}(1)-\mathrm{C}(12)$ | $1.465(4)$ | $\mathrm{N}(4)-\mathrm{C}(31)$ | $1.411(3)$ |
| $\mathrm{N}(4)-\mathrm{C}(36)$ | $1.466(3)$ |  |  |
| $\mathrm{P}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | $108.47(16)$ | $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{P}(2)$ | $111.33(15)$ |
| $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{C}(6)$ | $99.75(10)$ | $\mathrm{C}(2)-\mathrm{P}(2)-\mathrm{C}(22)$ | $102.04(10$ |
| $\mathrm{C}(7)-\mathrm{N}(1)-\mathrm{C}(12)$ | $116.2(2)$ | $\mathrm{C}(31)-\mathrm{N}(4)-\mathrm{C}(37)$ | $115.4(2)$ |

## 2.4 $\mathbf{P t}^{\text {II }}$ and $\mathbf{P d}^{\text {II }}$ Complexes

Reaction of 1 equiv. of dmape or dmapcp with $\mathrm{PtCl}_{2}(\operatorname{cod})$ or trans $-\mathrm{PdCl}_{2}(\mathrm{PhCN})_{2}$ gives the $1: 1$ complexes $\mathrm{MCl}_{2}(\mathrm{P}-\mathrm{P})$ or $[\mathrm{MCl}(\mathrm{P}-\mathrm{P})] \mathrm{Cl}$ quantitatively. The reactions proceed swiftly in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at r.t., except that of dmapcp with $\mathrm{PtCl}_{2}$ (cod) which was successful when conducted in refluxing $\mathrm{CH}_{2} \mathrm{ClCH}_{2} \mathrm{Cl}$. An alternate synthesis of $\left[\mathrm{PtCl}\left(P, P^{\prime}, N-\right.\right.$ dmapcp) $] \mathrm{Cl}$ involves reaction of the ligand with cis $-\mathrm{PtCl}_{2}(\mathrm{MeCN})_{2}$ in refluxing MeCN . The complexes have been characterised by ${ }^{1} \mathrm{H},{ }^{1} \mathrm{H}\left\{{ }^{31} \mathrm{P}\right\}$ and ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopies and elemental analysis and, in the Pt cases, by X-ray crystallography. The molecular structure of $\left[\mathrm{PdCl}\left(P, P^{\prime}, N-\mathrm{dmapcp}\right)\right] \mathrm{Cl}$ was also determined but could not be refined sufficiently well for publication. The following sections describe in detail the coordination modes of the ligands with each metal, and the solution behaviour of the complexes. With the exception of organometallic intermediates resulting from reactions of dmapm with $\mathrm{PdX}_{2}$ (diolefin) $(\mathrm{X}=$ halide; diolefin $=\operatorname{cod}, \mathrm{nbd})($ Section 2.5.8), dmapm complexes are discussed in Chapter 3.

### 2.4.1 Dmapcp complexes

### 2.4.1.1 Platinum

The number and relative integrations of the singlets due to the $\mathrm{NCH}_{3}$ protons in the ${ }^{1} \mathrm{H}$ NMR spectra of anilinyldiphosphine complexes constitute an invaluable diagnostic tool for determining the overall structure of the molecule. The two anilinyl substituents on each P-atom in dmapcp are diastereotopic and are related to those on the opposite P -atom by a $C_{2}$ axis, i.e., the ligand bears homotopic pairs of diastereotopic anilinyl rings and the ${ }^{1} \mathrm{H}$ NMR spectrum therefore shows two singlets due to the $\mathrm{NCH}_{3}$ protons ( $\delta 2.55$ and 2.63). In the case of $\left[\operatorname{PtCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl}$, the $C_{2}$ symmetry is lifted and 4 sharp peaks due to $\mathrm{NCH}_{3}$ protons are apparent at $\delta 3.50,3.05,2.67$ and 2.22 in a 1:1:2:2 ratio (i.e., 3:3:6:6 protons). The remaining 6 protons are manifested by a broad peak at $\delta 2.32$ (Figure 2.3). The pattern of $\mathrm{NCH}_{3}$ peaks defines a $P, P^{\prime}, N$ coordination mode for the ligand; the cartoon in Chart 2.9 gives a representation of the grouping of $\mathrm{NCH}_{3}$ groups in the $\left[\mathrm{PtCl}\left(P, P^{\prime}, N \text {-dmapcp }\right)\right]^{+}$cation. On the basis of integration, the two most downfield singlets (equivalent to 3 protons each) are assigned unequivocally to methyl groups a and b which are associated with the Pt-bound N -atom: these peaks show the most dramatic
coordination shifts from their position in the free ligand ( $\Delta \delta=0.91$ and 0.46 ppm ), and they show 3-bond $\mathrm{H}^{195} \mathrm{Pt}$ coupling (with magnitudes of 17 and 22 Hz , respectively).


Figure 2.3 The $\delta 1-4$ region of the ${ }^{1} \mathrm{H}\left\{{ }^{31} \mathrm{P}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ) spectrum of $\left[\mathrm{PtCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl}$. Asterisks $\left(^{*}\right)$ and number symbols (\#) indicate peaks due to the $\mathrm{CH}_{2}$ and CH protons, respectively, in the ligand "backbone". Other assignments are discussed in the text. The singlet at $\delta 1.56$ is due to $\mathrm{H}_{2} \mathrm{O}$.

## Chart 2.9



For a structure like the one shown in Chart 2.9, 3 equal-intensity peaks due to methyl groups associated with free N -atoms are expected: $\mathbf{c}, \mathbf{d}, \mathbf{e}, \mathbf{f}$ and $\mathbf{g}, \mathbf{h}$. Peaks due to the last two pairs should have similar chemical shifts, while that due to $\mathbf{c}, \mathbf{d}$ is expected to be somewhat removed from the others. On this basis, the peak at $\delta 2.67$ ( 6 protons) is due to methyl groups $\mathbf{c}$ and $\mathbf{d}$ and those at $\delta 2.32$ ( 6 protons) and 2.22 ( 6 protons) are due to groups $\mathbf{e}-\mathbf{h}$.

The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum reveals chemically inequivalent P -atoms. A positive assignment of the peaks is possible because of the relative magnitudes of the associated ${ }^{1} J_{\mathrm{PPt}}$ values. ${ }^{1} J_{\mathrm{PPt}}$ values for P-atoms trans to Cl are typically on the order of 3500 Hz , e.g., 3490 Hz for $\mathrm{PtCl}_{2}$ (dpypcp) and 3480 Hz for $\mathrm{PtCl}_{2}$ (dpype) (Sections 4.7.7 and 4.7.10, respectively), and are lower for P trans to N, e.g., 3200 Hz for $\left[\mathrm{Pt}_{2}(\text { dpype })_{2}\right]^{4+}$ (Section 4.7.21). Thus, the peak at $\delta 18.9\left({ }^{1} J_{\mathrm{PPt}}=3490 \mathrm{~Hz}\right)$ is due to $\mathrm{P}_{\mathrm{A}}$ (trans to Cl$)$ while that at $\delta$ $28.6\left({ }^{1} J_{\mathrm{PPt}}=3400 \mathrm{~Hz}\right)$ is due to $\mathrm{P}_{\mathrm{B}}($ trans to N$)$.

The structure of $\left[\mathrm{PtCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl} \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2} \cdot 1.46 \mathrm{H}_{2} \mathrm{O}$ was determined by X-ray crystallography (Figure 2.4) using crystals prepared by Meessen, and selected bond distances and angles are given in Table 2.3. The metal coordination sphere is approximately square planar, and in agreement with the solution NMR data, the ligand adopts a $P, P^{\prime}, N$-configuration.

The absolute configurations of $\mathrm{P}(1)$ and the methine C -atoms $\mathrm{C}(1)$ and $\mathrm{C}(2)$ are $R, S, S$, respectively, and the 5 -membered chelate ring is in the $\delta$-configuration. As the space group is $\mathrm{P} \overline{1}$ and $\mathrm{Z}=2$, the mirror image is present in the unit cell, but the diastereomeric forms $R, R, R$ and $S, S, S$ are absent. This is consistent with the fact that the substituents on the P -atoms of a chiral $C_{2}$-symmetric ligand are presented as pseudo-axial and pseudo-equatorial pairs, and the hypothesis that only the equatorial of these are sterically available for binding to a square planar metal centre. Thus, the $R, R, R$ and $S, S, S$ forms of $\left[\mathrm{PtCl}\left(P, P^{\prime}, N \text {-dmapcp }\right)\right]^{+}$cannot arise. In order to show this, a $2 \mathrm{D}{ }^{1} \mathrm{H}$ EXSY experiment was conducted (Figure 2.5).


Figure 2.4 ORTEP representation (50 \% ellipsoids) of $\left[\mathrm{PtCl}\left(P, P^{\prime}, N \text {-dmapcp }\right)\right]^{+} . \mathrm{H}-$ atoms have been omitted for clarity.

Table 2.3 Selected bond distances $(\AA)$ and angles $\left({ }^{\circ}\right)$ for $\left[\operatorname{PtCl}\left(P, P^{\prime}, N-\right.\right.$ dmapcp) $] \mathrm{Cl} \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2} \cdot 1.46 \mathrm{H}_{2} \mathrm{O}$ with estimated standard deviations given in parentheses.

| $\mathrm{Pt}(1)-\mathrm{P}(1)$ | $2.2012(12)$ | $\mathrm{Pt}(1)-\mathrm{P}(2)$ | $2.2646(10)$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{Pt}(1)-\mathrm{N}(1)$ | $2.184(3)$ | $\mathrm{Pt}(1)-\mathrm{Cl}(1)$ | $2.3642(13)$ |
| $\mathrm{P}(1)-\mathrm{C}(1)$ | $1.822(4)$ | $\mathrm{P}(1)-\mathrm{C}(6)$ | $1.782(4)$ |
| $\mathrm{P}(1)-\mathrm{C}(14)$ | $1.814(5)$ | $\mathrm{P}(2)-\mathrm{C}(2)$ | $1.848(4)$ |
| $\mathrm{P}(2)-\mathrm{C}(22)$ | $1.819(5)$ | $\mathrm{P}(2)-\mathrm{C}(30)$ | $1.829(4)$ |
| $\mathrm{N}(1)-\mathrm{C}(7)$ | $1.481(6)$ | $\mathrm{N}(1)-\mathrm{C}(12)$ | $1.490(6)$ |
| $\mathrm{N}(1)-\mathrm{C}(13)$ | $1.496(6)$ | $\mathrm{N}(2)-\mathrm{C}(15)$ | $1.452(6)$ |
| $\mathrm{N}(2)-\mathrm{C}(20)$ | $1.500(6)$ | $\mathrm{N}(2)-\mathrm{C}(21)$ | $1.449(6)$ |
| $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{N}(1)$ | $84.07(11)$ | $\mathrm{P}(2)-\mathrm{Pt}(1)-\mathrm{Cl}(1)$ | $94.08(4)$ |
| $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{P}(2)$ | $87.43(4)$ | $\mathrm{Cl}(1)-\mathrm{Pt}(1)-\mathrm{N}(1)$ | $94.53(11)$ |
| $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{C}(6)$ | $112.1(2)$ | $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{C}(14)$ | $109.1(2)$ |
| $\mathrm{C}(6)-\mathrm{P}(1)-\mathrm{C}(14)$ | $115.9(2)$ | $\mathrm{C}(12)-\mathrm{N}(1)-\mathrm{C}(13)$ | $109.8(3)$ |
| $\mathrm{C}(7)-\mathrm{N}(1)-\mathrm{C}(12)$ | $108.3(4)$ | $\mathrm{C}(7)-\mathrm{N}(1)-\mathrm{C}(13)$ | $109.2(4)$ |
| $\mathrm{C}(20)-\mathrm{N}(2)-\mathrm{C}(15)$ | $114.6(4)$ | $\mathrm{C}(20)-\mathrm{N}(2)-\mathrm{C}(21)$ | $109.5(4)$ |
| $\mathrm{C}(15)-\mathrm{N}(2)-\mathrm{C}(21)$ | $109.9(4)$ |  |  |



Figure 2.5 The $\delta 2-4$ range of the $2 \mathrm{D}{ }^{1} \mathrm{H}$ EXSY $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right)$ spectrum of $\left[\mathrm{PtCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl}$.

If the "pendant" and bound N -atoms are in free chemical exchange, the stereogenic P-atoms should be racemized. If, however, only pseudo-equatorial anilinyl rings can bind the square planar metal centre, then methyl groups $\mathbf{a}$ and $\mathbf{b}$ cannot be in exchange with $\mathbf{c}$ and d, i.e., with methyl groups associated with the other (pseudo-axial) anilinyl group attached to the same (bound) P-atom. Rather, $\mathbf{a}$ and $\mathbf{b}$ can only be in exchange with the $\mathrm{NCH}_{3}$ protons of the corresponding pseudo-equatorial anilinyl ring on the other P -atom. This is clearly demonstrated in Figure 2.5: $\mathbf{a}$ and $\mathbf{b}$ are in chemical
exchange with $\mathbf{g}, \mathbf{h}$ and not with $\mathbf{c , d}$ or $\mathbf{e}, \mathbf{f}$. Instead, $\mathbf{c}, \mathbf{d}$ and $\mathbf{e}, \mathbf{f}$ are in exchange with one another. If it is assumed that an associative mechanism is more likely than a dissociative one for a $\mathrm{d}^{8}$ square planar metal centre, these data can be interpreted in light of the exchange pathways illustrated in Scheme 2.5 (for clarity, "bonding" anilinyl rings have been simplified to ethyl chains, while "pendant" rings have been omitted altogether. The single positive charge on each ion has also been omitted.)

## Scheme 2.5



I

Only one diastereomer of the postulated trigonal bipyramidal $P, P^{\prime}, N, N^{\prime}$ intermediate can lead to the exchange of P -atoms. Inspection of the crystal structure (Figure 2.4) shows no obvious reason why the "non-productive" diastereomer (I) should not also form, however. The broad appearance of the peak due to e,f is tentatively attributed to the rapid equilibrium formation of this intermediate, i.e., to the reversible binding of N(3) in Figure 2.4.

The aqueous conductivity of $\left[\mathrm{PtCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl}$ is $150 \mathrm{ohm}^{-1} \mathrm{~mol}^{-1} \mathrm{~cm}^{2}$, consistent with a 1:1 conductor, i.e., the second chloride ligand does not dissociate. In
addition, the $\mathrm{Cl}^{-}$counter-ion is easily exchanged for $\mathrm{PF}_{6}{ }^{-}$by reaction with $\mathrm{NH}_{4} \mathrm{PF}_{6}$ in acetone. Even in the presence of a vast excess of the ammonium salt, only the ionic chloride is replaced under these conditions.

### 2.4.1.2 Palladium

The ${ }^{1} \mathrm{H}$ NMR spectrum of $\left[\operatorname{PdCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl}$ is similar to that of $[\mathrm{PtCl}(\mathrm{dmapcp})] \mathrm{Cl}$, and shows 5 chemically inequivalent $\mathrm{NCH}_{3}$ peaks in the 1:1:2:2:2 integration ratio expected for a $P, P^{\prime}, N$ coordination mode of dmapcp (Section 2.4.1.1). In addition, the crystal structure (Figure 2.6) reveals a cation very similar to $[\mathrm{PtCl}(\mathrm{dmapcp})]^{+}$(Figure 2.4). However, the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ spectrum shows two closelyseparated singlets at $\delta 48.7$ and 49.6 instead of the anticipated AX pattern. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ spectra of $\left[\mathrm{MCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl}(\mathrm{M}=\mathrm{Pt}, \mathrm{Pd})$ are shown for comparison in Figure 2.7.


Figure 2.6 PLUTO representation of the molecular structure of $\left[\mathrm{PdCl}\left(P, P^{\prime}, N-\right.\right.$ dmapcp) $]^{+}$. H -atoms are omitted for clarity.


Figure 2.7 ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \quad \mathrm{NMR}\left(121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right)$ spectra of $\left[\mathrm{MCl}\left(P, P^{\prime}, N-\right.\right.$ dmapcp) $] \mathrm{Cl}(\mathrm{M}=\mathrm{Pt}, \mathrm{Pd})$. Peaks due to ${ }^{31} \mathrm{P}-{ }^{195} \mathrm{Pt}$ coupling fall outside the range given for the Pt spectrum.

The 2D ${ }^{1} \mathrm{H}$ EXSY spectrum of $\mathrm{PdCl}_{2}$ (dmapcp) is similar to that of the Pt analogue, pointing to the same type of exchange between coordinated and free anilinyl N atoms. In light of these data, the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum is difficult to interpret: it suggests that the P -atoms are rendered chemically equivalent by the exchange.

Rapid exchange between P -atoms whose pendant N -containing "arms" are either coordinated or free has been observed by Stelzer and coworkers for the compound $\left[\mathrm{PdCl}\left(P, P^{\prime}, N-p y\left(\mathrm{CH}_{2}\right)_{2} \mathrm{P}(\mathrm{Me})\left(\mathrm{CH}_{2}\right)_{3} \mathrm{P}(\mathrm{Me})\left(\mathrm{CH}_{2}\right)_{2} \mathrm{py}\right)\right] \mathrm{Cl}$ (py $=o$-pyridyl), which gives rise to two ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ singlets at $\delta 13.7$ and $15.5 .{ }^{29}$ In the same manner that $\left[\mathrm{PtCl}\left(P, P^{\prime}, N-\right.\right.$ dmapcp) $]^{+}$gives the expected AX pattern, the analogous Pt complex of Stelzer gives two well separated signals for the chemically inequivalent $P$-atoms at $\delta-6.2$ and -12.9 .

Reaction of $\left[\mathrm{PdCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl}$ with an excess of the mild halideabstracting reagent $\mathrm{NH}_{4} \mathrm{PF}_{6}$ in acetone gives $\left[\mathrm{PdCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right]\left[\mathrm{PF}_{6}\right]$. In water, however, the molar conductivity is $200 \mathrm{ohm}^{-1} \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$ which perhaps indicates that the second chloride dissociates to give $\left[\mathrm{Pd}\left(\mathrm{OH}_{2}\right)\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl}_{2}$.

### 2.4.2 Dmape complexes

### 2.4.2.1 Solution equilibrium

The r.t. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of $\mathrm{PtCl}_{2}$ (dmape) consists of several very broad, illdefined peaks in the range $15-70 \mathrm{ppm}$. At less than $c a .250 \mathrm{~K}$, the spectrum resolves into 3 singlets and associated Pt "satellites" (Figure 2.8). The peak at $\delta 46$ is due to $\mathrm{PtCl}_{2}\left(P, P^{\prime}\right.$-dmape) and those at $\delta 32$ and 53 correspond to the chemically inequivalent P atoms of $\left[\mathrm{PtCl}\left(P, P^{\prime}, N\right.\right.$-dmape $\left.)\right] \mathrm{Cl}$.


Figure 2.8 The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 240 \mathrm{~K}$ ) spectrum of $\mathrm{PtCl}_{2}$ (dmape). The * symbol designates peaks due to $\mathrm{PtCl}_{2}\left(P, P^{\prime}\right.$-dmape) and \# denotes those due to $\left[\mathrm{PtCl}\left(P, P, N^{\prime}\right.\right.$-dmape $\left.)\right] \mathrm{Cl}$.

The peak assignments were confirmed by the following experiment. $\mathrm{PtCl}_{2}$ (dmape) was reacted with $\mathrm{NH}_{4} \mathrm{PF}_{6}$ in acetone to give $\left[\mathrm{PtCl}\left(P, P^{\prime}, N\right.\right.$-dmape $\left.)\right]\left[\mathrm{PF}_{6}\right]$. Elemental analysis confirmed that even though a large excess of the halide abstracting reagent was used, only one chloride ligand was removed. The r.t. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of this complex showed singlets at $\delta 31.6$ and 52.7 which correspond closely to two of the three peaks observed in the low temperature spectra of $\mathrm{PtCl}_{2}$ (dmape). As for $\left[\mathrm{PtCl}\left(P, P^{\prime}, N-\right.\right.$ dmapcp) $]^{+}$, 2-bond PP coupling was not observed. The remaining singlet must
correspond to a $C_{2}$-symmetric complex which could be either $\mathrm{PtCl}_{2}\left(P, P^{\prime}\right.$-dmape) or $\left[\operatorname{Pt}\left(P, P^{\prime}, N, N^{\prime}\right.\right.$-dmape $\left.)\right] \mathrm{Cl}_{2}$, but the failure to generate the latter compound synthetically rules it out.

The Pd analogue $\mathrm{PdCl}_{2}$ (dmape) exhibited analogous behaviour. Its r.t. $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ solution ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum showed a single broad peak centred at $c a .66 \mathrm{ppm}$. At lower temperatures (less than ca. 250 K ), this peak diminished and two new singlets at $\delta$ 60.5 and 73.4 appeared. Reaction of $\mathrm{PdCl}_{2}$ (dmape) with excess $\mathrm{NH}_{4} \mathrm{PF}_{6}$ in acetone gave $\left[\mathrm{PdCl}\left(P, P^{\prime}, N\right.\right.$-dmape $\left.)\right]\left[\mathrm{PF}_{6}\right]$ with two ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ singlets at $\delta 60.5$ and 73.4. The $\delta 66.4$ singlet is due to the chemically equivalent P -atoms of $\mathrm{PdCl}_{2}\left(P, P^{\prime}\right.$-dmape) while those at $\delta 60.5$ and 73.4 belong to the inequivalent P -atoms of $\left[\mathrm{PdCl}\left(P, P^{\prime}, N\right.\right.$-dmape $\left.)\right] \mathrm{Cl}\left({ }^{2} J_{\mathrm{PP}}\right.$ is unresolved for this compound).

Varying the temperature at which the spectra of $\mathrm{MCl}_{2}$ (dmape) $(\mathrm{M}=\mathrm{Pt}, \mathrm{Pd})$ were acquired reversibly altered the relative peak intensities showing that $\mathrm{MCl}_{2}\left(P, P^{\prime}\right.$-dmape) and $\left[\mathrm{MCl}\left(P, P^{\prime}, N\right.\right.$-dmape $\left.)\right] \mathrm{Cl}$ are in thermal equilibrium in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution. With use of the protocol given in Section 2.9.6, K values for the equilibrium shown in Chart 2.10 were determined at $210-250 \mathrm{~K}$ by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy; the resulting Van't Hoff plots appear in Figure 2.9.

## Chart 2.10





Figure 2.9 Van't Hoff plot for the $\mathrm{MCl}_{2}\left(P, P^{\prime}\right.$-dmape $) \rightleftharpoons\left[\mathrm{MCl}\left(P, P^{\prime}, N\right.\right.$-dmape $\left.)\right] \mathrm{Cl}$ equilibrium.

The determined thermodynamic parameters are $\Delta \mathrm{H}^{\circ}=-19 \pm 4 \mathrm{~kJ} \mathrm{~mol}^{-1}$ and $\Delta \mathrm{S}^{\circ}=$ $-100 \pm 30 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$ for $\mathrm{PtCl}_{2}$ (dmape), and $\Delta \mathrm{H}^{\circ}=-11 \pm 7 \mathrm{~kJ} \mathrm{~mol}^{-1}$ and $\Delta \mathrm{S}^{\circ}=-$ $60 \pm 20 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$ for $\mathrm{PdCl}_{2}$ (dmape). The entropy decrease must be the result of solvent ordering about the charged species, and the exothermicity is due predominantly to the formation of strong $\mathrm{M}-\mathrm{N}$ bonds ( $\nu s . \mathrm{M}-\mathrm{Cl}$ ) with that for Pt being stronger than for Pd . The large error values result from less than ideal reproducibility between separate measurements.

### 2.4.2.2 Structure

The structure of $\mathrm{PtCl}_{2}$ (dmape) $\cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$ was determined by X-ray crystallography using crystals prepared by Meessen (Figure 2.10); selected bond distances and angles are given in Table 2.4.


Figure 2.10 ORTEP representation ( $50 \%$ ellipsoids) of the molecular structure of $\mathrm{PtCl}_{2}$ (dmape). Except for those in the "backbone" of the ligand, H -atoms have been omitted for clarity.

Table 2.4 Selected bond distances $(\AA)$ and angles $\left({ }^{\circ}\right)$ for $\mathrm{PtCl}_{2}($ dmape $) \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$ with estimated standard deviations given in parentheses.

| $\mathrm{Pt}(1)-\mathrm{P}(1)$ | $2.2317(13)$ | $\mathrm{Pt}(1)-\mathrm{P}(2)$ | $2.2355(13)$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{Pt}(1)-\mathrm{Cl}(1)$ | $2.3728(12)$ | $\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | $2.3776(13)$ |
| $\mathrm{P}(1)-\mathrm{C}(1)$ | $1.8819(5)$ | $\mathrm{P}(1)-\mathrm{C}(3)$ | $1.810(4)$ |
| $\mathrm{P}(1)-\mathrm{C}(11)$ | $1.818(7)$ | $\mathrm{P}(2)-\mathrm{C}(2)$ | $1.833(5)$ |
| $\mathrm{P}(2)-\mathrm{C}(19)$ | $1.844(7)$ | $\mathrm{P}(2)-\mathrm{C}(27)$ | $1.813(4)$ |
| $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | $92.74(5)$ | $\mathrm{P}(2)-\mathrm{Pt}(1)-\mathrm{Cl}(1)$ | $91.25(5)$ |
| $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{P}(2)$ | $86.07(5)$ | $\mathrm{Cl}(1)-\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | $90.99(5)$ |
| $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{C}(3)$ | $109.2(2)$ | $\mathrm{C}(3)-\mathrm{P}(1)-\mathrm{C}(11)$ | $105.5(3)$ |
| $\mathrm{C}(11)-\mathrm{P}(1)-\mathrm{C}(1)$ | $109.2(3)$ | $\mathrm{C}(2)-\mathrm{P}(2)-\mathrm{C}(19)$ | $106.2(3)$ |
| $\mathrm{C}(19)-\mathrm{P}(2)-\mathrm{C}(27)$ | $105.7(3)$ | $\mathrm{C}(2)-\mathrm{P}(2)-\mathrm{C}(27)$ | $110.2(2)$ |

### 2.5 Organometallic Pd Anilinyldiphosphine Intermediates

In contrast to the reaction between dmapcp and trans $-\mathrm{PdCl}_{2}(\mathrm{PhCN})_{2}$ which gives $\left[\mathrm{PdCl}\left(P, P, N^{\prime}-\mathrm{dmapcp}\right)\right] \mathrm{Cl}$ cleanly, the ligand reacts with $\mathrm{PdCl}_{2}(\operatorname{cod})$ to give not only this product, but also another whose ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum is characterised by an AX pattern ( $\delta_{\mathrm{A}} 36.5$ (d), $\delta_{\mathrm{X}} 47.8$ (d), ${ }^{2} J_{\mathrm{PAPX}}=8.8 \mathrm{~Hz}$ ) (Figure 2.11). Because of several reasons: the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum depends both on the nature of the diolefin and the halide (Section 2.5.3); the product is a kinetic one (Section 2.5.5) and not the result of a "back-reaction" (Section 2.5.4); and finally, ${ }^{1}$ H NMR peaks characteristic of coordinated olefin are seen (Section 2.5.6), the second product is proposed to be an organometallic intermediate bearing both the diolefin and the anilinyldiphosphine ligand. Based on these observations, on the limiting coordination number of 5 for $\mathrm{Pd}^{\mathrm{II}}$, and on the known susceptibility of Pd-coordinated olefins to nucleophilic attack (Section 2.5.2), the structure of the intermediate is proposed to be that depicted in Chart 2.11 (three of the anilinyl rings have been omitted for clarity.)


Figure 2.11 The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ) spectrum of the isolated product mixture from the reaction between dmapcp and $\mathrm{PdCl}_{2}(\operatorname{cod})$. The * symbol denotes peaks due to $\left[\mathrm{PdCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl}$.

## Chart 2.11



### 2.5.1 An introduction to 5-coordinate Pt and Pd complexes

Most 5-coordinate complexes of Pt and Pd are trigonal bipyramidal (rather than square pyramidal) and have the general formula $\mathrm{M}(\mathrm{N}-\mathrm{N})($ olefin $)(\mathrm{X})(\mathrm{Y}),{ }^{30}$ where $\mathrm{N}-\mathrm{N}$ is a bulky bidentate N -ligand such as 2,9-dimethyl-1,10-phenanthroline (dmphen), and X and Y are either two anions (usually halides or alkyl groups) or one anion and one neutral ligand.

Conditions favouring the formation of trigonal bipyramidal over square planar complexes of the group 10 metals are summarised in the following statements: ${ }^{31}$
(1) The strongest $\pi$-acceptor ligand (the olefin) lies in the equatorial plane where the greatest degree of back-bonding is expected.
(2) The most hindered ligand (typically the chelating $\mathrm{N}-\mathrm{N}$ ligand) occupies the two remaining equatorial sites so as to minimise its steric interactions with other ligands in the coordination sphere. Axial-equatorial dispositions of this ligand, though rare, are also known, e.g., in $\operatorname{PtMe}(d m p h e n)(E-$ $\mathrm{NCCH}=\mathrm{CHCN})\left(\mathrm{CH}\left(\mathrm{CO}_{2} \mathrm{Me}_{2}\right)^{2}{ }^{31}\right.$
(3) The strongest donor ligands occupy the axial positions.

Of particular relevance to this work is the reaction shown in Scheme 2.6.32 The Pt reactant is the product of the reaction between $\mathrm{PtCl}_{2}(\operatorname{cod})$ and $\mathrm{NaOMe},{ }^{33-35}$ while the product is very similar to that shown in Chart 2.11. The olefinic moiety is "held fast" because it is part of a chelating $\eta^{1}, \eta^{2}$ modified cod ligand.

The complex shown in Chart 2.11 may represent a new class of complexes. To date, the only known 5 -coordinate, $\mathrm{Pd}^{\mathrm{II}}$-phosphine-olefin complexes have the general formula $\left[\mathrm{Pd}(\mathrm{Cp})(\text { olefin })\left(\mathrm{PR}_{3}\right)\right]^{+} .36,37$

## Scheme 2.6



### 2.5.2 Nucleophilic attack on coordinated olefin

It has been known since the 1930s that coordination of olefins to platinum group metals renders them susceptible to nucleophilic attack. ${ }^{38}$ Of particular relevance to this thesis is attack by amines ${ }^{39}$ and phosphines. ${ }^{40,41}$ However, there have been no reports of the particular type of reaction described here, i.e., nucleophilic attack by one donor atom of a polydentate ligand that gives rise to a complex in which at least one of the donors is bound to the metal and one has reacted with the olefin (in this case to generate an ammonium species).

The 5-coordinate organometallic intermediate proposed in the reaction between dmapcp and $\mathrm{PdCl}_{2}$ (cod) results from nucleophilic attack by an anilinyl N -atom at one of the coordinated olefinic C -atoms, causing a slip in the diolefin coordination mode from $\eta^{2}, \eta^{2}$ to $\eta^{1}, \eta^{2}$; this prevents displacement of the $C_{8}$ moiety. Whether coordination of the metal by $P$ precedes the nucleophilic attack at the bound olefin is unknown. The presence of multiple P - and N -atoms seems necessary for the formation of the 5 -coordinate complex: for example, an in situ reaction of $\mathrm{PdCl}_{2}(\operatorname{cod})$ with PMA gave the simple substitution product, $\mathrm{PdCl}_{2}(\mathrm{PMA})$, and no intermediates were detected ( $\mathrm{PMA}=\mathrm{Ph}_{2} \mathrm{P}$-o$\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{NMe}_{2}$ ).

### 2.5.3 Variation of diolefin and halide

Table 2.5 summarises the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR data for the reaction shown in Scheme 2.7. The data for pure $\left[\mathrm{PdCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl}$ dissolved in $\mathrm{CDCl}_{3}$ and $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ are included for reference purposes.

## Scheme 2.7

$$
\mathrm{PdX}_{2}(\text { diolefin })+\text { dmapcp } \rightarrow\left[\operatorname{PdX}\left(P, P^{\prime}, N \text {-dmapcp }\right)\right] \mathrm{X}(\mathbf{a})+\mathbf{b}
$$

Table 2.5 Summary of ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}(121 \mathrm{MHz}, 300 \mathrm{~K})$ data for the series of reactions shown in Scheme 2.7.

| Reaction | Solvent | diolefin | X | ${ }^{31} \mathrm{P}\left\{{ }^{\mathrm{I}} \mathrm{H}\right\}$ NMR chemical shift (ppm) $\left[^{2} J_{\mathrm{PP}}(\mathrm{Hz})\right]$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  | $\mathbf{a}^{\text {a }}$ | $\mathrm{b}^{\text {b }}$ |
| 1 | $\mathrm{CDCl}_{3}$ | cod | Cl | 48.4 | 36.8 [10.3] |
|  |  |  |  | 48.9 | 47.9 [10.3] |
| 2 | $\mathrm{CDCl}_{3}$ | nbd | Cl | 48.4 | 33.1 [13.0] |
|  |  |  |  | 49.0 | 49.6 [13.0] |
| 3 | $\mathrm{CDCl}_{3}$ | dcp | Cl | 48.4 | [13.0] |
|  |  |  |  | 48.9 |  |
| 4 | $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ | cod | Br | 47.0 | 34.7 [10.0] |
|  |  |  |  | 50.0 | 47.5 [10.0] |
| 5 | $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ | cod | I | 39.9 | - |
|  |  |  |  | 50.4 |  |
| Compound |  |  |  |  |  |
| $\begin{gathered} \text { Dmapcp } \\ {\left[\mathrm{PdCl}\left(P, P^{\prime}, N \text {-dmapcp }\right)\right] \mathrm{Cl}} \end{gathered}$ | $\mathrm{CDCl}_{3}$ |  |  | -25.6 |  |
|  | $\mathrm{CDCl}_{3}$ |  |  | 48.4 |  |
|  |  |  |  | 48.9 |  |
| $\left[\mathrm{PdCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl}$ | $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ |  |  | 48.6 |  |
|  |  |  |  | 48.8 |  |

[^0]The downfield ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ shifts given in Table 2.5 indicate that both P -atoms are bound to Pd . Peaks due to a are necessarily independent of the diolefin. Changing, however, from Cl to Br to I causes the downfield singlet due to $\mathbf{a}$ to shift from $\delta 48.9$ to $\delta$ 50.4 , and the upfield singlet to shift from $\delta 48.4$ to $\delta 39.9$.

Table 2.5 clearly shows that both the diolefin and the halide are implicated in the second product $\mathbf{b}$ : variation of either results in variation of the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ shifts.

The r.t. reaction between $\mathrm{PdI}_{2}(\operatorname{cod})$ and dmapcp did not produce $\mathbf{b}$ in detectable concentration. An independent synthesis of $\left[\operatorname{PdI}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right]$ I (Section 2.9.2.7) via
halide metathesis of $\left[\mathrm{PdCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl}$ with NaI gave a compound whose ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum was identical to that of the product of reaction 5 in Table 2.5. The reaction of dmapcp with $\mathrm{PdCl}_{2}(\mathrm{dcp})$ did not produce $\mathbf{b}$, either (reaction 3); an in situ NMR investigation revealed that $\left[\mathrm{PdCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl}$ was the sole product at r.t. These results indicate that the nature of the halide and olefin dramatically affect the stability of the 5-coordinate intermediate.

Reaction 2 was monitored by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy over the course of 10 d at r.t. Twenty minutes after the reagents had been mixed, integration revealed the mixture to be approximately $60 \% \mathbf{b}, 40 \% \mathbf{a}$. After 2 d , the mixture contained ca. $52 \% \mathbf{b}, 48 \% \mathbf{a}$ and after 10 d , this had dropped to $45 \% \mathbf{b}, 55 \% \mathbf{a}$. In order to ensure that all of $\mathbf{b}$ converts to a and that no decomposition occurs, this experiment needs to be repeated in the presence of an inert internal concentration standard.

### 2.5.4 Reaction between diolefin and $[\mathbf{P d C l}(P, P \prime, N$-dmapcp $)] \mathbf{C l}$

In situ NMR measurements revealed that $\left[\operatorname{PdCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl}$ did not react with 100 -fold excesses of cod, nbd or hxd, demonstrating that the diolefin-containing product $\mathbf{b}$ is a true intermediate en route to the formation of $\left[\operatorname{PdCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl}$ and not the result of a back-reaction between the product and the displaced diolefin.

### 2.5.5 Low temperature in situ reaction between $\mathbf{P d C l}_{2}(\operatorname{cod})$ and dmapep

The reaction between dmapcp and $\mathrm{PdCl}_{2}$ (cod) was followed by low temperature ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy. In this experiment, $\mathrm{CDCl}_{3}$ was added by vacuum transfer to an NMR tube containing the solid reagents held at 77 K . The solvent was allowed to melt at 230 K within the spectrometer probe. Within the time taken to make the first measurement ( 6 min ), the intermediate $\mathbf{b}$ had begun to form. It was not until after about 1 h that peaks due to $\left[\operatorname{PdCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl}$ appeared. At this point, the ligand had almost completely been consumed.

### 2.5.6 ${ }^{1} \mathrm{H}$ NMR spectroscopy

The ${ }^{1} \mathrm{H}$ NMR spectrum of the isolated product mixture from the reaction of $\mathrm{PdCl}_{2}(\operatorname{cod})$ and dmapcp with or without added $\mathrm{NH}_{4} \mathrm{PF}_{6}$ shows several peaks in addition to those due to $\left[\operatorname{PdCl}\left(P, P^{\prime}, N \text {-dmapcp }\right)\right]^{+}$(see Section 2.9.4.1 for full ${ }^{1} \mathrm{H}$ NMR data for the product of the reaction in the presence of $\mathrm{NH}_{4} \mathrm{PF}_{6}$ ). Most prominent are a pair of pseudoquartets that
appear at $\delta 5.23$ and 5.65 ; by virtue of their integrations and chemical shifts, these can be assigned to 2 inequivalent olefinic protons of a coordinated $\mathrm{C}_{8} \mathrm{H}_{12}$ moiety (Figure 2.12). (For useful reference, the olefinic protons of $\mathrm{PdCl}(\mathrm{Me})(\mathrm{cod})$ give rise to multiplets at $\delta$ 5.15 and $5.90,{ }^{42}$ while those of $[\mathrm{Pd}(\mu-\mathrm{Cl})(\mathrm{MeO}-c o d)]_{2}$ appear at $\delta 5.45$ and $\left.5.90 .4^{43}\right){ }^{1} \mathrm{H}^{1} \mathrm{H}$ COSY measurements reveal that each of these peaks is coupled to two others in the aliphatic region of the spectrum, consistent with the presence of a saturated organic component. In all, 9 protons of the anticipated 12 could be clearly identified with the aid of the COSY spectrum. A multiplet at high field ( $\delta 1.05$ ) is tentatively assigned to the proton attached to the Pd -bound C -atom. This proton is strongly coupled to another at much lower field ( $\delta 4.15$ ) which is therefore assigned as proton bound to the C -atom which has undergone the postulated nucleophilic attack by N . In addition, the $\mathrm{NCH}_{3}$ region shows an "extra" 4 singlets at $\delta 2.90,2.85,2.21$ and 2.18 in a $1: 2: 4: 1$ ratio, consistent with the number and type of $\mathrm{NCH}_{3}$ protons illustrated in Chart 2.11. Presumably, the two $1: 1$ singlets are due to the methyl groups bonded to the N -atom responsible for the nucleophilic attack. Because these are well separated, it is concluded that the N -atom in $\mathbf{b}$ is a different type from that in the thermodynamic product $[\operatorname{PdCl}(P, P ', N$-dmapcp $)] \mathrm{Cl}$.


Figure 2.12 The $\delta 4.8-6.0$ region of the ${ }^{1} \mathrm{H} \mathrm{NMR}\left(121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right)$ spectrum of the isolated product mixture from the r.t. reaction between $\mathrm{PdCl}_{2}$ (cod) and dmapcp.

### 2.5.7 Comparison between the isolated product mixtures from low and r.t. reactions

Section 2.9.4.1 describes the isolation of product mixtures from the reactions of dmapcp with $\mathrm{PdCl}_{2}(\operatorname{cod})$ in the presence of the mild halide-abstracting reagent $\mathrm{NH}_{4} \mathrm{PF}_{6}$ at r.t. and
$-40^{\circ} \mathrm{C}$. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra of these are shown in Figure 2.13; spectral data appear in Table 2.6.


Figure $2.13{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ) of the isolated product mixtures from the reaction between $\mathrm{PdCl}_{2}(\mathrm{cod})$ and dmapcp at (i) r.t. and (ii) $40^{\circ} \mathrm{C}$ recorded 0.5 h after making the samples. Spectrum (iii) shows the evolution of (ii) after 6 h at r.t. Peaks marked by asterisks are due to $\left[\mathrm{PdCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right]\left[\mathrm{PF}_{6}\right]$. Other assignments are discussed in the text.

Table 2.6 Summary of the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR data for the spectra shown in Figure 2.13, excluding peaks due to $\left[\mathrm{PdCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right]\left[\mathrm{PF}_{6}\right]$.

|  | ${ }^{31} \mathrm{P}\{\mathrm{H}\} \mathrm{NMR}$ chemical shift (ppm) $\left[^{2} J_{\mathrm{PP}}(\mathrm{Hz})\right]^{\mathrm{a}}$ |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Spectrum | $\mathbf{b}$ | $\mathbf{c}$ | $\mathbf{d}$ | $\mathbf{e}$ |  |  |
| (i) | $36.8[10.3]$ | - | - | - |  |  |
|  | $47.9[10.3]$ |  |  | - |  |  |
| (ii) | - | $33.8[111]$ | - |  |  |  |
|  |  | $38.6[111]$ |  |  |  |  |
| (iii) | $36.8[10.3]$ | $33.8[111]$ | $24.7[85.5]$ | $26.4[102]$ |  |  |
|  | $47.9[10.3]$ | $38.6[111]$ | $50.3[85.5]$ | $41.4[102]$ |  |  |

[^1]As spectrum (i) clearly demonstrates, the single organometallic product $\mathbf{b}$ resulting from the r.t. reaction in the presence of the halide-abstracting reagent is identical to the kinetic product of the $-40^{\circ} \mathrm{C}$ reaction in its absence (Section 2.5.5). The low temperature reaction in the presence of $\mathrm{NH}_{4} \mathrm{PF}_{6}$, however, produces a different result. Spectrum (ii) shows the two peaks due to $\left[\operatorname{PdCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right]\left[\mathrm{PF}_{6}\right]$ and an AX pattern due to another product, c. After 6 h at r.t., 5 species are seen: $\left[\operatorname{PdCl}\left(P, P^{\prime}, N-\right.\right.$ dmapcp) $]\left[\mathrm{PF}_{6}\right], \mathbf{b}, \mathbf{c}$, and new complexes $\mathbf{d}$ and $\mathbf{e}$ (spectrum (iii)); b-e all show AX patterns.

The most significant difference between $\mathbf{b}$ and $\mathbf{c}-\mathbf{e}$ is that $\mathbf{b}$ has a small ${ }^{2} J_{\mathrm{PP}}$ value of 10.3 Hz , while c-e have corresponding values in the range $85-111 \mathrm{~Hz}$. The small coupling constant observed for $\mathbf{b}$ is consistent with a cis disposition of P -atoms coordinated to Pd or Pt for the anilinyldiphosphine ligand family, e.g., ${ }^{2} J_{\mathrm{PP}}=12.3 \mathrm{~Hz}$ for $\operatorname{PtCl}\left(P, P^{\prime}, N\right.$-dmapcp $\left.)\right] \mathrm{Cl}$ (Section 2.9.2.1) and is too small to be observed for $\left[\mathrm{PtCl}\left(P, P^{\prime}, N\right.\right.$-dmape $\left.)\right]\left[\mathrm{PF}_{6}\right]$ (Section 2.9.2.4), $\left[\mathrm{PdCl}\left(P, P^{\prime}, N-\mathrm{L}\right)\right]\left[\mathrm{PF}_{6}\right]$ (L $=$ dmape (Section 2.9.2.10), or dmapcp (Section 2.9.2.8)). This, together with the NMe "fingerprint" in the ${ }^{1}$ H NMR spectrum of $\mathbf{b}$ (Section 2.5.6), is consistent with the structure given in Chart 2.11 , i.e., a structure in which both P -atoms are bound to Pd and one of the anilinyl N atoms acts as a nucleophile to attack the originally coordinated cod.

An alternate view has the anilinyldiphosphine ligand $P, N$-bound to the metal and one of the P-atoms acting as the nucleophile. In this case, 3-bond PP coupling should be observed. The only comparison available for the anilinyldiphosphine ligands are the complexes $[\mathrm{PdCl}(\text { dmapeO })]_{2}\left[\mathrm{PF}_{6}\right]_{2}\left({ }^{3} J_{\mathrm{PP}}=66.2 \mathrm{~Hz}\right.$; see Section 2.6.1 for discussion and Section 2.9.2.12 for synthesis) and $\mathrm{PdCl}(\mathrm{Me})\left(P, N\right.$-dmape) $\left({ }^{3} J_{\mathrm{PP}}=44.1 \mathrm{~Hz}\right.$; from the in situ reaction between $\mathrm{PdCl}(\mathrm{Me})(\mathrm{cod})$ and dmape). Although these couplings are on the order of $1 / 2$ of magnitude of those observed for $\mathbf{c}-\mathbf{e}$, they are much larger than observed for $\mathbf{b}$, and may indicate structures of the type shown in Chart 2.12 (anilinyl rings not involved in bonding have been omitted for clarity, and the counterion in each case is $\mathrm{PF}_{6}{ }^{-}$).

## Chart 2.12






The structures in Chart 2.12 are depicted as unipositive ions. If these complexes were dipositive, i.e., chloride free, they could not serve as intermediates en route to the formation of $\left[\mathrm{PdCl}\left(P, P^{\prime}, N \text {-dmapcp }\right)\right]^{+}$which is the ultimate product at r.t.

Clearly, the presence of a halide-abstracting reagent significantly impacts the path of the reaction at low temperature. However, the specific role of $\mathrm{NH}_{4} \mathrm{PF}_{6}$ is not understood, and positive assignments of $\mathbf{c}-\mathbf{e}$ cannot be made.

### 2.5.8 Variation of the anilinyldiphosphine ligand

The r.t. reaction between the $\mathrm{CH}_{2}$-bridged anilinyldiphosphine ligand dmapm and $\mathrm{PdCl}_{2}(\operatorname{cod})$ produces not one but two olefin-bearing intermediates en route to the formation of the intended product, $\mathrm{PdCl}_{2}(\mathrm{dmapm})$. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of an in situ reaction given by Scheme $2.8(\mathrm{X}=\mathrm{Cl})$ is shown in Figure 2.14; $\mathrm{PdCl}_{2}(\mathrm{dmapm})$ exists in organic solution as an equilibrium mixture of $\mathrm{PdCl}_{2}\left(P, P^{\prime}\right.$-dmapm) and $\mathrm{PdCl}_{2}(P, N-$ dmapm) (see Section 3.3.1).

Scheme 2.8

$$
\mathrm{PdX}_{2}(\text { diolefin })+\mathrm{dmapm} \rightarrow \mathrm{PdX}_{2}\left(P, P^{\prime}-\mathrm{dmapm}\right)(\mathbf{f})+\mathrm{PdX}_{2}(P, N-\mathrm{dmapm})(\mathbf{g})+\mathbf{h}+\mathbf{i}
$$



Figure 2.14 ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ) spectrum of the in situ reaction between dmapm and $\mathrm{PdCl}_{2}$ (cod). The ${ }^{*}$ symbol denotes peaks due to $\mathrm{PdCl}_{2}\left(P, N\right.$-dmapm) and \# identifies that due to $\mathrm{PdCl}_{2}\left(P, P^{\prime}-\mathrm{dmapm}\right)$. Other labels are discussed in the text.

Table 2.7 Summary of ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}(121 \mathrm{MHz}, 300 \mathrm{~K})$ data for a series of reactions of the type shown in Scheme 2.8. ${ }^{\text {a }}$

| Reaction | diolefin | X | ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR chemical shift (ppm) [ $\left.{ }^{2} J_{\mathrm{PP}}(\mathrm{Hz})\right]$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | $\mathbf{f}^{b}$ | $\mathbf{g}^{\mathbf{c}}$ | $\mathbf{h}^{\text {c }}$ | $i^{c}$ |
| 1 | cod | Cl | $-56.8$ | -40.0 [108] | 18.8 [83.3] | 19.6 [79.4] |
|  |  |  |  | 33.5 [108] | 46.4 [83.3] | 49.0 [79.4] |
| $2^{\text {d }}$ | nbd | Cl | -56.8 | -40.0 [108] | 16.3 [13:7] | - |
|  |  |  |  | 33.5 [108] | 33.8 [13.7] |  |
| 3 | cod | Br | -58.5 | -40.4 [112] | 16.2 [84.5] | 17.8 [80.6] |
|  |  |  |  | 32.4 [112] | 46.3 [84.5] | 49.4 [80.6] |
| Compound |  |  | -36.0 |  |  |  |
| dmapm |  |  |  |  |  |  |
| $\mathrm{PdCl}_{2}(P, N \text {-dmapm })^{\text {e }}$ |  |  | - | -40.0 [108] | - | - |
|  |  |  |  | 33.5 [108] |  |  |
| $\mathrm{PdCl}_{2}\left(P, P^{\prime}-\mathrm{dmapm}\right)^{\text {e }}$ |  |  | -56.8 | - | - | - |

${ }^{\text {a }}$ Measured in $\mathrm{CDCl}_{3}$ unless otherwise noted.
${ }^{\mathrm{b}}$ Singlets.
${ }^{\mathrm{c}}$ Doublets.
${ }^{\mathrm{d}}$ Measured in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$.
${ }^{\mathrm{e}}$ See Section 3.3.1.

Complexes containing P -atoms involved 4 -membered metallacycles (such as $\mathbf{f}$ ) give rise to ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR singlets in the high-field region, ${ }^{44}$ e.g., $\delta-56.8$ for $\mathrm{PdCl}_{2}\left(P, P^{\prime}-\right.$
dmapm). As peaks due to $\mathbf{h}$ and $\mathbf{i}$ are dramatically shifted from that of free dmapm, fall in the low-field region, and are well separated from each other, one P-atom of the ligand is likely involved in a 5 -membered $P, N$-chelate with $\mathrm{Pd}^{44}$ and the other probably participates in another type of interaction. Comparing reactions 1 and 2 in Table 2.7, it is evident that this second interaction (manifested by the doublets at $\delta 46.4$ and 33.8 , respectively) is very sensitive to the nature of the diolefin.

Consistent with these findings, and those for the reaction of $\mathrm{PdCl}_{2}(\operatorname{cod})$ with dmapcp, are the structures shown in Chart 2.13 (3 anilinyl rings have been omitted for clarity in each case). No concrete assignment of the isomers $\mathbf{h}$ and $\mathbf{i}$ is possible, however. These structures differ from that proposed for intermediate $\mathbf{b}$ (Section 2.5.3) in that a Patom rather than an N -atom attacks the coordinated olefin. This alleviates the 4 membered ring strain that would result if the N -atom were the nucleophile (Chart 2.11). Moreover, there are no known 5-coordinate $\mathrm{Pt} / \mathrm{Pd}^{\mathrm{II}}$-olefin complexes containing 4membered chelates.

## Chart 2.13




The distribution of products for reaction 1 (Table 2.7), for example, varies with time. Within the time taken to make the first NMR measurement, isomer i dominates. After $48 \mathrm{~h}, \mathbf{h}$ is more abundant than $\mathbf{i}$, and peaks due to $\mathrm{PdCl}_{2}(P, N$-dmapm) (f) and $\mathrm{PdCl}_{2}\left(P, P^{\prime}-\mathrm{dmapm}\right)(\mathrm{g})$ are also marginally larger than they were initially.

Shown in Figure 2.15 are the ${ }^{1} \mathrm{H}$ and ${ }^{1} \mathrm{H}\left\{{ }^{31} \mathrm{P}\right\}$ NMR spectra of the mixture isolated from the reaction of $\mathrm{PdCl}_{2}(\operatorname{cod})$ and dmapm; this spectrum is more complicated in the $\delta$
4.0-6.0 region than that of $\mathrm{PdCl}_{2}(\operatorname{cod})(\mathrm{dmapcp})$ because of the presence of not only olefinic but also methylene peaks due to the $\mathrm{PCH}_{2} \mathrm{P}$ protons.


Figure 2.15 ${ }^{1} \mathrm{H}\left\{{ }^{31} \mathrm{P}\right\}$ (top) and ${ }^{1} \mathrm{H}$ (bottom) NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ) spectra of the product mixture from the reaction between $\mathrm{PdCl}_{2}(\operatorname{cod})$ and dmapm. Peak assignments are discussed in the text.

The peaks labelled " $o$ " correspond to the protons due to the coordinated olefinic moiety. Those with the prefix " m " correspond to the methylene protons in the "backbone" of the dmapm liganḍ. In each case, there are two sets reflecting the organometallic intermediates $\mathbf{h}$ and $\mathbf{i}$.

The olefinic protons $\mathbf{o}(\mathbf{h})$ and $\mathbf{o}(\mathbf{i})$ are represented by pseudo-quartets in both the ${ }^{1} \mathrm{H}$ and ${ }^{1} \mathrm{H}\left\{{ }^{31} \mathrm{P}\right\}$ spectra, i.e., these protons are not strongly coupled to $P$. The chemical shifts of $\mathbf{o}(\mathbf{h})$ and $\mathbf{o}(\mathbf{i})$ are in the range typical for 5 -coordinate alkene complexes of $\mathrm{Pd}^{\mathrm{II}} .32,45{ }^{1} \mathrm{H}^{1} \mathrm{H}$ COSY measurements show each of the pair of $\mathbf{o}(\mathbf{h})$ and $\mathbf{o}(\mathbf{i})$ peaks to be coupled to one another and also to be coupled to several peaks in the aliphatic region of the spectrum ( $1-4 \mathrm{ppm}$ ), consistent with assignment of these to coordinated olefin.

The methylene protons $\mathbf{m}(\mathbf{h})$ and $\mathbf{m}(\mathbf{i})$ are represented by doublets in the ${ }^{1} \mathrm{H}\left\{{ }^{31} \mathrm{P}\right\}$ spectrum and their assignment is unequivocal: each proton is coupled only to one other
proton (the large magnitude, 19 Hz , identifies it as geminal coupling) and to two inequivalent P -atoms. This gives rise to a ddd pattern for each of the $\mathbf{m}(\mathbf{h})$ and $\mathbf{m}(\mathbf{i})$ peaks in the absence of the P -decoupler.

The multiplet at $\delta 4.15$ which collapses to a pseudo-triplet on P-decoupling is tentatively assigned to the proton bound to the C -atom which has undergone nucleophilic attack. This proton should be coupled to 2 inequivalent P -atoms via $\mathrm{P}-\mathrm{C}-H$ and $\mathrm{P}-\mathrm{C}-\mathrm{P}-$ $H$ connectivities. The corresponding "formerly olefinic" proton, which is bound to the C -atom bound to Pd , is identified by its characteristic upfield shift (a multiplet at $\delta 1.00$ ) and response to the P -decoupler (collapse to a pseudo-triplet). This proton is coupled to 2-inequivalent P -atoms through $\mathrm{P}-\mathrm{Pd}-\mathrm{C}-H$ and $\mathrm{P}-\mathrm{C}-\mathrm{C}-H$ linkages.

### 2.6 Reactions of $\mathbf{P d C l}_{2}$ (dmape) with Bases

### 2.6.1 Reaction with KOH

In an attempt to make anilinyldiphosphine analogues of the well-documented hydroxobridged $\mathrm{Pd}_{2}$ compounds of the type illustrated in Chart 2.14 (left; $\mathrm{P}=$ a tertiary phosphine ligand), ${ }^{46,47} \mathrm{PdCl}_{2}$ (dmape) was reacted with KOH according to the protocol outlined in Section 2.9.2.12. Pale yellow single crystals of $[\mathrm{PdCl}(\mathrm{dmapeO})]_{2}\left[\mathrm{PF}_{6}\right]_{2}$ (Chart $2.14,6$ anilinyl rings have been omitted for clarity) deposited from $\mathrm{CDCl}_{3}$ solution. The ORTEP representation is shown in Figure 2.16, and selected bond distances and angles appear in Table 2.8.

## Chart 2.14




### 2.6.1.1 Structure of $[\mathrm{PdCl}(\text { dmape } O)]_{2}{ }^{2+}$



Figure 2.16 ORTEP representation (50 \% ellipsoids) of the molecular structure of the $[\mathrm{PdCl}(\text { dmape })]_{2}{ }^{2+}$ cation. H -atoms are omitted for clarity.

Table 2.8 Selected bond distances $(\AA)$ and angles $\left({ }^{\circ}\right)$ for $[\mathrm{PdCl}(\text { dmapeO })]_{2}\left[\mathrm{PF}_{6}\right]_{2} \cdot 4 \mathrm{CDCl}_{3}$ with estimated standard deviations given in parentheses.

| $\mathrm{Pd}(1)-\mathrm{Cl}(1)$ | $2.296(2)$ | $\mathrm{Pd}(1)-\mathrm{N}(1)$ | $2.114(5)$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{Pd}(1)-\mathrm{P}(1)$ | $2.182(2)$ | $\mathrm{Pd}(1)-\mathrm{O}(1 \mathrm{~A})$ | $2.124(4)$ |
| $\mathrm{P}(2)-\mathrm{O}(1)$ | $1.515(4)$ | $\mathrm{Pd}(1)-\mathrm{Pd}\left(1^{*}\right)$ | $4.873(2)$ |
|  |  | $\mathrm{Cl}(1)-\mathrm{Pd}(1)-\mathrm{O}(1 \mathrm{~A})$ | $95.71(13)$ |
| $\mathrm{P}(1)-\mathrm{Pd}(1)-\mathrm{N}(1)$ | $87.17(14)$ | $\mathrm{P}(1)-\mathrm{C}(17)-\mathrm{C}(18)$ | $113.8(5)$ |
| $\mathrm{Pd}(1)-\mathrm{P}(1)-\mathrm{C}(17)$ | $111.2(2)$ | $\mathrm{C}(18)-\mathrm{P}(2)-\mathrm{O}(1)$ | $108.7(3)$ |
| $\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{P}(2)$ | $111.2(5)$ |  |  |
| $\mathrm{P}(2)-\mathrm{O}(1)-\mathrm{Pd}(1 \mathrm{~A})$ | $137.1(3)$ |  |  |

The structure consists of 2 face-to-face $\mathrm{Pd}^{\mathrm{II}}$ square planes in a head-to-tail (HT) orientation (i.e., they are related by an inversion centre which lies at the mid-point of the $\mathrm{Pd}-\mathrm{Pd}$ axis). The metal centres are separated by a distance of $4.873 \AA$; each is $P, N$ chelated by the monooxide derivative of dmape, and $P, O$-bridged to the other. A 12membered ring containing the metal centres results, and this is flanked on either side by $\mathrm{CDCl}_{3}$ molecules (not shown in Figure 2.16).

The $\mathrm{P}-\mathrm{C}-\mathrm{C}$ angles in the dmapeO ligand "backbone" (113.8 and $111.2^{\circ}$ ) are very similar to that found for dmape ( $110.7^{\circ}$; Figure 2.1 ), indicating that the ligand is unstressed and that the Pd centres are too far removed from one another to interact. The $\mathrm{Pd}-\mathrm{P}$ and $\mathrm{Pd}-\mathrm{N}$ bond lengths ( 2.182 and $2.114 \AA$ ) as well as the $\mathrm{P}-\mathrm{Pd}-\mathrm{N}$ angle $\left(87.17^{\circ}\right)$ are similar to those found for $\mathrm{PdCl}_{2}(P, N$-dmapm) ( 2.178 and $2.132 \AA$, and $86.10^{\circ}$, respectively; Figure 3.4 , p. 94).

The P - O bond length ( $1.515 \AA$ ) is almost identical to those found recently within this laboratory for coordinated BINAPO in the complexes $[\mathrm{RuCl}(\mathrm{BINAPO})(\mathrm{N}-\mathrm{N})]\left[\mathrm{PF}_{6}\right]$ (1.518 $\AA$ for $\mathrm{N}-\mathrm{N}=$ bipy and $1.515 \AA$ for $\mathrm{N}-\mathrm{N}=$ phen), ${ }^{48}$ and is in the range typically found for coordinated $\mathrm{R}_{3} \mathrm{P}=\mathrm{O}(1.49-1.52 \AA) .49$

### 2.6.1.2 Formation of $[\mathrm{PdCl}(\text { dmape } \mathrm{O})]_{2}{ }^{2+}$

The dmapeO ligand represents an example of a bis(phosphine) monooxide (BPMO). Complexes of this ligand class have been investigated since 1996 in hydroformylation, ${ }^{50,51}$ hydrosilylation, ${ }^{52}$ hydrovinylation ${ }^{53}$ and oligomerisation and polymerisation reactions. ${ }^{54}$ Although BPMOs are now routinely made via metal-free organic synthesis (e.g., by benzylation followed by basic hydrolysis of the resulting phosphonium salt ${ }^{55}$ ) or with the aid of a Pd catalyst, ${ }^{56}$ this brief introduction will deal only with those BPMOs which result from reactions of metal-phosphine complexes and, once formed, remain bound to the metal. An excellent and more detailed introduction to the syntheses and uses of BPMOs can be found in the PhD thesis of Cyr. ${ }^{48}$

While there are several examples of oxidation of "dangling" P-atoms in complexes bearing polydentate ligands (e.g., $\mathrm{PdCl}_{2}\left(P, N\right.$-dmapmO) from $\mathrm{PdCl}_{2}$ (dmapm) (Section 3.3.5), and in $\mathrm{Co},{ }^{57,58} \mathrm{Mo},{ }^{59} \mathrm{Rh},{ }^{60}$ and other $\mathrm{Pd}{ }^{61,62}$ systems), in only a few cases do coordinated phosphine oxides result. ${ }^{58,59}$ Even more rare is the oxidation of a
coordinated diphosphine to give a BPMO in which both the $\mathrm{P}^{\mathrm{III}}$-atom and the O -atom are bound. Two examples of this are the formation of $\left[\left(\mathrm{Cp}^{*}\right) \mathrm{Ru}\left(\mathrm{O}_{2}\right)(P, O\right.$-dppmO $\left.)\right]\left[\mathrm{BF}_{4}\right]$ from $\left[\left(\mathrm{Cp}^{*}\right) \mathrm{Ru}\left(\mathrm{H}_{2}\right)\left(P, P^{\prime}-\mathrm{dppm}\right)\right]\left[\mathrm{BF}_{4}\right]$ via a multistep process ${ }^{63}$ and the oxidation of $\mathrm{RuCl}_{2}(\mathrm{BINAP})(\mathrm{N}-\mathrm{N})(\mathrm{N}-\mathrm{N}=$ bipy, phen) in MeOH to give $[\mathrm{RuCl}(\mathrm{BINAPO})(\mathrm{N}-\mathrm{N})] \mathrm{Cl}$ in which the BINAPO ligand is coordinated not only via the P - and O -atoms but also through 2 C -atoms of one of the naphthyl rings. ${ }^{48}$ The reaction of $\mathrm{PdCl}_{2}$ (dmape) with base represents another example of this uncommon occurrence, the reaction again probably requiring multiple steps (vide infra).

Alper and coworkers have shown that in the biphasic carbonylation of ArX catalysed by $\mathrm{PdCl}_{2}\left(\mathrm{PR}_{3}\right)_{2}$ in the presence of alkali, the active species is a $\mathrm{Pd}^{0}$ phosphine complex generated by the in situ reduction of $\mathrm{Pd}^{\text {II }}$ by $\mathrm{PR}_{3} / \mathrm{OH}^{-} .{ }^{64}$ Indeed, in many Pd catalysed coupling reactions (e.g., the Heck, ${ }^{65}$ Stille ${ }^{66}$ and Suzuki ${ }^{67}$ reactions, as well as aminations, ${ }^{68,69}$ and diaryl ether formations ${ }^{70}$ ), the true $\mathrm{Pd}^{0}$ active species is generated in situ by reduction of $\mathrm{Pd}^{\text {II }}$. In the Heck reaction, for example, the active catalyst is often derived from a mixture of $\mathrm{Pd}(\mathrm{OAc})_{2}$ and a phosphine ligand. The formation of $\mathrm{Pd}^{0}$ from this combination has been studied in detail by Amatore et al. ${ }^{71}$

The basic principle of $\mathrm{Pd}^{\mathrm{II}}$ reduction by $\mathrm{PR}_{3} / \mathrm{OH}^{-}$is outlined in Scheme 2.9.

## Scheme 2.9

$$
\mathrm{L}_{\mathrm{n}} \mathrm{Pd}^{\mathrm{II}}-\mathrm{PR}_{3}+\mathrm{OH}^{-} \rightarrow \mathrm{L}_{\mathrm{n}} \mathrm{Pd}^{0}+\mathrm{OPR}_{3}+\mathrm{H}^{+}
$$

The compound $[\mathrm{PdCl}(\mathrm{dmapeO})]_{2}\left[\mathrm{PF}_{6}\right]_{2}$ probably arises in two steps. First, reduction of $\mathrm{PdCl}_{2}$ (dmape) by $\mathrm{OH}^{-}$gives " $\mathrm{Pd}(\mathrm{dmapeO})$ " or " $\mathrm{Pd}(\mathrm{dmapeO}) \mathrm{Cl}$ "' which then reacts with the chlorinated solvent to generate the $\mathrm{Pd}^{\mathrm{II}}$ product. Reactions of $\mathrm{M}^{0}$ (phosphine) complexes $(\mathrm{M}=\mathrm{Pd}, \mathrm{Pt})$ with chlorinated solvents to generate the corresponding $\mathrm{M}^{\mathrm{II}}$ chloro species are well documented, ${ }^{72}$ and are also investigated in this thesis (Section 4.4.3.1).

In order to test this hypothesis, two concurrent experiments were conducted (Table 2.9). In the first, the reaction was performed as outlined in Section 2.9.2.12, while in the second, both the reduction and analysis of the product were done in the absence of a chlorinated solvent (Section 2.9.4.2).

Table 2.9 Colour changes observed for the reaction between $\mathrm{PdCl}_{2}$ (dmape) and KOH in $\mathrm{H}_{2} \mathrm{O} / \mathrm{CH}_{2} \mathrm{Cl}_{2}$ (I) and in $\mathrm{H}_{2} \mathrm{O} / \mathrm{CH}_{3} \mathrm{NO}_{2}$ (II).

|  | Prior to KOH addition |  | Upon KOH addition |  | After 20 h |  |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Layer | I | II | $\mathbf{I}$ | $\mathbf{I I}$ | I | $\mathbf{I I}$ |
| Aqueous | Colourless | Colourless | Colourless | Colourless | Colourless | Red |
| Organic | Yellow | Yellow | Orange | Yellow | Orange | Orange |

The two experiments differ significantly. Analysis of the organic fraction of experiment II by acetone- $\mathrm{d}_{6}$ solution ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy reveals broad peaks $(\delta 61,73)$ of the starting material $\mathrm{PdCl}_{2}$ (dmape). The baseline of this spectrum is undulating in the lowfield region, possibly reflecting the presence of fluxional " $\mathrm{Pd}^{0}$ (dmapeO)" and/or " $\mathrm{Pd}^{0} \mathrm{Cl}(\mathrm{dmapeO})$ ") species. (Variable temperature NMR experiments are needed to probe this phenomenon.) Most importantly, the spectrum does not contain peaks attributable to $[\mathrm{PdCl}(\text { dmape })]_{2}{ }^{2+}$, which supports the hypothesis that this cation results from the reaction of a $\mathrm{Pd}^{0}$ species with the chlorinated solvent.

### 2.6.2 Reaction of $\mathbf{P d C l}_{2}($ dmape $)$ with $K_{2} \mathbf{C O}_{3}, \mathrm{KO}^{t} \mathbf{B u}$ and $\mathbf{P d}_{2}(\mathbf{d b a})_{3} \cdot \mathbf{C H C l}_{3}$

An attempt was made to make the $O, O^{\prime}$-bonded maleate complex $\operatorname{Pd}(P, P-d m a p e)\left(O, O^{\prime}-\right.$ maleate) because of potential implication of the compound in the Pd-catalysed hydration of water-soluble olefins (see Chapter 5). Thus, an acetone solution containing $\mathrm{PdCl}_{2}$ (dmape) and an excess of maleic acid was stirred together with solid $\mathrm{K}_{2} \mathrm{CO}_{3}$; this resulted in a colour change from yellow to deep orange. Analysis of the orange product by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ spectroscopy revealed that two species were formed: one gave rise to a singlet at $\delta 35.2$ and the other to a pair of doublets ( $\delta 70.8$ and 86.2 ) which showed severe second-order distortion. Moreover, the same two products resulted from the reaction of $\mathrm{PdCl}_{2}$ (dmape) in the absence of maleic acid (Section 2.9.4.5) which showed that the olefin had not been incorporated. Further investigations showed that not only did these products arise from the reaction of $\mathrm{PdCl}_{2}$ (dmape) with $\mathrm{K}_{2} \mathrm{CO}_{3}$, but that they also resulted from the reaction with $\mathrm{KO}^{t} \mathrm{Bu}$ (Section 2.9.4.5). Moreover, reaction of trans$\mathrm{PdCl}_{2}\left(\mathrm{PhCN}_{2}, \mathrm{Pd}_{2}(\mathrm{dba})_{3} \cdot \mathrm{CHCl}_{3}\right.$ and dmape, which was done with the conscious aim of producing dmape-bridged $\mathrm{Pd}_{2}{ }^{\mathrm{I}}$ compounds, gave the same products (Section 2.9.2.13). These findings suggest that the base is acting to reduce the Pd , and that the products are likely to be $\mathrm{Pd}_{2}{ }^{1}$ complexes; those shown in Chart 2.15 would satisfy the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR
data (anilinyl rings not involved in coordination have been omitted for clarity). Unlike in the reaction of $\mathrm{PdCl}_{2}$ (dmape) with KOH , phosphine oxidation did not result in the analogous reactions with $\mathrm{K}_{2} \mathrm{CO}_{3}$ and $\mathrm{KO}^{\prime} \mathrm{Bu}$, pointing to a different reduction mechanism for these bases.

## Chart 2.15




### 2.7 Conclusions

An effective synthesis has been established for a family of $o$-anilinyldiphosphine ligands whose members differ from one another in the number and arrangement of C -atoms in the "bridge" linking the two P-atoms. The nature of this bridge is the determining factor in the mode of coordination of the ligands to $\mathrm{Pt}^{\mathrm{II}}$ and $\mathrm{Pd}^{\mathrm{II}}$. The "cyclopentyl-bridged" dmapcp binds in a $P, P^{\prime}, N$ fashion, while the "ethyl-bridged" dmape forms complexes which are in equilibrium between their $\mathrm{MX}_{2}\left(P, P^{\prime}\right.$-dmape) and [MX $\left(P, P^{\prime}, N\right.$-dmape $\left.)\right] \mathrm{X}$ isomers ( $\mathrm{X}=$ halide). The thermodynamic parameters associated with this equilibrium have been evaluated by variable temperature ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy to be: $\Delta \mathrm{H}^{\circ}=-$ $19 \pm 4 \mathrm{~kJ} \mathrm{~mol}^{-1}, \Delta \mathrm{~S}^{\circ}=-100 \pm 30 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$ for $\mathrm{M}=\mathrm{Pt}$, and $\Delta \mathrm{H}^{\circ}=11 \pm 7 \mathrm{~kJ} \mathrm{~mol}^{-1}, \Delta \mathrm{~S}^{\circ}$ $=-60 \pm 20 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$ for $\mathrm{M}=\mathrm{Pd}$. Two-dimensional ${ }^{1} \mathrm{H}$ EXSY measurements demonstrate that free and bound N -atoms in the complexes $\left[\mathrm{MCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl}$ are in chemical exchange via one of two diastereomeric 5-coordinate $P, P^{\prime}, N, N$, intermediates. Only enantiomers result from the combination of $R, R$ - or $S, S$-dmapcp with Pd and Pt , with the absolute configuration at the stereogenic P -centre being opposite to that of the methine C-atoms in the ligand "backbone": exchange does not occur between a coordinated anilinyl ring and the free ring associated with the same, i.e, bound, P-atom.

Water-soluble complexes $\left[\mathrm{MCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl}$ result via displacement of halide from the metal coordination sphere.

The reactions between dmapcp or dmapm and $\mathrm{PdX}_{2}$ (diolefin) ( $\mathrm{X}=$ halide; diolefin $=\operatorname{cod}, \operatorname{nbd})$ result in a mixture of products. The thermodynamic product is $\left[\operatorname{PdX}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{X}$, and the kinetic products are likely to be trigonal bipyramidal compounds with the general formula $\left[\operatorname{PdX}\left(\eta^{1}, \eta^{2}\right.\right.$-diolefin $\left.)(\mathrm{L})\right] \mathrm{X}$ where $\mathrm{L}=P, P^{\prime}$-dmapcp or $P, N$-dmapm. In these compounds, either a P - or an N -atom of the anilinyldiphosphine ligand participates in a nucleophilic attack on the coordinated diolefin.
$\mathrm{PdCl}_{2}$ (dmape) reacts with KOH in a $\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{H}_{2} \mathrm{O}$ mixture to form the bimetallic head-to-tail complex $[\mathrm{PdCl}(\mathrm{dmapeO})]_{2}{ }^{2+}$. This compound arises in two steps: reduction of $\mathrm{Pd}^{\mathrm{II}}$ to $\mathrm{Pd}^{0}$ by $\mathrm{OH}^{-}$with concomitant oxidation of phosphine to phosphine oxide, followed by oxidation of the metal by solvent to give the final product.
$\mathrm{PdCl}_{2}$ (dmape) also reacts with other bases $\left(\mathrm{K}_{2} \mathrm{CO}_{3}, \mathrm{KO}^{t} \mathrm{Bu}\right)$ and with $\mathrm{Pd}^{0}$ to give the dmape-bridged bimetallic complex $\mathrm{Pd}_{2} \mathrm{Cl}_{2}$ (dmape).

### 2.8 Recommendations for Future Work

### 2.8.1 Preparation of $\mathbf{P t}^{\mathbf{0}}$ and $\mathbf{P d}^{\mathbf{0}}$ complexes

In contrast to the $1: 1$ reactions of the pyridyldiphosphine ligands with $\mathrm{M}\left(\mathrm{PPh}_{3}\right)_{4}(\mathrm{M}=\mathrm{Pd}$, $\mathrm{Pd})$ which quickly generate $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}(\mathrm{P}-\mathrm{P})\left(\mathrm{P}-\mathrm{P}=\right.$ dpype, dpypcp) or $\mathrm{Pd}(\mathrm{P}-\mathrm{P})_{2}$ (Sections 4.5.22-25), the anilinyldiphosphine ligands do not react under the conditions tested, possibly for steric reasons. Other attempts were made during the course of this work to synthesise $\mathrm{M}^{0}$ complexes of the anilinyldiphosphine ligands; the most promising involved either reduction of the corresponding $\mathrm{M}^{\text {II }}$ complexes using $\mathrm{Na} / \mathrm{Hg}$, or photolysis of a $\mathrm{M}^{\mathrm{II}}$ (oxalate) complex.

Sodium amalgam reduction of $\mathrm{PtCl}_{2}$ (dmape) (Section 2.9.4.3) produced an orange product whose ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum showed the product to bear equivalent P -atoms ( $\delta_{\mathrm{P}} 38.9, \mathrm{~s},{ }^{1} J_{\mathrm{PPt}}=3580 \mathrm{~Hz}$ ). This product remains poorly characterised, but it could be the tetrahedral complex $\operatorname{Pt}\left(P, P^{\prime}, N, N^{\prime}\right.$-dmape $)$. Further work along the lines of this reaction will, in all likelihood, yield a new class of highly reactive $\mathrm{Pt}^{0}$ complexes.

Trogler's group pioneered the use of UV light to effect the reductive elimination of $\mathrm{CO}_{2}$ from Pt and Pd oxalate complexes (Scheme 2.10, Reaction 1). ${ }^{73}$ During this thesis work, the analogous reaction with $\operatorname{Pt}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)\left(P, P^{\prime}-\mathrm{dmape}\right)$ was attempted in the presence of dmm (Section 2.9.4.4), the function of the olefin being to trap the reactive, photochemically generated "Pt(dmape)" (Scheme 2.10, reaction 2).

## Scheme 2.10

$$
\begin{align*}
& \mathrm{Pt}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right) \mathrm{L}_{2} \rightarrow \text { '"PtLe" }+2 \mathrm{CO}_{2}  \tag{1}\\
& \mathrm{Pt}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)\left(P, P^{\prime} \text {-dmape }\right)+\mathrm{dmm} \rightarrow \mathrm{Pt}\left(\eta^{2}-\mathrm{dmm}\right)\left(P, P^{\prime} \text {-dmape }\right)+2 \mathrm{CO}_{2} \tag{2}
\end{align*}
$$

As judged by the NMR data, the reaction was successful. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of the product consists of a singlet at $\delta 43.8\left({ }^{1} J_{\mathrm{PPt}}=3910 \mathrm{~Hz}\right)$, and the ${ }^{1} \mathrm{H}$ spectrum contains peaks which may be attributed to $\mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}$ and $\mathrm{CH}=\mathrm{CH}$ protons of coordinated dmm. All the $\mathrm{NCH}_{3}$ protons in the product are equivalent (giving rise to a singlet at $\delta 2.50$ ), which demonstrates that there are no coordinated N -atoms.

An effective general strategy for the synthesis of $\mathrm{M}^{0}$ complexes of the anilinyldiphosphine ligands is a goal worthy of future attention.

### 2.8.2 Preparation and investigation of allyl complexes

In order to determine whether the anilinyldiphosphine ligands would participate in nucleophilic attack on coordinated allyl as they do on coordinated cod, dmape was reacted with $\left[\mathrm{Pd}(\mu-\mathrm{Cl})\left(\eta^{3} \text {-allyl }\right)\right]_{2}$ in the presence of $\mathrm{NH}_{4} \mathrm{PF}_{6}$ (Section 2.9.2.14). The product of this reaction was $\left[\operatorname{Pd}\left(\eta^{3}\right.\right.$-allyl $)\left(P, P^{\prime}\right.$-dmape $\left.)\right]\left[\mathrm{PF}_{6}\right]$, i.e., no nucleophilic attack occurred. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum shows a sharp singlet at $\delta 44.2$ which is invariant from $230-300 \mathrm{~K}$. Sharp peaks, all of which may be assigned, appear in the ${ }^{1} \mathrm{H}$ spectrum. If the reaction is performed in the absence of the halide-abstracting reagent, the ${ }^{31} \mathrm{P}$ peak now appears at $\delta 28.4$, and the ${ }^{1} \mathrm{H}$ spectrum is broad and ill-defined. The system is further complicated, if the anilinyldiphosphine is varied: reaction of $\left[\mathrm{Pd}(\mu-\mathrm{Cl})\left(\eta^{3} \text {-allyl) }\right]_{2}\right.$ with dmapm gave 3 products as determined by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy, while reaction with dmapcp in the presence of $\mathrm{NH}_{4} \mathrm{PF}_{6}$ gave a compound whose ${ }^{31} \mathrm{P}$ spectrum was illdefined at r.t. and showed 8 peaks in the range $\delta-25$ to 52 at 220 K . The possibilities of equilibria between $\eta^{3}$ - and $\eta^{1}$ - allyl, coordinated and free $\mathrm{Cl}^{-}$, and different coordination
modes of the anilinyldiphosphine ligands, and for nucleophilic attack on the allyl moiety, deserve attention. A recent publication by Braunstein et al. describes an equilibrium between $\eta^{3}$ - and $\eta^{1}$ - allyl at a $\operatorname{Pd}(P N P)$ complex. ${ }^{74}$

### 2.8.3 Catalytic $\mathbf{C - C}$ and $\mathrm{C}-\mathrm{N}$ bond formations

While the Heck reaction ${ }^{75}$ (C-C coupling) catalysed by Pd-dmapm complexes forms the basis of Chapter 3 of this thesis, catalysts based on dmapcp and dmape remain unexplored. The use of Pd -anilinyldiphosphine complexes in catalytic $\mathrm{C}-\mathrm{N}$ bond forming reactions is also a worthy focal point for future research. Over the last few years, this reaction has been developed primarily by Buchwald and coworkers into a useful synthetic tool. ${ }^{76-80}$ The reason for suggesting Pd -anilinyldiphosphine complexes as potential $\mathrm{C}-\mathrm{X}$ bond forming catalysts is that it has been found, e.g., in the amination of arylbromides by $\mathrm{Pd}(\mathrm{OAc})_{2} / \mathrm{BINAP}$ catalysts, that oxidative addition is rate limiting ${ }^{79}$ and requires the predissociation of BINAP from $\mathrm{Pd}(\mathrm{BINAP})_{2} .{ }^{77}$ Presumably, the corresponding "Pd" (dmape)" or " $\mathrm{Pd}^{0}$ (dmapcp)" species would not suffer from this slowdown, as the labile " N -arms" should dissociate easily.

In preliminary studies, $\mathrm{PdCl}_{2}$ (dmape) was used as the catalyst precursor in the amination of PhBr by aniline (Section 2.9.5). At $70^{\circ} \mathrm{C}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$ solution with $\mathrm{KO}^{t} \mathrm{Bu}$ as the base and a catalyst loading of $2 \mathrm{~mol} \%$, the conversion to $\mathrm{Ph}_{2} \mathrm{NH}$ was $11 \%$ after 3 h ( $\mathrm{TON}=6$ ). While not impressive, the result does indicate that the complexes here under study have potential as amination catalysts, and further work in this area is warranted.

### 2.8.4 Ruthenium complexes: novel coordination modes, and reactivity

Water-soluble $\mathrm{Ru}^{\text {II }}$-phosphine complexes are attractive targets both for the homogeneous catalysis and pharmaceutical industries. In the course of this study, it was found that dmape reacted with $\mathrm{RuCl}_{2}\left(\mathrm{PPh}_{3}\right)_{3}$ (Section 2.9.3.1) to give cis- and trans$\operatorname{RuCl}_{2}(P, P$ ', $N, N$ '-dmape) (Chart 2.16 , p. 64; arcs terminated by ' N " represent $o$ $\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{NMe}_{2}$ ), while dmapcp did not react. High temperature and r.t. reactions give different product distributions: only the cis isomer resulted from the r.t. reaction, while a mixture of the cis and trans (ca. 9:1) was formed at $80^{\circ} \mathrm{C}$. Cis- $\mathrm{RuCl}_{2}$ (dmape) is freely soluble in $\mathrm{H}_{2} \mathrm{O}\left(\Lambda_{\mathrm{M}}=211 \mathrm{ohm}^{-1} \mathrm{~mol}^{-1} \mathrm{~cm}^{2}\right)$ with the assumed dissociation of both chlorides to give cis- $\left[\mathrm{Ru}\left(\mathrm{OH}_{2}\right)_{2}\left(P, P^{\prime}, N, N^{\prime}\right.\right.$-dmape $\left.)\right] \mathrm{Cl}_{2}$; it is a non-conductor in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$.

The chloro compound reacts with $\mathrm{NH}_{4} \mathrm{PF}_{6}$ in acetone to give a mixture of products $\left[\mathrm{Ru}(\mathrm{S})_{n}\left(P_{2,}, N_{4-n}\right.\right.$-dmape $\left.)\right]\left[\mathrm{PF}_{6}\right]_{2}\left(\mathrm{~S}=\right.$ acetone, $\left.\mathrm{H}_{2} \mathrm{O} ; n=1-4\right)$. The solvent ligands can be removed by heating the compound in vacuo; the hexa-coordinated product, $\left[\mathrm{Ru}\left(P, P^{\prime}, N, N^{\prime}, N^{\prime}, N^{\prime \prime}{ }^{\prime}-\right.\right.$ dmape $\left.)\right]\left[\mathrm{PF}_{6}\right]_{2}$ is very reactive, presumably because of strain built up in the ligand: it reacts in the solid-state with trace $\mathrm{H}_{2} \mathrm{O}$ in H.P. Ar, and in solution with $\mathrm{H}_{2} \mathrm{~S}$ (the solid-state reaction with $\mathrm{H}_{2} \mathrm{~S}$ has not yet been attempted). A summary of the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR data for the Ru complexes and for reactions of the halide-free compound with $\mathrm{H}_{2} \mathrm{E}(\mathrm{E}=\mathrm{O}, \mathrm{S})$ is given in Table 2.10.

Table 2.10
${ }^{31} \mathrm{P}$ NMR data for a variety of Ru (dmape) complexes and for the in situ reactions of $\operatorname{Ru}\left(P, P^{\prime}, N, N^{\prime}, N^{\prime \prime}, N^{\prime \prime \prime}-\right.$-dmape $\left.)\right]\left[\mathrm{PF}_{6}\right]_{2}$ with $\mathrm{H}_{2} \mathrm{O}$ and $\mathrm{H}_{2} \mathrm{~S}$.

| Compound or Reaction | Solvent | ${ }^{31} \mathbf{P}\left\{{ }^{1} \mathbf{H}\right\}$ chemical shift ${ }^{\mathrm{a}, \mathrm{b}}$ (ppm) $\left[{ }^{2} J_{\mathrm{PP}}(\mathrm{Hz})\right]$ |
| :---: | :---: | :---: |
| cis-RuCl ${ }_{2}\left(P, P^{\prime}, N, N^{\prime}\right.$-dmape) | $\mathrm{CDCl}_{3}$ | 94.6 |
|  | $\mathrm{D}_{2} \mathrm{O}$ | $83.1{ }^{\text {c }}$ |
| trans $-\mathrm{RuCl}_{2}\left(P, P^{\prime}, N, N^{\prime}\right.$-dmape $)$ | $\mathrm{CDCl}_{3}$ | 26.0 |
| $\left[\mathrm{Ru}\left(P, P^{\prime}, N, N^{\prime}, N^{\prime}, N^{\prime \prime}{ }^{\prime \prime}\right.\right.$-dmape $\left.)\right]\left[\mathrm{PF}_{6}\right]_{2}$ | $\mathrm{CDCl}_{3}$ | 95.6 |
| $\begin{aligned} & {\left[\operatorname{Ru}\left(P, P^{\prime}, N, N^{\prime}, N^{\prime}, N^{\prime \prime} \text {-dmape }\right)\right]\left[\mathrm{PF}_{6}\right]_{2}+} \\ & \mathrm{H}_{2} \mathrm{O} \end{aligned}$ | $\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{H}_{2} \mathrm{O}$ | $74.0,78.1[20]^{\text {d }}$ |
|  |  | 75.3, 88.7 [unresolved] ${ }^{\text {d }}$ |
|  |  | 79.6, $93.9[20]^{\text {d }}$ |
|  |  | $80.8,83.1$ [24] ${ }^{\text {d }}$ |
|  |  | $82.7{ }^{\text {d }}$ |
| $\begin{aligned} & {\left[\operatorname{Ru}\left(P, P^{\prime}, N, N^{\prime}, N^{\prime}, N^{\prime \prime} \text {-'dmape }\right)\right]\left[\mathrm{PF}_{6}\right]_{2}+} \\ & \mathrm{H}_{2} \mathrm{~S} \end{aligned}$ | $\mathrm{CDCl}_{3}$ | 66.9, 97.7 [13] |
|  |  | 74.1, 89.7 [14] |
|  |  | 77.1 |
|  |  | 79.5, 95.5 [20] |
|  |  | 85.8 |

[^2]
## Chart 2.16




The reactions of $\left[\mathrm{Ru}\left(P, P^{\prime}, N, N^{\prime}, N^{\prime \prime}, N^{\prime \prime \prime}\right.\right.$-dmape $\left.)\right]\left[\mathrm{PF}_{6}\right]_{2}$ with $\mathrm{H}_{2} \mathrm{E}$ yield several products because of the possibility for geometrical isomers and, assuming the P -atoms remain coordinated, the binding of up to (theoretically) $4 \mathrm{H}_{2} \mathrm{E}$ molecules. In addition, it is not known whether the $\mathrm{H}_{2} \mathrm{E}$ ligands are deprotonated, as in the case of the reaction between $\mathrm{H}_{2} \mathrm{~S}$ and cis-Ru(H) $2(\mathrm{dppm})_{2}$ which gives cis- $\mathrm{Ru}(\mathrm{SH})_{2}(\mathrm{dppm})_{2}+2 \mathrm{H}_{2},{ }^{81}$ or not deprotonated, as the in the reaction of $\mathrm{RuCl}_{2}(P, N-\mathrm{PMA})\left(\mathrm{PPh}_{3}\right)$ with $\mathrm{H}_{2} \mathrm{~S}$ which gives $\mathrm{Ru}\left(\mathrm{SH}_{2}\right)(P, N$-PMA $)\left(\mathrm{PPh}_{3}\right) \cdot{ }^{82,83}$ Further investigations in this area are worthwhile as there are no known complexes bearing more than one coordinated $\mathrm{H}_{2} \mathrm{~S}$. In addition, it would be of interest to attempt the reaction between $\left[\operatorname{Ru}\left(P, P^{\prime}, N, N^{\prime}, N^{\prime}, N^{\prime \prime}{ }^{\prime \prime}-\mathrm{dmape}\right)\right]\left[\mathrm{PF}_{6}\right]_{2}$ and $\mathrm{N}_{2} \mathrm{O} .{ }^{84}$

### 2.9 Experimental

### 2.9.1 Ligand syntheses

### 2.9.1.1 1,1-bis(di(o- $N, N$-dimethylanilinyl)phosphino)methane, dmapm

To a solution of $n-\mathrm{BuLi}$ in hexanes $\left(1.6 \mathrm{~mol} \mathrm{~L}{ }^{-1}, 16.5 \mathrm{~mL}, 26.4 \mathrm{mmol}\right)$, cooled to $-40{ }^{\circ} \mathrm{C}$ on a dry ice $/ \mathrm{CH}_{3} \mathrm{CN}$ bath, was added o-bromo- $N, N$-dimethylaniline ( $5.05 \mathrm{~g}, 25.2 \mathrm{mmol}$ ) in $\mathrm{Et}_{2} \mathrm{O}(20 \mathrm{~mL})$ via cannula over a period of 20 min . The yellow solution was stirred for 15 min and a white precipitate formed. The slurry was allowed to warm to r.t. and stirring was continued for 1 h . After the solution was cooled again to $-40^{\circ} \mathrm{C}, 1,1-$ bis(dichlorophosphino)methane ( $1.33 \mathrm{~g}, 6.09 \mathrm{mmol}$ ) in $\mathrm{Et}_{2} \mathrm{O}(15 \mathrm{~mL})$ was added over 5 min . The resulting orange-red slurry was stirred for 15 min and then allowed to warm to r.t.. Stirring was continued for 1 h and then $\mathrm{HCl}\left(c a .1 \mathrm{~mol} \mathrm{~L}^{-1}, 50 \mathrm{~mL}\right)$ was added. The organic layer was removed and $\mathrm{KOH}\left(c a .2 \mathrm{~mol} \mathrm{~L}^{-1}\right.$ ) was added dropwise to the aqueous layer until it was neutral. The aqueous fraction was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 20 \mathrm{~mL})$ and the combined extracts were dried over $\mathrm{MgSO}_{4}$. The solvent was removed in vacuo and EtOH ( 15 mL ) was added. The slurry was refluxed for 0.5 h , cooled to r.t. and filtered to give a white powder that was washed with cold $\mathrm{EtOH}(3 \times 5 \mathrm{~mL})$ and dried in vacuo. Yield: $1.84 \mathrm{~g}(54 \%)$. Anal. Calcd for $\mathrm{C}_{33} \mathrm{H}_{42} \mathrm{~N}_{4} \mathrm{P}_{2}$ : C, 71.2; H, 7.6; N, 10.1. Found: C, $71.0 ; \mathrm{H}, 7.8 ; \mathrm{N}, 9.9{ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta 2.23\left(\mathrm{t}, 2 \mathrm{H}, \mathrm{CH}_{2}\right.$, ${ }^{2} J_{\mathrm{HP}}=4.2$ ), $2.68\left(\mathrm{~s}, 24 \mathrm{H}, \mathrm{NCH}_{3}\right), 7.02(\mathrm{pt}, 2 \mathrm{H}, \mathrm{Ar}), 7.11(\mathrm{pd}, 4 \mathrm{H}, \mathrm{Ar}), 7.25(\mathrm{pt}, 4 \mathrm{H}, \mathrm{Ar})$,
7.40 (pd, 4H, Ar). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta-36.0(\mathrm{~s}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(50 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta 28.0\left(\mathrm{CH}_{2},{ }^{1} J_{\mathrm{CP}}=26.2\right), 45.3\left(\mathrm{NCH}_{3}\right), 119.7(\mathrm{CH}), 124.2$ $(\mathrm{CH}), 128.6(\mathrm{CH}), 132.3(\mathrm{CH}), 139.2(\mathrm{CN}), 157.1(\mathrm{CP})$.

### 2.9.1.2 1,2-bis(di(o-N,N-dimethylanilinyl)phosphino)cyclopentane, dmapcp

The synthesis of this compound corresponds to that of dmapm (Section 2.9.1.1). Thus, reaction of $n-\mathrm{BuLi}$ in hexanes $\left(1.6 \mathrm{~mol} \mathrm{~L}^{-1}, 23.0 \mathrm{~mL}, 36.8 \mathrm{mmol}\right)$, o-bromo- $N, N$ dimethylaniline $(6.83 \mathrm{~g}, 34.1 \mathrm{mmol})$ and 1,2-bis(dichlorophosphino)cyclopentane ( 2.33 g , $8.57 \mathrm{mmol})$ at $-40^{\circ} \mathrm{C}$ gave $2.72 \mathrm{~g}(52 \%)$ of a white powder. Anal. Calcd for $\mathrm{C}_{37} \mathrm{H}_{48} \mathrm{~N}_{4} \mathrm{P}_{2}$ : C 72.8; H 8.0; N 9.2. Found: C 72.9; H 8.1; N 9.1. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 300 \mathrm{~K}$ ): $\delta 1.51\left(2 \mathrm{H}, \mathrm{m}, \mathrm{CH}_{2}\right), 1.69\left(2 \mathrm{H}, \mathrm{m}, \mathrm{CH}_{2}\right), 2.23\left(2 \mathrm{H}, \mathrm{m}, \mathrm{CH}_{2}\right), 2.55\left(12 \mathrm{H}, \mathrm{s}, \mathrm{NCH}_{3}\right.$, obscures CH protons), $2.63\left(12 \mathrm{H}, \mathrm{s}, \mathrm{NCH}_{3}\right), 6.49(2 \mathrm{H}, \mathrm{m}, \mathrm{Ar}), 6.71(2 \mathrm{H}, \mathrm{m}, \mathrm{Ar})$, 6.96-7.28 ( $12 \mathrm{H}, \mathrm{m}, \mathrm{Ar}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $50 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 24.7\left(\mathrm{CH}_{2}\right), 29.9$ $\left(\mathrm{CH}_{2}\right), 40.4(\mathrm{CH}), 45.1\left(\mathrm{NCH}_{3}\right), 120.0(\mathrm{Ar}), 124.2(\mathrm{Ar}), 128.6(\mathrm{Ar}), 133.1(\mathrm{Ar}), 137.9$ (Ar), 157.7 (Ar). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ) $\delta-25.6$ (s). Crystals of dmapcp suitable for X-ray analysis deposited from a $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution containing dmapcp onto which EtOH had been layered.

### 2.9.1.3 1,2-bis(di(o-N,N-dimethylanilinyl)phosphino)ethane, dmape

The synthesis of this compound follows that of dmapm (Section 2.9.1.1). Thus, reaction of $n-\mathrm{BuLi}\left(1.6 \mathrm{~mol} \mathrm{~L}^{-1}, 17.4 \mathrm{~mL}, 27.8 \mathrm{mmol}\right)$, o-bromo- $N, N$-dimethylaniline $(5.56 \mathrm{~g}$, 27.8 mmol ) and 1,2-bis(dichlorophosphino)ethane ( $1.61 \mathrm{~g}, 6.94 \mathrm{mmol}$ ) gave 2.44 g ( 61 $\%$ ) of a white powder. Anal. Calcd for $\mathrm{C}_{34} \mathrm{H}_{44} \mathrm{~N}_{4} \mathrm{P}_{2}$ : C, 71.6; H, 7.8; N, 9.8. Found: C, 71.0; H, 7.6; N, 9.5. ${ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 300 \mathrm{~K}\right): \delta 1.86\left(\mathrm{t}, 4 \mathrm{H}, \mathrm{CH}_{2},{ }^{2} \mathrm{~J}_{\mathrm{HP}}=14\right.$ ), $2.62\left(\mathrm{~s}, 24 \mathrm{H}, \mathrm{NCH}_{3}\right), 6.95(\mathrm{~m}, 8 \mathrm{H}, \mathrm{Ar}), 7.11(\mathrm{~m}, 4 \mathrm{H}, \mathrm{Ar}), 7.25(\mathrm{~m}, 4 \mathrm{H}, \mathrm{Ar}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $\left.50 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta 24.4\left(\mathrm{CH}_{2}\right), 45.3\left(\mathrm{NCH}_{3}\right), 113.1$ (Ar), 119.9 ( Ar ), 128.9 (Ar), 132.5 (Ar), 137.0 (Ar), 157.8 (Ar). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(121 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 300 \mathrm{~K}\right)$ $\delta-27.5$ (s). Crystals of dmape suitable for analysis by X-ray diffraction deposited from a $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution containing dmape onto which EtOH had been layered.

### 2.9.2 Syntheses of Pt and Pd complexes

### 2.9.2.1 $\quad[\mathrm{PtCl}(P, P,, N$-dmapep $)] \mathrm{Cl} \cdot \mathrm{H}_{2} \mathrm{O}$

This compound could be made either from $\mathrm{PtCl}_{2}$ via cis $-\mathrm{PtCl}_{2}(\mathrm{MeCN})_{2}$, or from $\mathrm{PtCl}_{2}$ (cod).
(a) From $\mathrm{PtCl}_{2}$. To a Schlenk tube containing $\mathrm{PtCl}_{2}$ ( $100 \mathrm{mg}, 0.38 \mathrm{mmol}$ ) was added $\mathrm{CH}_{3} \mathrm{CN}(10 \mathrm{~mL})$ and the slurry refluxed for 2 h , during which the solid dissolved to give a yellow solution. Dmapcp ( $230 \mathrm{mg}, 0.38 \mathrm{mmol}$ ) was then added to the hot solution which became colourless. The solvent was removed in vacuo and the residue was redissolved in the minimum $\mathrm{CH}_{2} \mathrm{Cl}_{2}$. Addition of $\mathrm{Et}_{2} \mathrm{O}(20 \mathrm{~mL})$ gave a white powder that was isolated by filtration, washed with $\mathrm{Et}_{2} \mathrm{O}$ and dried in vacuo at $78^{\circ} \mathrm{C}$. Yield: 240 mg ( $72 \%$ ).
(b) From $\mathrm{PtCl}_{2}($ cod $)$. To a Schlenk tube charged with $\mathrm{PtCl}_{2}$ (cod) $(97 \mathrm{mg}$, 0.26 mmol ) and dmapcp ( $160 \mathrm{mg}, 0.26 \mathrm{mmol}$ ) was added 1,2-dichloroethane ( 15 mL ), and the resulting colourless solution refluxed for 17 h . The work up was the same as that for the $\mathrm{PtCl}_{2}$ route. Yield: 150 mg ( $66 \%$ ).

The routes gave identical NMR spectra and very similar elemental analyses. Several independent syntheses of $\left[\mathrm{PtCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl} \cdot \mathrm{H}_{2} \mathrm{O}$ analysed as the monohydrate, and ${ }^{1} \mathrm{H}$ NMR spectroscopy confirmed the presence of $\mathrm{H}_{2} \mathrm{O}$. Moreover, crystals of this compound contained $1.46 \mathrm{H}_{2} \mathrm{O}$ per unit cell (vide infra). Anal. Calcd for $\mathrm{C}_{37} \mathrm{H}_{42} \mathrm{~N}_{4} \mathrm{Cl}_{2} \mathrm{P}_{2} \mathrm{Pt} \cdot \mathrm{H}_{2} \mathrm{O}$ : C 49.7; H 5.6; N 6.3; Found: C 50.0; H 5.7; N 6.1. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 1.30\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{CH}_{2}\right), 1.60\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{H}_{2} \mathrm{O}\right), 1.70\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{CH}_{2}\right)$, $1.90\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.22\left(\mathrm{~s}, 12 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.35\left(\mathrm{~m}, 3 \mathrm{H}, \mathrm{CH}\right.$ and $\left.\mathrm{CH}_{2}\right), 2.67\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{NCH}_{3}\right)$, $3.05\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right), 3.50\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right), 3.72(\mathrm{~m}, 1 \mathrm{H}, \mathrm{CH}), 6.70(\mathrm{~m}, 2 \mathrm{H}, \mathrm{Ar}), 7.05(\mathrm{~m}$, $1 \mathrm{H}, \mathrm{Ar}), 7.3-7.9(\mathrm{~m}, 11 \mathrm{H}, \mathrm{Ar}), 8.24(\mathrm{~m}, 1 \mathrm{H}, \mathrm{Ar}), 9.32(\mathrm{~m}, 1 \mathrm{H}, \mathrm{Ar}) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right) \delta 18.9\left(\mathrm{~d},{ }^{1} J_{\mathrm{PPt}}=3490,{ }^{2} J_{\mathrm{PP}}=12.3\right), 28.6\left(\mathrm{~d},{ }^{1} J_{\mathrm{PPt}}=3400,{ }^{2} J_{\mathrm{PP}}\right.$ $=12.3) . \Lambda_{\mathrm{M}}\left(\mathrm{H}_{2} \mathrm{O}, 298 \mathrm{~K}\right)$ : 150. Colourless, X-ray diffraction quality crystals of $\left[\mathrm{PtCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl} \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2} \cdot 1.46 \mathrm{H}_{2} \mathrm{O}$ were grown over 4 d by evaporation of a $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution containing the compound onto which EtOH had been layered $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}: \mathrm{EtOH} 2: 5\right.$ by vol).

### 2.9.2.2 $\quad[\mathbf{P t C l}(P, P, N$-dmapcp $)]\left[\mathrm{PF}_{6}\right]$

To a Schlenk tube charged with $\left[\operatorname{PtCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl}(38 \mathrm{mg}, 0.043 \mathrm{mmol})$ and $\mathrm{NH}_{4} \mathrm{PF}_{6}(7.0 \mathrm{mg}, 0.045 \mathrm{mmol})$ was added acetone $(10 \mathrm{~mL})$. The resulting white suspension was stirred at r.t. for 1 h and then filtered through Celite 545 . The Celite was washed with acetone ( $3 \times 10 \mathrm{~mL}$ ) and the combined filtrate was reduced to $c a .1 \mathrm{~mL}$ in vacuo. The product was afforded as a white powder by the addition of $\mathrm{Et}_{2} \mathrm{O}(20 \mathrm{~mL})$, isolated by filtration, washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 3 \mathrm{~mL})$ and dried in vacuo at $100^{\circ} \mathrm{C}$. Yield: 21 mg (49 \%). Anal. Calcd for $\mathrm{C}_{37} \mathrm{H}_{48} \mathrm{~N}_{4} \mathrm{ClF}_{6} \mathrm{P}_{3} \mathrm{Pt}$ : C 45.1; H 4.9; N 5.7. Found: C 44.8; H 4.9; N 5.6. The $\mathrm{CDCl}_{3}$ solution ${ }^{1} \mathrm{H}$ NMR spectrum of $\left[\mathrm{PtCl}\left(P, P^{\prime}, N-\mathrm{dmapcp}\right)\right]\left[\mathrm{PF}_{6}\right]$ was almost identical to that of $\left[\mathrm{PtCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl} .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(121 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.$, $300 \mathrm{~K}) \delta 17.0\left(\mathrm{~d},{ }^{1} J_{\mathrm{PPt}}=3510,{ }^{2} J_{\mathrm{PP}}=13.7\right), 26.7\left(\mathrm{~d},{ }^{1} J_{\mathrm{PPt}}=3390,{ }^{2} J_{\mathrm{PP}}=13.7\right),-145(\mathrm{spt}$, $\left.{ }^{1} J_{\mathrm{PF}}=710, \mathrm{PF}_{6}{ }^{-}\right)$.

### 2.9.2.3 $\quad \mathrm{PtCl}_{2}(P, P$ '-dmape $)$ and $[\mathrm{PtCl}(P, P, N$-dmape $)] \mathrm{Cl}$

This complex was synthesised according to the two routes detailed for the preparation of $\left[\mathrm{PtCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl}$ (Section 2.9.2.1). Thus, reaction of $\mathrm{PtCl}_{2}(105 \mathrm{mg}, 0.40 \mathrm{mmol})$ and dmape ( $230 \mathrm{mg}, 0.40 \mathrm{mmol}$ ) yielded $130 \mathrm{mg}(40 \%)$ of a white powder; and reaction of $\mathrm{PtCl}_{2}(\mathrm{cod})(110 \mathrm{mg}, 0.28 \mathrm{mg})$ with the same ligand ( $160 \mathrm{mg}, 0.28 \mathrm{mmol}$ ) gave 200 mg ( $85 \%$ ) of $\mathrm{PtCl}_{2}$ (dmape). However, elevated temperatures were not required for the latter preparation that was conducted in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at r.t. Anal. Calcd for $\mathrm{C}_{34} \mathrm{H}_{44} \mathrm{~N}_{4} \mathrm{Cl}_{2} \mathrm{P}_{2} \mathrm{Pt}$ : C 48.8; H 5.3; N 6.7; Found: C 48.5; H 5.3; N 6.5. $\mathbf{P t C l}_{2}$ (P,P'-dmape): ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 233 \mathrm{~K}$ ): $\delta 48.0\left(\mathrm{br} \mathrm{s},{ }^{1} J_{\mathrm{PPt}}=3750\right.$ ). The ${ }^{1} \mathrm{H}$ NMR spectrum of this compound is broad and uninformative, even at low temperature, and could not be resolved from that of $\left[\mathrm{PtCl}\left(P, P^{\prime}, N\right.\right.$-dmape $\left.)\right] \mathrm{Cl}$. The $\mathrm{NCH}_{3}$ protons and the methylene protons in the ligand "backbone" fall in the $2-4 \mathrm{ppm}$ range, while the peaks due to aromatic protons lie between $6.5-9 \mathrm{ppm}$. $[\mathbf{P t C l}(\boldsymbol{P}, \boldsymbol{P}, N$-dmape $)] \mathbf{C l}:{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 233 \mathrm{~K}$ ): $\delta 34.0$ (br s, ${ }^{1} J_{\mathrm{PPt}}=3510$ ), 55.1 (br s, ${ }^{1} J_{\mathrm{PPt}}=3460$ ). Evaporation over a period of 3 d of a $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution containing the compound onto which EtOH had been layered $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right.$ : EtOH $1: 1$ by vol) yielded colourless, X-ray diffraction quality crystals of $\mathrm{PtCl}_{2}\left(P, P^{\prime}-\right.$ dmape $) \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$.

### 2.9.2.4 $\quad\left[\mathrm{PtCl}\left(P, P{ }^{\prime}, N\right.\right.$-dmape $\left.)\right]\left[\mathrm{PF}_{6}\right]$

This compound was prepared in the same manner as outlined for $\left[\mathrm{PtCl}\left(P, P^{\prime}, N-\right.\right.$ dmape) $]\left[\mathrm{PF}_{6}\right]$ (Section 2.9.2.2), except that the acetone was removed at the pump and the residue taken up in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$ before filtration through Celite 545 . This removed excess $\mathrm{NH}_{4} \mathrm{PF}_{6}$ which is insoluble in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$. Thus, reaction of $\mathrm{PtCl}_{2}$ (dmape) ( 92 mg , $0.11 \mathrm{mmol})$ and $\mathrm{NH}_{4} \mathrm{PF}_{6}(42 \mathrm{mg}, 0.26 \mathrm{mmol})$ gave $48 \mathrm{mg}(47 \%)$ of a white powder. Anal. Calcd for $\mathrm{C}_{34} \mathrm{H}_{44} \mathrm{~N}_{4} \mathrm{ClF}_{6} \mathrm{P}_{3} \mathrm{Pt}$ : C 43.2; H 4.7; N 5.9. Found: C 43.3; H 4.9; N 5.8. ${ }^{1} \mathrm{H}$ NMR ( $200 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 2.2-3.6\left(\mathrm{br} \mathrm{m}, 28 \mathrm{H}, \mathrm{CH}_{2}\right.$ and $\mathrm{NCH}_{3}$ ), $7.10-7.80(\mathrm{br}$ $\mathrm{m}, 12 \mathrm{H}, \mathrm{Ar}), 8.05(\mathrm{~m}, 4 \mathrm{H}, \mathrm{Ar}) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(81 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta 31.6\left(\mathrm{~s},{ }^{1} J_{\mathrm{PPt}}=\right.$ $3540,{ }^{2} J_{\mathrm{PP}}$ not observed), 52.7 (s, ${ }^{1} J_{\mathrm{PPt}}=3446,{ }^{2} J_{\mathrm{PP}}$ not observed), -145 ( $\mathrm{spt},{ }^{1} J_{\mathrm{PF}}=710$, $\mathrm{PF}_{6}{ }^{-}$).

### 2.9.2.5 $\quad \operatorname{Pt}(\mathrm{ox})\left(P, P^{\prime}\right.$-dmape $)$

To a $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$ solution containing $\mathrm{PtCl}_{2}$ (dmape) ( $85.3 \mathrm{mmol}, 0.10 \mathrm{mmol}$ ) was added $\mathrm{H}_{2} \mathrm{O}(10 \mathrm{~mL})$ followed by solid $\mathrm{Na}_{2} \mathrm{ox}$ under air. The biphasic system was stirred overnight and the aqueous layer was removed. The organic fraction was washed with $\mathrm{H}_{2} \mathrm{O}(2 \times 10 \mathrm{~mL})$ and $\mathrm{EtOH}(5 \mathrm{~mL})$ was added. The solvent volume was reduced to $c a .1$ mL in vacuo and the product was afforded as a fine white precipitate by the addition of $\mathrm{Et}_{2} \mathrm{O}(20 \mathrm{~mL})$. This was isolated by filtration, washed with $\mathrm{Et}_{2} \mathrm{O}(2 \times 5 \mathrm{~mL})$ and air-dried. Yield: $56 \mathrm{mg}(65 \%)$. Anal. Calcd for $\mathrm{C}_{36} \mathrm{H}_{44} \mathrm{~N}_{4} \mathrm{O}_{4} \mathrm{P}_{2} \mathrm{Pt}$ : C, $50.6 ; \mathrm{H}, 5.2 ; \mathrm{N}, 6.6$. Found: C , 50.0; H, 5.5; N 6.4. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 2.43\left(\mathrm{~s}, 24 \mathrm{H}, \mathrm{NCH}_{3}\right), 3.17(\mathrm{~m}$, $2 \mathrm{H}, \mathrm{CH}_{2}$ ), 7.32 (pt, 4H, Ar), 7.55 (pt, 4H, Ar), 7.63 (pt, 4H, Ar), 7.85 (m, 4H, Ar). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 35.2\left(\mathrm{~s},{ }^{1} J_{\mathrm{PPt}}=3750 \mathrm{~Hz}\right)$.

### 2.9.2.6 $\quad[\mathbf{P d C l}(P, P \prime, N$-dmapcp $)] C l$

To a Schlenk tube containing trans $-\mathrm{PdCl}_{2}(\mathrm{PhCN})_{2}(55 \mathrm{mg}, 0.14 \mathrm{mmol})$ and dmapcp ( $86 \mathrm{mg}, 0.14 \mathrm{mmol}$ ) was added $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$, and the initially orange solution stirred for 15 min during which it became yellow. The volume was reduced under vacuum to $c a$. 1 mL and addition of $\mathrm{Et}_{2} \mathrm{O}(20 \mathrm{~mL})$ gave the yellow solid product. This was isolated by filtration, washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 3 \mathrm{~mL})$ and dried in vacuo. Yield: $109 \mathrm{mg}(98 \%)$. Anal. Calcd for $\mathrm{C}_{37} \mathrm{H}_{48} \mathrm{~N}_{4} \mathrm{Cl}_{2} \mathrm{P}_{2} \mathrm{Pd}$ : C 56.4; H 6.1; N 7.1. Found: C 56.1; H 6.3; N 7.0. ${ }^{1} \mathrm{H}$ NMR
( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 1.42\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{CH}_{2}\right), 1.65$ (br m, $1 \mathrm{H}, \mathrm{CH}_{2}$ ), 1.83 (br m, 1 H , $\mathrm{CH}_{2}$ ), 2.15 (br m, $1 \mathrm{H}, \mathrm{CH}_{2}$ ), 2.29 ( $\mathrm{s}, 13 \mathrm{H}, \mathrm{NCH}_{3}$ and $\mathrm{CH}_{2}$ obscured), 2.45 (br m, 1 H , $\mathrm{CH}_{2}$ ), $2.73\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.93\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right), 3.14(\mathrm{br} \mathrm{m}, 1 \mathrm{H}, \mathrm{CH}), 3.30\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right)$, 4.05 (br m, 1H, CH), $6.73(\mathrm{~m}, 1 \mathrm{H}, \mathrm{Ar}), 6.82(\mathrm{pt}, 1 \mathrm{H}, \mathrm{Ar}), 7.08(\mathrm{pt}, 1 \mathrm{H}, \mathrm{Ar}), 7.58(\mathrm{~m}, 11 \mathrm{H}$, Ar), $8.21(\mathrm{pt}, 1 \mathrm{H}, \mathrm{Ar}), 9.43(\mathrm{~m}, 1 \mathrm{H}, \mathrm{Ar}) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta 48.7$ (s), 49.6 (s). UV-vis: 334 [6100] $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right) ; 378$ [3900] $\left(\mathrm{H}_{2} \mathrm{O}\right) . \Lambda_{\mathrm{M}}\left(\mathrm{H}_{2} \mathrm{O}, 298 \mathrm{~K}\right): 200$.

### 2.9.2.7 $\quad\left[\operatorname{PdII}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] I$

To a Schlenk tube containing solid trans $-\mathrm{PdCl}_{2}\left(\mathrm{PhCN}_{2}\right)(71 \mathrm{mg}, 0.19 \mathrm{mmol})$ and dmapcp ( $110 \mathrm{mg}, 0.190 \mathrm{mmol}$ ) was added $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$, and the resulting orange solution was stirred for 0.5 h during which time it became yellow. To this was added solid NaI ( 97 mg , 0.65 mmol ) followed by acetone ( 5 mL ). The solution immediately became orange and turbid, and was stirred for a further 0.5 h . The solvent was removed in vacuo. The residue was taken up in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$ and the mixture was filtered through Celite 545 . The volume of the filtrate was reduced in vacuo to $c a .2 \mathrm{~mL}$ and the product was afforded as a fine, orange powder by the addition of $\mathrm{Et}_{2} \mathrm{O}(20 \mathrm{~mL})$. It was isolated by filtration, washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 3 \mathrm{~mL})$ and dried in vacuo. Yield: $130 \mathrm{mg}(72 \%)$. Anal. Calcd for $\mathrm{C}_{37} \mathrm{H}_{48} \mathrm{~N}_{4} \mathrm{I}_{2} \mathrm{P}_{2} \mathrm{Pd}: ~ \mathrm{C}, 45.8 ; \mathrm{H}, 5.0 ; \mathrm{N}, 5.8$. Found: C, $45.9 ; \mathrm{H}, 5.1 ; \mathrm{N}, 5.6{ }^{1}{ }^{\mathrm{H}} \mathrm{H}$ NR ( $200 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 1.80$ (br m, $2 \mathrm{H}, \mathrm{CH}_{2}$ ), 2.35 (br s, $12 \mathrm{H}, \mathrm{NCH}_{3}$ ), 2.70 (br s, $6 \mathrm{H}, \mathrm{NCH}_{3}$ ), 3.05 (br s, $3 \mathrm{H}, \mathrm{NCH}_{3}$ ), $3.70\left(\mathrm{br} \mathrm{s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right.$ ), 3.95 (br m, $1 \mathrm{H}, \mathrm{CH}$ ), 6.80 (br $\mathrm{m}, 1 \mathrm{H}, \mathrm{Ar}$ ), 7.05 (br m, 2H, Ar), $7.30-8.00$ (br m, 13H, Ar), 8.20 (br m, 1H, Ar), 9.40 (br $\mathrm{m}, 1 \mathrm{H}, \mathrm{Ar}$ ). The peaks due to the remaining $\mathrm{CH}_{2}$ protons in the ligand "backbone" are obscured by the broad $\mathrm{NCH}_{3}$ peaks. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $81 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ) $\delta 39.9$ (s), 50.4 (s). 2-bond PP coupling could not be resolved.

### 2.9.2.8 $\quad[\mathrm{PdCl}(P, P, N$-dmapcp $)]\left[\mathrm{PF}_{6}\right]$

This complex was made in the same manner as outlined for $\left[\mathrm{PtCl}\left(P, P^{\prime}, N\right.\right.$-dmape $\left.)\right]\left[\mathrm{PF}_{6}\right]$ (Section 2.9.2.2). Thus, reaction of $\left[\mathrm{PdCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl}(150 \mathrm{mg}, 0.19 \mathrm{mmol})$ and $\mathrm{NH}_{4} \mathrm{PF}_{6}(157 \mathrm{mg}, 0.97 \mathrm{mmol})$ gave $174 \mathrm{mg}(91 \%)$ of a yellow powder. Anal. Calcd for $\mathrm{C}_{37} \mathrm{H}_{48} \mathrm{~N}_{4} \mathrm{ClF}_{6} \mathrm{P}_{3} \mathrm{Pd}: \mathrm{C} 49.5$; H 5.4; N 6.2. Found: C 49.7 ; H 5.4; N 5.8. The ${ }^{1} \mathrm{H}$ NMR spectrum of this compound is essentially the same as that for $[\operatorname{PdCl}(P, P, N-\mathrm{dmapcp})] \mathrm{Cl}$
and the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum is identical save for the presence of the spt $(\delta-145)$ due to $\mathrm{PF}_{6}{ }^{-}$.

### 2.9.2.9 $\quad \mathbf{P d C l}_{2}\left(P, P^{\prime}\right.$-dmape $)$ and $\left[\mathbf{P d C l}\left(P, P{ }^{\prime}, N\right.\right.$-dmape $\left.)\right] \mathbf{C l}$

This complex was prepared in the same manner as outlined for $\mathrm{PtCl}_{2}$ (dmape) (Section 2.9.2.3). Thus, reaction of trans $-\mathrm{PdCl}_{2}(\mathrm{PhCN})_{2}(56 \mathrm{mg}, 0.15 \mathrm{mmol})$ and dmape ( 83 mg , 0.15 mmol ) gave $88 \mathrm{mg}(81 \%)$ of a yellow powder. Anal. Calcd for $\mathrm{C}_{34} \mathrm{H}_{44} \mathrm{~N}_{4} \mathrm{Cl}_{2} \mathrm{P}_{2} \mathrm{Pd}$ : C 54.6; H 5.9; N 7.5; Found: C 54.6; H 5.9; N 7.6. The ${ }^{1} \mathrm{H}$ NMR spectrum of an equilibrium mixture of the two compounds is uninformative throughout the temperature range $220-300 \mathrm{~K}$ because the peaks are broad and overlapped. $\mathbf{P d C l}_{\mathbf{2}}$ ( $\boldsymbol{P}, \boldsymbol{P}$ '-dmape): ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 233 \mathrm{~K}$ ): $\delta 66.4$ (br s). [ $\mathbf{P d C l}(\boldsymbol{P}, \boldsymbol{P}, \boldsymbol{N}$-dmape)]Cl: ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 233 \mathrm{~K}$ ): 73.4 (br s), 60.5 (br s).

### 2.9.2.10 $\quad\left[\mathrm{PdCl}\left(P, P{ }^{\prime}, N\right.\right.$-dmape $\left.)\right]\left[\mathrm{PF}_{6}\right]$

This complex was prepared in the same manner as outlined for $\left[\operatorname{PtCl}\left(P, P^{\prime}, N-\right.\right.$ dmape) $]\left[\mathrm{PF}_{6}\right]$ (Section 2.9.2.4). Thus, reaction of $\mathrm{PdCl}_{2}$ (dmape) ( $83 \mathrm{mg}, 0.11 \mathrm{mmol}$ ) and $\mathrm{NH}_{4} \mathrm{PF}_{6}(93 \mathrm{mg}, 0.57 \mathrm{mmol})$ gave $60 \mathrm{mg}(63 \%)$ of a yellow powder. Anal. Calcd for $\mathrm{C}_{34} \mathrm{H}_{44} \mathrm{~N}_{4} \mathrm{ClF}_{6} \mathrm{P}_{3} \mathrm{Pd}: \mathrm{C} 47.6$; H 5.2; N 6.5. Found: C $47.4 ; \mathrm{H} 5.4 ; \mathrm{N} 6.4$. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 2.6$ (br s, $24 \mathrm{H}, \mathrm{NCH}_{3}$ ), 6.8-8.0 (br m, $16 \mathrm{H}, \mathrm{Ar}$ ). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 300 \mathrm{~K}$ ) $\delta 73.4$ (s), 60.5 (s).

### 2.9.2.11 $\quad \operatorname{Pd}\left(\mathrm{OAc}_{2}{ }_{2}\left(P, P^{\prime}\right.\right.$ '-dmape)

This complex was made in a manner similar to that outlined for $[\mathrm{PdCl}(\mathrm{dmapcp})] \mathrm{Cl}$ (Section 2.9.2.6). Thus an overnight reaction between $\mathrm{Pd}(\mathrm{OAc})_{2}(37 \mathrm{mg}, 0.17 \mathrm{mmol})$ and dmape ( $96 \mathrm{mg}, 0.17 \mathrm{mmol}$ ) gave $92 \mathrm{mg}(70 \%)$ of a yellow powder. Acceptable elemental analysis was not obtained for this complex. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 2.59$ (br s, $24 \mathrm{H}, \mathrm{NCH}_{3}$ ), 3.64 (br m, $4 \mathrm{H}, \mathrm{CH}_{2}$ ), $7.08-7.56$ (m, 12H, Ar), 8.00 (br m, $4 \mathrm{H}, \mathrm{Ar}$ ). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, 300 \mathrm{~K}$ ): $\delta 61(\mathrm{br} \mathrm{s}), 74(\mathrm{br} \mathrm{s})\left[\mathrm{D}_{2} \mathrm{O}\right] ; \delta 70(\mathrm{br} \mathrm{s})\left[\mathrm{CDCl}_{3}\right]$.

### 2.9.2.12 $\quad[\mathrm{PdCl}(\text { dmape }))_{2}\left[\mathrm{PF}_{6}\right]_{2}$

To a $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$ solution containing $\mathrm{PdCl}_{2}$ (dmape) $(30 \mathrm{mg}, 0.041 \mathrm{mmol})$ was added an aqueous KOH solution ( $5 \mathrm{~mL}, 1 \mathrm{~mol} \mathrm{~L}^{-1}$ ), this causing an immediate colour change in
the organic layer from yellow to orange-red. The two phase mixture was stirred for 1 h and then the aqueous layer was removed. $\mathrm{H}_{2} \mathrm{O}(5 \mathrm{~mL})$ was added, followed by $\mathrm{KPF}_{6}$ ( $83 \mathrm{mg}, 0.45 \mathrm{mmol}$ ), and stirring was continued for 0.5 h . The aqueous layer was removed and the $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ phase was washed with $\mathrm{H}_{2} \mathrm{O}(3 \times 10 \mathrm{~mL})$ before being filtered through Celite 545 . The filtrate was reduced to dryness in vacuo and taken up in $\mathrm{CDCl}_{3}$ for analysis by solution NMR spectroscopy. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta$ $28.1\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=62.2\right), 29.3\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=62.2\right), 31.5\left(\mathrm{~s}\right.$, dmape $\left.(\mathrm{O})_{2}\right),-144\left(\mathrm{spt}, \mathrm{PF}_{6}{ }^{-},{ }^{1} J_{\mathrm{PF}}=\right.$ 710). A small crop of X-ray diffraction quality crystals of the title complex formed by slow evaporation of the $\mathrm{CDCl}_{3}$ solution.

### 2.9.2.13 $\quad \mathbf{P d}_{2} \mathbf{C l}_{2}$ (dmape)

To a combination of trans $-\mathrm{PdCl}_{2}(\mathrm{PhCN})_{2}(35 \mathrm{mg}, 0.091 \mathrm{mmol}), \mathrm{Pd}_{2}(\mathrm{dba})_{3} \cdot \mathrm{CHCl}_{3}(47 \mathrm{mg}$, $0.046 \mathrm{mmol})$ and dmape ( $52 \mathrm{mg}, 0.091 \mathrm{mmol}$ ) was added $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$, and the resulting purple solution was stirred over night. The brown solution was filtered through Celite 545 and the volume of the filtrate was reduced in vacuo to $c a .1 \mathrm{~mL}$. Addition of $\mathrm{Et}_{2} \mathrm{O}(20 \mathrm{~mL})$ gave a green-brown precipitate $(57 \mathrm{mg}) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy revealed that this solid contained a symmetric ( $\delta_{\mathrm{P}}=35.2$ ) and an asymmetric ( $\delta_{\mathrm{P}}=70.8$, 86.2) product. The former was isolated by column chromatography using silica gel as the stationary phase ( $20 \mathrm{~cm} \times 0.8 \mathrm{~cm}$ i.d.) and $\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{EtOH}$ ( $19: 1$ by vol.) as eluent. The first band (orange) was collected and reduced to $c a .1 \mathrm{~mL}$ in vacuo. Addition of $\mathrm{Et}_{2} \mathrm{O}$ $(10 \mathrm{~mL})$ gave an orange precipitate that was washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 2 \mathrm{~mL})$ and dried under vacuum at $78{ }^{\circ} \mathrm{C}$. Yield: 15 mg ( $19 \%$ ). The NMR data are consistent with the title formulation but, for reasons that remain unclear, the elemental analysis is poor. Anal. Calcd for $\mathrm{C}_{34} \mathrm{H}_{44} \mathrm{~N}_{4} \mathrm{Cl}_{2} \mathrm{P}_{2} \mathrm{Pd}_{2}$ : C, 47.8; H, 5.2; $\mathrm{N}, 6.6$. Found: C, $45.9 ; \mathrm{H}, 5.1 ; \mathrm{N}, 6.1 .{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 2.38\left(\mathrm{~s}, 12 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.77\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 2.87(\mathrm{~s}, 6 \mathrm{H}$, $\mathrm{NCH}_{3}$ ), 3.11 ( $\mathrm{s}, 6 \mathrm{H}, \mathrm{NCH}_{3}$ ), 7.01 (pt, 2H, Ar), 7.15 (pt, 4H, Ar), 7.29 (m, 2H, Ar), 7.42 (m, 4H, Ar), $7.54(\mathrm{~m}, 2 \mathrm{H}, \mathrm{Ar}), 7.62(\mathrm{~m}, 2 \mathrm{H}, \mathrm{Ar}) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(121 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.$, 300 K ): $\delta 35.2$ (s).

### 2.9.2.14 $\quad\left[P d\left(\eta^{3}\right.\right.$-allyl $)\left(P, P{ }^{\prime}\right.$-dmape $\left.)\right]\left[P_{6}\right]$

To a combination of $\left[\operatorname{Pd}(\mu-\mathrm{Cl})\left(\eta^{3} \text {-allyl) }\right]_{2} \quad(39 \mathrm{mg}, 0.11 \mathrm{mmol})\right.$, dmape $(120 \mathrm{mg}$, $0.21 \mathrm{mmol})$ and $\mathrm{NH}_{4} \mathrm{PF}_{6}(120 \mathrm{mg}, 0.72 \mathrm{mmol})$ was added $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ and acetone
( 5 mL ), and the resulting slurry was stirred for 0.5 h . The solvent was removed in vacuo and the work-up procedure was identical to that for $\left[\mathrm{PtCl}\left(P, P^{\prime}, N\right.\right.$-dmape $\left.)\right]\left[\mathrm{PF}_{6}\right]$ (Section 2.9.2.4). Yield: $160 \mathrm{mg}(86 \%)$. Acceptable elemental analysis was not obtained for this complex. ${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta 2.27\left(\mathrm{~s}, 24 \mathrm{H}, \mathrm{NCH}_{3}\right), 4.42(\mathrm{~d}, 2 \mathrm{H}$, CHH ), 3.07 (d, 2H, CHH), 5.57 (qn, 1H, CH), 7.1-7.6(m, 16H, Ar). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 44.2(\mathrm{~s}),-144\left(\mathrm{spt},{ }^{1} J_{\mathrm{PF}}=710, \mathrm{PF}_{6}{ }^{-}\right.$).

### 2.9.3 Syntheses and reactions of $R u$ complexes

### 2.9.3.1 $\quad \mathrm{RuCl}_{2}\left(P, P, N, N^{\prime}\right.$ 'dmape $)$

The title compound was made under two different sets of conditions.
(a) $\mathrm{CH}_{2} \mathrm{Cl}_{2}$, r.t., overnight reaction. To a combination of $\mathrm{RuCl}_{2}\left(\mathrm{PPh}_{3}\right)_{3}(71 \mathrm{mg}$, 0.074 mmol ) and dmape ( $43 \mathrm{mg}, 0.075 \mathrm{mmol}$ ) was added $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$. The brown solution was stirred magnetically overnight at r.t. The volume of the solvent was reduced in vacuo to ca. 2 mL and $\mathrm{Et}_{2} \mathrm{O}(20 \mathrm{~mL})$ and hexanes ( 20 mL ) were added; when the solvent volume was reduced to $c a .20 \mathrm{~mL}$ under vacuum, the product precipitated solely as the cis isomer. Yield: 24 mg ( 43 \%). Anal. Calcd for $\mathrm{C}_{34} \mathrm{H}_{44} \mathrm{~N}_{4} \mathrm{Cl}_{2} \mathrm{P}_{2} \mathrm{Ru}$ : C, 55.0; H , 6.0; N, 7.5. Found: C, $55.1 ; \mathrm{H}, 6.1 ; \mathrm{N}, 7.4 \%{ }^{1} \mathrm{H}$ NMR ( $200 \mathrm{MHz}, \mathrm{D}_{2} \mathrm{O}, 300 \mathrm{~K}$ ): $\delta 1.70$ $\left(\mathrm{m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 2.50\left(\mathrm{~s}, 12 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.90\left(\mathrm{~s}, 12 \mathrm{H}, \mathrm{NCH}_{3}\right), 7.2-8.0(\mathrm{~m}, 16 \mathrm{H}, \mathrm{Ar}) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{D}_{2} \mathrm{O}, 300 \mathrm{~K}$ ): $\delta 83.1(\mathrm{~s}) . \Lambda_{\mathrm{M}}(298 \mathrm{~K}): 211\left(\mathrm{H}_{2} \mathrm{O}\right),<1\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$.
(b) $\mathrm{CH}_{2} \mathrm{ClCH}_{2} \mathrm{Cl}$, reflux, 2.5 h reaction. To a combination of $\mathrm{RuCl}_{2}\left(\mathrm{PPh}_{3}\right)_{3}$ ( $230 \mathrm{mg}, 0.24 \mathrm{mmol}$ ) and dmape ( $140 \mathrm{mg}, 0.25 \mathrm{mmol}$ ) was added 1,2-dichloroethane $(10 \mathrm{~mL})$ and the resulting brown solution refluxed for 2.5 h . The orange solution was reduced to dryness in vacuo and $\mathrm{Et}_{2} \mathrm{O}(10 \mathrm{~mL})$ was added. Tritulation gave a yellow powder which was isolated by filtration, washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 5 \mathrm{~mL})$ and dried in vacuo. Yield: $157 \mathrm{mg}(86 \%)$. This procedure gave predominantly the cis isomer with ca. $5-10 \%$ of the trans. Cis-RuCl $_{2}$ (P,P',N,N'-dmape): ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 2.25\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.45\left(\mathrm{brm}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 2.63\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.93\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{NCH}_{3}\right)$, $3.36\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{NCH}_{3}\right), 7.05-7.70(\mathrm{~m}, 16 \mathrm{H}, \mathrm{Ar}) .{ }^{31} \mathrm{P}\left\{{ }^{\mathrm{l}} \mathrm{H}\right\} \mathrm{NMR}\left(121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta$ 94.6 (s). Trans-RuCl $\mathbf{Z}_{\mathbf{2}} \boldsymbol{P}, \boldsymbol{P}^{\prime}, N, N^{\prime}$-dmape): ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \operatorname{NMR}\left(121 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.$, r.t.): $\delta 26.0$ (s). ${ }^{1} \mathrm{H}$ NMR peaks were completely obscured by those of the cis isomer and could not be identified.

### 2.9.3.2 $\quad\left[\mathrm{Ru}\left(P, P^{\prime}, N, N^{\prime}, N^{\prime}, N^{\prime}{ }^{\prime \prime}\right.\right.$-dmape $\left.)\right]\left[\mathrm{PF}_{6}\right]_{2}$

To a combination of $\mathrm{RuCl}_{2}\left(P, P^{\prime}, N, N^{\prime}-\right.$ dmape $)(71 \mathrm{mg}, 0.096 \mathrm{mmol})$ and $\mathrm{NH}_{4} \mathrm{PF}_{6}(80 \mathrm{mg}$, 0.49 mmol ) was added acetone ( 6 mL ), and the yellow suspension stirred for 1 h . The solvent was removed in vacuo and the residue taken up in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$ which was then filtered through Celite 545 . The yellow filtrate was reduced to $c a .1 \mathrm{~mL}$ at the pump and the product was afforded as a pale yellow powder by the addition of $\mathrm{Et}_{2} \mathrm{O}(10 \mathrm{~mL})$. This was isolated by filtration and washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 2 \mathrm{~mL})$. The yield could not be determined accurately at this point due to the product being a mixture of solventcoordinated species, $\left[\mathrm{Ru}(\mathrm{S})_{n}\left(P_{2}, N_{4-n}\right.\right.$-dmape $\left.)\right]\left[\mathrm{PF}_{6}\right]_{2}\left(\mathrm{~S}=\right.$ acetone, $\left.\mathrm{H}_{2} \mathrm{O} ; n=1-4\right)$, but was approximately $70 \%$. The product on drying thoroughly in vacuo at $78{ }^{\circ} \mathrm{C}$ changed from yellow to orange-red. Anal: Calcd for $\mathrm{C}_{34} \mathrm{H}_{44} \mathrm{~N}_{4} \mathrm{~F}_{12} \mathrm{P}_{4} \mathrm{Ru}$ : C, 42.5 ; H, 4.6; N, 5.8. Found: C, 42.4; H, 4.9; N, $6.0 \%$. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 220 \mathrm{~K}$ ): $\delta 2.30\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 1.70$ (br s, $6 \mathrm{H}, \mathrm{NCH}_{3}$ ), 2.67 (br s, $12 \mathrm{H}, \mathrm{NCH}_{3}$ ), 3.10 (br s, $6 \mathrm{H}, \mathrm{NCH}_{3}$ ), $7.0-7.8$ (br m, 16 H , Ar). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 220 \mathrm{~K}$ ): $\delta 95.6$ (s).

### 2.9.3.3 Reaction of [Ru(P,P, $N, N^{\prime}, N^{\prime}, N^{\prime \prime}{ }^{\prime \prime}$-dmape $\left.)\right]\left[\mathrm{PF}_{6}\right]_{2}$ with $\mathrm{H}_{2} \mathrm{~S}$

An NMR tube containing $c a .5 \mathrm{mg}$ of $\left[\mathrm{Ru}(\mathrm{S})_{n}\left(P_{2}, N_{4-n}\right.\right.$-dmape) $]\left[\mathrm{PF}_{6}\right]_{2}$ (see Section 2.9.3.2, above) and fitted with a J. Young tap was evacuated at $100^{\circ} \mathrm{C}$ for 5 min . In this time, the solid reagent changed from yellow to orange-red. $\mathrm{CDCl}_{3}$ (ca. 0.5 mL ) was then condensed into the tube, and 1 atm of $\mathrm{H}_{2} \mathrm{~S}$ was admitted. The solution changed colour from red to yellow. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR data for this reaction are reported in Table 2.10.

### 2.9.3.4 Reaction of [Ru(P,P', $N, N^{\prime}, N^{\prime}, N^{\prime \prime}{ }^{\prime \prime}$-dmape $\left.)\right]\left[P_{6}\right]_{2}$ with $\mathrm{H}_{2} \mathrm{O}$

An NMR tube charged with $\left[\operatorname{Ru}(S)_{n}\left(P_{2}, N_{4-n}\right.\right.$-dmape) $]\left[\mathrm{PF}_{6}\right]_{2}$ (ca. 45 mg ; Section 2.9.3.2) was placed uncapped in a Schlenk tube connected to a vacuum pump. The Schlenk tube was immersed in an oil-bath set at $100^{\circ} \mathrm{C}$ and evacuated for 10 min . To $\mathrm{CH}_{2} \mathrm{Cl}_{2}(20 \mathrm{~mL})$, freshly-distilled from $\mathrm{CaH}_{2}$, was added $\mathrm{H}_{2} \mathrm{O}(20 \mu \mathrm{~L})$ and the mixture was shaken thoroughly. Analysis by Carl-Fisher titration showed the $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ to contain 850 ppm $\mathrm{H}_{2} \mathrm{O}$. Under a flow of Ar , this solution ( $c a .1 .5 \mathrm{~mL}$ ) was used to dissolve the $\left[\mathrm{Ru}\left(P, P^{\prime}, N, N^{\prime}, N^{\prime \prime}, N^{\prime \prime \prime}\right.\right.$-dmape $\left.)\right]\left[\mathrm{PF}_{6}\right]_{2}$ generated in the NMR tube, which was then capped and sealed with Parafilm. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR data for this reaction are reported in Table 2.10.

### 2.9.4 Miscellaneous reactions

### 2.9.4.1 Reactions between dmapcp and $\mathrm{PdCl}_{2}(\mathbf{c o d})$

The title reaction was conducted both at r.t. and at $-40^{\circ} \mathrm{C}$.
(a) At r.t. To a combination of solid $\mathrm{PdCl}_{2}(\operatorname{cod})(44 \mathrm{mg}, 0.15 \mathrm{mmol})$ and dmapep ( $91 \mathrm{mg}, 0.15 \mathrm{mmol}$ ) was added $\mathrm{CH}_{2} \mathrm{Cl}_{2}(8 \mathrm{~mL})$. The resulting orange solution was stirred at r.t. for 1 h when it became bright yellow. $\mathrm{NH}_{4} \mathrm{PF}_{6}(126 \mathrm{mg}, 0.77 \mathrm{mmol})$ was added followed by acetone ( 7 mL ). The solution became cloudy instantly. Stirring was continued for an additional 1 h before the suspension was reduced to dryness in vacuo. The residue was taken up in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$ and the mixture was filtered through Celite 545. The filtrate was reduced to $c a .1 \mathrm{~mL}$ at the pump and ether $(20 \mathrm{~mL})$ was added to give the product mixture as a yellow powder. This was isolated by filtration, washed with $\mathrm{Et}_{2} \mathrm{O}$ and dried in vacuo. Yield: 145 mg . The product is a mixture of $\left[\operatorname{PdCl}\left(P, P^{\prime}, N-\right.\right.$ dmapcp) $]\left[\mathrm{PF}_{6}\right]$ and an organometallic intermediate as discussed in Section 2.5.7; the ${ }^{1} \mathrm{H}$ and ${ }^{31} \mathrm{P}$ NMR spectra contain peaks due to $\left[\operatorname{PdCl}\left(P, P^{\prime}, N \text {-dmapcp }\right)\right]^{+}$(Section 2.9.2.6) and these others (assignments followed by "?" are tentative): ${ }^{1} \mathrm{H} \mathrm{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.$, $300 \mathrm{~K}): \delta 0.90\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{CH}_{2}\right.$ of $\mathrm{C}_{8} \mathrm{H}_{8}$ moiety), $1.05\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{HC}-\mathrm{Pd}\right.$ ?), $1.60\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{CH}_{2}\right.$ of dmapcp), $1.80\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{CH}_{2}\right.$ of $\mathrm{C}_{8} \mathrm{H}_{8}$ moiety), $1.90\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{CH}_{2}\right.$ of $\mathrm{C}_{8} \mathrm{H}_{8}$ moiety), 2.05 (m, 1H, CH2 of dmapcp), 2.18 (s, $3 \mathrm{H}, \mathrm{NCH}_{3}$ ), 2.21 ( $\mathrm{s}, 12 \mathrm{H}, \mathrm{NCH}_{3}$ ), $2.85\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{NCH}_{3}\right)$, $2.90\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right), 3.40\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{CH}_{2}\right.$ of $\mathrm{C}_{8} \mathrm{H}_{8}$ moiety), $3.70(\mathrm{~m}, 1 \mathrm{H}, \mathrm{CH}$ of dmapcp), $4.15\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{N}^{+}-\mathrm{CH}\right.$ ?), $5.23(\mathrm{~m}, 1 \mathrm{H}, \mathrm{CH}=\mathrm{C} H), 5.65(\mathrm{~m}, 1 \mathrm{H}, \mathrm{C} H=\mathrm{C} H)$. Except for a prominent multiplet at $\delta 8.67$, peaks due to the intermediate overlap with those due to $\left[\mathrm{PdCl}\left(P, P^{\prime}, N \text {-dmapcp }\right)\right]^{+}$in the aromatic region and could not be discerned. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 36.5\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=8.8\right), 47.8\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=8.8\right)$.
(b) At $-40^{\circ} \mathrm{C}$. (In this procedure, "cold" and "cooled" refer to $-40^{\circ} \mathrm{C}$.) ${\mathrm{A} \mathrm{CH}_{2} \mathrm{Cl}_{2}}$ ( 5 mL ) slurry containing $\mathrm{PdCl}_{2}(\operatorname{cod})(94 \mathrm{mg}, 0.33 \mathrm{mmol})$ and $\mathrm{NH}_{4} \mathrm{PF}_{6}(160 \mathrm{mg}$, 0.98 mmol ) was cooled on a dry ice $/ \mathrm{CH}_{3} \mathrm{CN}$ bath. Over the course of 5 min , a cold $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ solution containing dmapcp ( $200 \mathrm{mg}, 0.33 \mathrm{mmol}$ ) was added to the slurry. After 5 min , cold acetone ( 5 mL ) was added and stirring was continued for 0.5 h . The solvent was removed in vacuo at $-40^{\circ} \mathrm{C}$, and the residue was taken up in cold $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ $(10 \mathrm{~mL})$ and the mixture was filtered through Celite 545 . The filtrate was reduced in vacuo to $c a .1 \mathrm{~mL}$ and cold $\mathrm{Et}_{2} \mathrm{O}(20 \mathrm{~mL})$ was added to give the product mixture as an
off-white powder that was recovered in the same manner as outlined in (a). Yield: 160 mg . The product is a mixture of $\left[\operatorname{PdCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right]\left[\mathrm{PF}_{6}\right]$ and several organometallic intermediates as discussed in Section 2.5.7. The ${ }^{31} \mathrm{P}$ NMR $(121 \mathrm{MHz}$, $\mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ) spectrum recorded 6 hours after making the sample contains peaks due to $\left[\mathrm{PdCl}\left(P, P^{\prime}, N \text {-dmapcp }\right)\right]^{+}$(Section 2.9.2.6) and these others: $\delta 33.8\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=111\right), 38.6$ $\left(\mathrm{d},{ }^{2} J_{\mathrm{PP}}=111\right), 24.7\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=85.5\right), 50.3\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=85.5\right), 26.4\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=102\right), 41.4(\mathrm{~d}$, ${ }^{2} J_{\mathrm{PP}}=102$ ). The ${ }^{1} \mathrm{H}$ NMR spectrum is too complicated for any definite assignments to be made, but evidence of coordinated olefin is given by a series of multiplets in the $\delta 4.6$ 6.4 range.

### 2.9.4.2 Halide-free reaction between $\mathrm{PdCl}_{2}$ (dmape) and KOH

The initial step of title reaction was performed as outlined in Section 2.9.2.12, except that the $\mathrm{PdCl}_{2}$ (dmape) $(100 \mathrm{mg}, 0.14 \mathrm{mmol})$ was dissolved in $\mathrm{CH}_{3} \mathrm{NO}_{2}(5 \mathrm{~mL})$ instead of in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$. After 2 h of reaction, the aqueous (red) and organic (orange) phases were separated. The aqueous phase was washed with $\mathrm{CH}_{3} \mathrm{NO}_{2}(3 \times 5 \mathrm{~mL})$ and the combined organic fractions were reduced to dryness in vacuo and the residue was taken up in acetone $(10 \mathrm{~mL})$. The volume of the red solution was reduced at the pump to $c a .1 \mathrm{~mL}$, and $\mathrm{Et}_{2} \mathrm{O}(20 \mathrm{~mL})$ was added to give the product as a clump which was broken up by sonication. Yield: $70 \mathrm{mg} .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 121 MHz , acetone- $\mathrm{d}_{6}, 300 \mathrm{~K}$ ): $\delta 61(\mathrm{br} \mathrm{s}), 73$ (br s).

### 2.9.4.3 Reduction of $\mathrm{PtCl}_{2}$ (dmape) by $\mathbf{N a} / \mathbf{H g}$

An amalgam was made by dissolving $\mathrm{Na}(20 \mathrm{mg})$ in $\mathrm{Hg}(3 \mathrm{~mL})$. Onto this was layered a THF ( 20 mL ) solution containing $\mathrm{PtCl}_{2}$ (dmape) ( $c a .50 \mathrm{mg}, 0.060 \mathrm{mmol}$ ). The colourless organic layer immediately became brown and a precipitate formed. After 20 min , the slurry was decanted into $\mathrm{C}_{6} \mathrm{H}_{6}(15 \mathrm{~mL})$ and the combined mixture was filtered through Celite 545. The red filtrate was reduced to dryness in vacuo yielding an orange solid. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}, 300 \mathrm{~K}$ ): $\delta 38.9\left(\mathrm{~s},{ }^{1} \mathrm{~J}_{\mathrm{PPt}}=3580\right)$.

### 2.9.4.4 In situ generation of $\operatorname{Pt}\left(\eta^{2}-\mathrm{dmm}\right)(P, P$ '-dmape $)$

To an NMR tube fitted with a J. Young screw cap was added $\operatorname{Pt}(\mathrm{ox})\left(P, P^{\prime}\right.$-dmape $)$ ( $7.4 \mathrm{mg}, 0.009 \mathrm{mmol}$ ), dmm ( $5.5 \mu \mathrm{~L}, 0.044 \mathrm{mmol}$ ) and $\mathrm{CD}_{2} \mathrm{Cl}_{2}(0.5 \mathrm{~mL})$. Three freeze-
pump-thaw cycles were performed. The tube was then subjected to UV irradiation by a Hg lamp for 2.25 h when the solution changed from colourless to yellow. The following peak assignments are tentative. ${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 300 \mathrm{~K}\right): \delta 2.50\left(\mathrm{NCH}_{3}\right)$, $3.20\left(\mathrm{CH}_{2}\right), 3.69$ and $3.73(\mathrm{CH}=\mathrm{CH}), 3.77\left(\mathrm{C}(\mathrm{O}) \mathrm{OCH}_{3}\right), 7.1-7.7(\mathrm{Ar}) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 300 \mathrm{~K}$ ): $\delta 43.8\left(\mathrm{~s},{ }^{1} J_{\mathrm{PPt}}=3910\right)$.

### 2.9.4.5 Reaction of $\mathbf{P d C l}_{\mathbf{2}}$ (dmape) and bases

(a) $\mathrm{K}_{2} \mathrm{CO}_{3}$. To a mixture of $\mathrm{PdCl}_{2}$ (dmape) $(15 \mathrm{mg}, 0.020 \mathrm{mmol})$ and $\mathrm{K}_{2} \mathrm{CO}_{3}$ ( 140 mg , 1.00 mmol ) was added acetone ( 5 mL ) and the resulting yellow slurry was stirred magnetically overnight when it turned orange-red. The solvent was removed in vacuo, the residue was taken up in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and the mixture filtered through Celite 545 . The filtrate was reduced to dryness under vacuum and the solid was dissolved in $\mathrm{CDCl}_{3}$ for solution NMR analysis. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta \delta 35.2$ (s), $70.8\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{PP}}=\right.$ 565), $86.2\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=565\right)$.
(b) $K O^{\mathrm{t}} \mathrm{Bu}$. To a $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ solution of $\mathrm{PdCl}_{2}$ (dmape) ( $110 \mathrm{mg}, 0.15 \mathrm{mmol}$ ) was added $\mathrm{KO}^{t} \mathrm{Bu}(16 \mathrm{mg}, 0.15 \mathrm{mmol})$. The yellow solution turned orange within 5 min and was stirred under Ar for 2 d during which a yellow precipitate formed. This was isolated by filtration, washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 3 \mathrm{~mL})$ and dried in vacuo. The yield was not recorded. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 35.2(\mathrm{~s}), 70.8\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=565\right), 86.2$ (d, ${ }^{2} J_{\mathrm{PP}}=565$ ).

### 2.9.5 Catalytic C-N bond formation

### 2.9.5.1 Experimental

To a $\mathrm{C}_{6} \mathrm{H}_{6}$ solution ( 5 mL ) containing $\operatorname{PhBr}(100 \mu \mathrm{~L}, 0.98 \mathrm{mmol})$, aniline $(90 \mu \mathrm{~L}$, $0.99 \mathrm{mmol})$ and $\mathrm{PdCl}_{2}$ (dmape) ( $15 \mathrm{mg}, 0.019 \mathrm{mmol}$ ) in a 3-neck round-bottom flask topped with a condenser and heated to $70^{\circ} \mathrm{C}$ was added $\mathrm{KO}^{t} \mathrm{Bu}(110 \mathrm{mg}, 0.98 \mathrm{mmol})$ under air. This marked the beginning of the reaction. At 30 min intervals, $2 \mu \mathrm{~L}$ samples were withdrawn by syringe, $0.1 \mu \mathrm{~L}$ of each being used for GC analysis.

### 2.9.5.2 GC analysis

GC parameters used in analysis of $\mathrm{C}-\mathrm{N}$ bond forming reactions are given in Table 2.11, and elution times under these conditions for components of interest appear in Table 2.12.

Table 2.11 GC parameters used in the determination of $\mathrm{C}-\mathrm{N}$ bond forming reaction components.

| Parameter | Setting |
| :--- | :--- |
| Initial oven temperature | $80^{\circ} \mathrm{C}$ |
| Final oven temperature | $220^{\circ} \mathrm{C}$ |
| Rate | $20^{\circ} \mathrm{C} \min ^{-1}$ |
| Initial time | $2 \min$ |
| Final time | $4 \min$ |
| Injector temperature | $220^{\circ} \mathrm{C}$ |
| Detector temperature | $220^{\circ} \mathrm{C}$ |
| Column head pressure | 105 kPa |

Table 2.12 Elution times for Heck reaction components under the GC conditions given in Table 2.11.

| Component | Retention time (min) |
| :--- | :--- |
| PhBr | 2.79 |
| Aniline | 3.90 |
| Diphenylamine | 9.15 |

### 2.9.6 Determination of equilibrium constants from ${ }^{31} P\left\{{ }^{1} \mathrm{H}\right\}$ VT NMR data

${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra were acquired for $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ solutions containing the appropriate complex (ca. 6-9 $\times 10^{-2} \mathrm{~mol} \mathrm{~L}^{-1}$ ) at various temperatures in the range $213-273 \mathrm{~K}$. In order to ensure accurate integrations, the delay between pulses was set to 4 s . This is reasonable in light of spin-inversion-recovery experiments which showed that the longest $\mathrm{T}_{1}$ relaxation of all the P-nuclei was approximately 0.75 s . The decoupler was set to fire only in the acquisition phase of the pulse program so as to minimise NOE perturbations. The acquisition time in all experiments was 0.4 s . An equilibration time of 0.5 h was allowed at each temperature before acquisition was begun.

### 2.9.6.1 The $\mathrm{PtCl}_{2}\left(P, P^{\prime}\right.$-dmape $) \rightleftharpoons\left[\mathrm{PtCl}\left(P, P^{\prime}, N \text {-dmape }\right)\right]^{+}+\mathrm{Cl}^{-}$equilibrium

 A typical ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum for the system is shown in Figure 2.17. The peaks due to $\left[\operatorname{PtCl}\left(P, P^{\prime}, N \text {-dmape }\right)\right]^{+}$are marked by the number symbol (\#). The peaks due to $\mathrm{PtCl}_{2}\left(P, P^{\prime}\right.$-dmape) are indicated by asterisks (*). Because some of the peaks are overlapped or closely juxtaposed, the 9 peaks have been divided into 7 groups (labelled$1-7$ ), with areas $\mathrm{A}_{1}-\mathrm{A}_{7}$, respectively. The total concentration of Pt is $\mathrm{Pt}_{\text {тот }}$. In order to determine the concentrations of $\mathrm{PtCl}_{2}\left(P, P^{\prime}\right.$-dmape $)$ and $\left[\mathrm{PtCl}\left(P, P^{\prime}, N \text {-dmape }\right)\right]^{+}$in solution and thus an equilibrium constant, K , at each temperature, the following procedure was adopted.


Figure 2.17 A typical low temperature ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 240 \mathrm{~K}$ ) spectrum of an equilibrium mixture of $\mathrm{PtCl}_{2}\left(P, P^{\prime}\right.$-dmape $)$ and $\left[\mathrm{PtCl}\left(P, P^{\prime}, N\right.\right.$-dmape $\left.)\right] \mathrm{Cl}$. Peak assignments are discussed in the text.

The area under the major peaks due to $\left[\operatorname{PtCl}\left(P, P^{\prime}, N \text {-dmape }\right)\right]^{+}$(APPN), i.e., not counting "satellites", is given by:

$$
\mathrm{A}_{\mathrm{PPN}}=\mathrm{A}_{3}+\mathrm{A}_{6}-\mathrm{A}_{2}
$$

The area under the corresponding peak due to $\mathrm{PtCl}_{2}\left(P, P^{\prime}-\mathrm{dmape}\right)$ ( $\mathrm{A}_{\mathrm{PP}}$ ) is:

$$
\mathrm{A}_{\mathrm{PP}}=\mathrm{A}_{4}-\mathrm{A}_{7}
$$

The concentration of $\left[\mathrm{PtCl}\left(P, P^{\prime}, N \text {-dmape }\right)\right]^{+}$in solution (PPN) is therefore:

$$
\mathrm{PPN}=\mathrm{A}_{\mathrm{PPN}} /\left(\mathrm{A}_{\mathrm{PPN}}+\mathrm{A}_{\mathrm{PP}}\right) \times \mathrm{Pt}_{\mathrm{TOT}}
$$

And, likewise, the concentration of $\mathrm{PtCl}_{2}\left(P, P^{\prime}\right.$-dmape $)(\mathrm{PP})$ is given by:

$$
\mathrm{PP}=\mathrm{A}_{\mathrm{PP}} /\left(\mathrm{A}_{\mathrm{PPN}}+\mathrm{A}_{\mathrm{PP}}\right) \times \mathrm{Pt}_{\mathrm{TOT}}
$$

For the equilibrium $\mathrm{PtCl}_{2}\left(P, P^{\prime}\right.$-dmape $) \rightleftharpoons\left[\mathrm{PtCl}\left(P, P^{\prime}, N \text {-dmape }\right)\right]^{+}+\mathrm{Cl}^{-}$,

$$
\mathrm{K}=\mathrm{PPN}^{2} / \mathrm{PP}
$$

### 2.9.6.2 The $\mathrm{PdCl}_{2}\left(P, P^{\prime}-\right.$ dmape $) \rightleftharpoons\left[\mathrm{PdCl}\left(P, P^{\prime}, N \text {-dmape }\right]^{+}+\mathrm{Cl}^{-}\right.$equilibrium

The case of Pd is simplified due to the absence of "satellites" and the spectrum contains only 3 peaks, labelled $1-3$, with areas $A_{1}-A_{3}$, respectively. A typical spectrum is shown in Figure 2.18. Once again, peaks due to the $P, P^{\prime}, N$-isomer $\left[\operatorname{PdCl}\left(P, P^{\prime}, N \text {-dmape }\right)\right]^{+}$are marked with the number symbol (\#) and that due to the $P, P^{\prime}$-isomer by an asterisk ( ${ }^{*}$ ). The calculation of equilibrium constants is performed in exactly the same manner as outlined above save for the fact that overlapping "satellites" do not have to be accounted for. As in the case of $\mathrm{PtCl}_{2}$ (dmape), the total concentration of Pd is $\mathrm{Pd}_{\mathrm{TOT}}$.


Figure 2.18 The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 233 \mathrm{~K}$ ) spectrum for the $\mathrm{PdCl}_{2}$ (dmape) system. Peak assignments are discussed in the text.

The area under the peaks due to $\left[\mathrm{PdCl}\left(P, P^{\prime}, N \text {-dmape }\right)\right]^{+}\left(\mathrm{A}_{\text {PPN }}\right)$ is given by:

$$
\mathrm{A}_{\mathrm{PPN}}=\mathrm{A}_{1}+\mathrm{A}_{3}
$$

The area under the peak due to $\mathrm{PdCl}_{2}\left(P, P^{\prime}\right.$-dmape $), \mathrm{A}_{\mathrm{PP}}=\mathrm{A}_{2}$. The concentration of $\left[\mathrm{PdCl}\left(P, P^{\prime}, N \text {-dmape }\right)\right]^{+}$in solution ( PPN ) is therefore:

$$
\mathrm{PPN}=\mathrm{A}_{\mathrm{PPN}} /\left(\mathrm{A}_{\text {PPN }}+\mathrm{A}_{\mathrm{PP}}\right) \times \mathrm{Pd}_{\mathrm{TOT}}
$$

And, likewise, the concentration of $\mathrm{PdCl}_{2}\left(P, P^{\prime}\right.$-dmape) ( PP ) is given by:

$$
\mathrm{PP}=\mathrm{A}_{\mathrm{PP}} /\left(\mathrm{A}_{\mathrm{PPN}}+\mathrm{A}_{\mathrm{PP}}\right) \times \mathrm{Pt}_{\mathrm{TOT}}
$$

For the equilibrium $\mathrm{PdCl}_{2}\left(P, P^{\prime}-\right.$ dmape $) \Longrightarrow\left[\mathrm{PdCl}\left(P, P^{\prime}, N \text {-dmape }\right)\right]^{+}+\mathrm{Cl}^{-}$,

$$
\mathrm{K}=\mathrm{PPN}^{2} / \mathrm{PP}
$$

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## 3 Late Transition Metal Complexes of dmapm, and the Heck Reaction

### 3.1 Introduction

The Pd-catalysed Heck reaction represents an important method for the formation of C-C bonds. Since its introduction in 1968, ${ }^{1}$ it has been the subject of intensive research, ${ }^{2}$ and mechanistic aspects ${ }^{3,4}$ have been elucidated. In addition, much work has focussed on improving the efficiency and scope of the reaction by tailoring the Pd catalyst and by varying the reaction conditions (solvent, temperature, base, additives).

The first use of Pd-phosphine complexes for vinylic hydrogen substitution reactions was by Dieck and Heck in $1974 .{ }^{5}$ Although the catalysts are most frequently generated in situ (e.g. from $\mathrm{Pd}(\mathrm{OAc})_{2}$ and a monodentate tertiary phosphine), ${ }^{6-9}$ many preformed catalysts are now being reported. These include Pd complexes of chelating $\mathrm{PP},{ }^{10} \mathrm{PC},{ }^{11} \mathrm{PCP},{ }^{12} \mathrm{SCS}^{13}$ and $\mathrm{PN}^{14}$ ligands. In general, these compounds demonstrate much higher catalytic activities and lifetimes than their predecessors (which typically required a $1-5 \mathrm{~mol} \%$ loading) and turnover numbers as high as $10^{6}$ have been observed. ${ }^{15}$

The appearance of Pd catalyst precursors bearing "PN" ligands, and the fact that the Heck and related reactions have been successfully conducted in water (in the presence of a quaternary ammonium salt), ${ }^{16}$ or in mixtures of polar organic solvents (e.g. DMF, THF, $i-\mathrm{PrOH}$, nitriles) and water using Pd complexes of sulphonated phosphines, ${ }^{17}$ or of guanadinium phosphines, ${ }^{18}$ prompted this author to investigate the anilinyldiphosphine complexes resulting from this work as catalyst candidates for the Heck reaction.

In addition, two other developments encouraged the investigation. The first was the observation by Bankston et al. that in an intramolecular Heck cyclization of a series of crotyl ethers, the use of $\mathrm{RhCl}\left(\mathrm{PPh}_{3}\right)_{3}$ in combination with $\mathrm{Pd}(\mathrm{OAc})_{2}$ yielded a system in which the rate of reaction and the selectivity for the endocyclic form of the bicyclic ether products were significantly enhanced as compared to the use of $\mathrm{Pd}(\mathrm{OAc})_{2}$ alone: ${ }^{19}$
the two metals were considered to interact synergistically to mediate the intramolecular coupling, although no concrete proof or mechanism was presented.

It was recognised early in this work that the strong tendency for $-\mathrm{CH}_{2}$ - tethered diphosphines to bridge metal centres ${ }^{20}$ combined, in the case of dmapm (Chart 3.1, left), with the possibility of five-membered PN chelate formation, gave access to a variety of homo- and heterobimetallic complexes of the general form illustrated in Chart 3.1 (right; $\mathrm{Ar}=o-\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{NMe}_{2}, \mathrm{X}=$ halide $)$.

## Chart 3.1




Use of these complexes as Heck catalysts allowed the assessment of the catalytic effects of a second metal centre, not supplied simply as an additive, as in Bankston's case, but rather as an integral component of a bimetallic catalyst.

Cooperative effects between adjacent metal centres in complexes containing two or more bridged metal ions are now established for a variety of homogeneous, catalytic transformations and continue to attract attention. The great majority of these employ homobimetallic catalyst precursors. Representative examples include bimetallic catalysts for phosphoester hydrolysis $\left(\mathrm{Co}_{2},{ }^{21} \mathrm{Cu}_{2},{ }^{22,23} \mathrm{Zn}_{2}{ }^{24}\right)$, nitrile hydration ( $\mathrm{Ni}_{2},{ }^{25,26} \mathrm{Pd}_{2}{ }^{27}$ ), hydroformylation $\left(\mathrm{Rh}_{2},{ }^{28-31} \mathrm{Ru}_{2}{ }^{32}\right)$, alkene ${ }^{33}$ and alkyne ${ }^{34}$ hydrogenation ( $\mathrm{Ir}_{2}$ ) and asymmetric epoxide ring-opening ${ }^{35}\left(\mathrm{Cr}_{2}\right)$. In addition, cooperative effects between two different metal centres have been invoked but not proven to be operative in the catalytic hydrogenation of cyclohexene ${ }^{36}$ (RuIr) and in hydroformylations ${ }^{30}$ (RhPd).

The second development which motivated the Heck study was the so-called "thermomorphic" method described by Bergbreiter and coworkers. ${ }^{37}$ In this system, a Pdcentre is covalently bound to a soluble polymer which is immiscible with the liquid reactants at r.t. At elevated temperature, the polymer and reactants become miscible and
the catalysis occurs. Once the reaction is complete and the temperature is lowered, the product and polymer separate into two phases and the catalyst containing phase can be reused. The catalytic conditions outlined in this chapter are similar in principle: at r.t. the reaction mixture comprises two phases, whereas at $100^{\circ} \mathrm{C}$ there is only one phase, and at r.t. after 3 h of reaction the product, stilbene, crystallises.

### 3.2 Scope

This chapter examines the coordination chemistry of $\mathrm{Pt}^{\mathrm{II}}, \mathrm{Pd}^{\mathrm{II}}$ and $\mathrm{Rh}^{\mathrm{I}}$ with the $\mathrm{CH}_{2}-$ bridged anilinyldiphosphine ligand, dmapm, (see Sections 3.9.1-3.9.16 for the syntheses of the compounds, and Sections 3.3-3.4.4 for discussion) and investigates a pair of the resulting homo- and heterobimetallic complexes as catalysts for the Heck coupling of iodobenzene and styrene paying particular attention to the possibility for cooperative effects (Section 3.6). A generally applicable cooperativity index is proposed as a kinetic complement to the Hill coefficient (Section 3.6.3).

The solution dynamics of the precursor used for the bulk of the work, $\mathrm{PdCl}_{2}$ (dmapm) (Section 3.3.1), and of the bimetallic complexes $\mathrm{MM}^{\prime} \mathrm{Cl}_{4}(\mathrm{dmapm})(\mathrm{M}=$ $\mathrm{Pd}^{\mathrm{II}} ; \mathrm{M}^{\prime}=\mathrm{Pd}^{\mathrm{II}}, \mathrm{Pt}^{\mathrm{II}}$; Section 3.4.1), as well as the structure and bonding of $\mathrm{PdCl}_{2}$ (dmapm) (Section 3.3.3), and its reactivity with halide and cyanide (Section 3.3.4), peroxide and sulphur (Section 3.3.5) and metal precursors (Sections 3.4.1 $\left[\mathrm{Pt}^{\mathrm{II}}\right.$ and $\left.\mathrm{Pd}^{\mathrm{II}}\right], 3.4 .3\left[\mathrm{Rh}^{\mathrm{I}}\right]$ and 3.4.5.1 $\left.\left[\mathrm{Pd}^{0}\right]\right)$, are examined in detail. The syntheses of metal-metal bonded homoand heterobimetallic $\mathrm{M}^{1}$ complexes both by conproportionation of $\mathrm{M}^{0}$ and $\mathrm{M}^{\mathrm{II}}$ (Section 3.9.17) and by 2 -electron reduction of $\mathrm{M}^{11}$ dimers (Section 3.9.18) are presented. The reactivities of these bimetallic complexes toward CO and diethylacetylene dicarboxylate (DEAD) are also described (Section 3.4.5.3).

### 3.3 Complexes Containing One Metal Centre

### 3.3.1 Solution dynamics

The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ solution NMR spectrum (at $25^{\circ} \mathrm{C}$ ) of the product of the reaction between dmapm and trans $-\mathrm{PdCl}_{2}(\mathrm{PhCN})_{2}$ shows that two species are formed (Section 3.9.1). The
spectrum consists of an upfield singlet ( $\delta-56.8$ ) indicative of a $C_{2}$-symmetric compound, in which both P -atoms are involved in a 4 -membered chelate with $\mathrm{Pd}, 38$ i.e., $\mathrm{PdCl}_{2}\left(P, P^{\prime}-\right.$ dmapm), and an AX pattern with high- and low-field doublets ( $\delta-40.0$ and $33.5,{ }^{2} J_{\mathrm{PP}}$, $=$ 108 Hz ), consistent with a complex bearing one "dangling" P-atom (high-field) and one P -atom involved in a 5 -membered chelate with Pd , i.e., $\mathrm{PdCl}_{2}(P, N$ - dmapm ) (see Figure 3.4 for the molecular structure of the latter isomer). Elemental analysis of the isolated solid is consistent with the formulation $\mathrm{PdCl}_{2}$ (dmapm), confirming that these are isomers. In addition, varying the temperature at which the spectrum is acquired reversibly alters the relative peak intensities, which shows that $\mathrm{PdCl}_{2}\left(P, P^{\prime}-\mathrm{dmapm}\right)$ and $\mathrm{PdCl}_{2}(P, N-$ dmapm) are in thermal equilibrium (Scheme 3.1; $\mathrm{Ar}=0-\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{NMe}_{2}$ ). In contrast to this is the fact that reaction of one equiv. of dmapm with $\mathrm{PtCl}_{2}(\operatorname{cod})$ generates $\mathrm{PtCl}_{2}\left(P, P^{\prime}-\right.$ dmapm) exclusively (Section 3.9.9).

## Scheme 3.1



The temperature-dependence of the $\mathrm{NCH}_{3}$ region of the ${ }^{1} \mathrm{H}$ NMR spectrum of an equilibrium mixture of $\mathrm{PdCl}_{2}(\mathrm{dmapm})$ isomers is given in Figure 3.1. At 300 K , five singlets due to $\mathrm{NCH}_{3}$ protons are apparent at $\delta 3.70,3.47,2.85,2.49$ and 2.35 with relative integrations of $1: 1: 2: 2: 3$, respectively. These peaks represent all $24 \mathrm{NCH}_{3}$ protons associated with $\mathrm{PdCl}_{2}\left(P, P^{\prime}-\mathrm{dmapm}\right)$ and 18 of the 24 corresponding protons of $\mathrm{PdCl}_{2}\left(P, \mathrm{~N}\right.$-dmapm). The remaining $6 \mathrm{NCH}_{3}$ protons of the latter are broadened into the baseline at r.t. and only become visible as the temperature approaches 240 K . These assignments are based on the following observations. When the solution is cooled from 300 to 215 K , the singlet which at 300 K appears at $\delta 2.35$ becomes less intense, broadens and eventually disappears, while two new peaks at $\delta 1.61$ and 2.93 grow in. All the other
peaks in this region maintain their relative intensities, but drift slightly in chemical shift (by less than 0.1 ppm ). As judged by the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ spectrum at 215 K which shows a greatly diminished singlet due to $\mathrm{PdCl}_{2}\left(P, P^{\prime}\right.$-dmapm), the ${ }^{1} \mathrm{H}$ spectrum at this temperature is due almost completely to $\mathrm{PdCl}_{2}(P, N$-dmapm). Therefore, the peak at $\delta$ 2.35 (essentially temperature-invariant) is due to all 24 chemically equivalent $\mathrm{NCH}_{3}$ protons of the $P, P^{\prime}$-isomer, while the singlets at $\delta 1.61$ and 2.93 are associated with the $P, N$-isomer. The two equal intensity peaks which at 300 K appear at $\delta 3.70$ and 3.47 are most likely due to the two diastereotopic methyl groups directly connected to the Pd bound N -atom as judged by the large coordination shifts from their positions in the free ligand ( $\Delta \delta=1.02$ and 0.79 , respectively). By virtue of integration, the 2 peaks which grow in at low temperature are thus due to the 2 methyl groups on the free anilinyl ring associated with the Pd -bound P -atom. The disappearance of these peaks at r.t. can be explained by assuming that $\mathrm{PdCl}_{2}(P, N$-dmapm) is in rapid equilibrium with the 5coordinate complex $\mathrm{PdCl}_{2}\left(P, N, N^{\prime}\right.$-dmapm) , in which both N -atoms associated with a single P -atom are bound to Pd . Such 5 -coordinate $\mathrm{MX}_{2}\left(P, N, N^{\prime}\right)$ complexes have been proposed by Xie in the cis-trans isomerisation of $\mathrm{PtI}_{2}\left(\mathrm{PN}_{1}\right)_{2} .{ }^{39}$ The equilibrium for the dmapm system is illustrated by the top and bottom lines of Scheme 3.2.


Figure 3.1 Temperature-dependence of the $\mathrm{NCH}_{3}$ region of the ${ }^{1} \mathrm{H}$ NMR $(400 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}\right)$ spectrum of an equilibrium mixture of $\mathrm{PdCl}_{2}\left(P, P^{\prime}\right.$-dmapm) and $\mathrm{PdCl}_{2}(P, N$-dmapm $)$.

## Scheme 3.2



Scheme 3.2 outlines all the possible intramolecular associative mechanisms for the interchange between $\mathrm{PdCl}_{2}\left(P, P^{\prime}-\mathrm{dmapm}\right)$ and $\mathrm{PdCl}_{2}(P, N-\mathrm{dmapm})$. In this scenario, the 5 -coordinate intermediates are present in concentrations beneath the level of detection by NMR spectroscopy and the overall equilibrium $\mathrm{PdCl}_{2}\left(P, P^{\prime}-\mathrm{dmapm}\right) \rightleftharpoons \mathrm{PdCl}_{2}(P, N-$ dmapm) is slow on the NMR timescale. The top and bottom rows of the scheme correspond to stereo inversions at the P -atoms, while the left and right columns represent exchange of the P -atoms. The $\mathrm{PdCl}_{2}(P, N$-dmapm) complexes represented at the corners of the scheme are indistinguishable in an achiral medium.

If all the equilibria are operative, all N -atoms on one dmapm ligand should be in chemical exchange with each other, even across isomers. That this is so has been shown by a $2 \mathrm{D}{ }^{1} \mathrm{H}$ EXSY experiment (Figure 3.2). Clearly indicated in this spectrum are offdiagonal peaks which demonstrate chemical exchange between all $\mathrm{NCH}_{3}$ groups.


Figure 3.2 The 2D ${ }^{1} \mathrm{H}$ EXSY spectrum ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ) of the $\mathrm{NCH}_{3}$ region of an equilibrium mixture of $\mathrm{PdCl}_{2}\left(P, P^{\prime}\right.$-dmapm) and $\mathrm{PdCl}_{2}(P, N-$ dmapm).

From the relative intensities of the peaks at $\delta 2.35$ and 3.70 in the spectra shown in Figure 3.1, equilibrium constants at each temperature can be calculated and the van't

Hoff plot shown in Figure 3.3 constructed. This yields $\Delta \mathrm{H}^{\circ}=-5.5 \pm 0.5 \mathrm{~kJ} \mathrm{~mol}^{-1}$ and $\Delta \mathrm{S}^{\circ}$ $=-10 \pm 1 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$ for the isomerisation process.


Figure 3.3 Van't Hoff plot for the $\mathrm{PdCl}_{2}\left(P, P^{\prime}-\right.$ dmapm $) \rightleftharpoons \mathrm{PdCl}_{2}(P, N$-dmapm $)$ equilibrium.

### 3.3.2 Four-membered ring strain

A direct comparison between $\mathrm{Pd}_{\mathrm{P}}-\mathrm{Ph}_{3}$ and Pd -py bond strengths was made by Partenheimer and $\mathrm{Hoy}^{40}$ who measured the heats of reaction for the following substitution processes in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution:

$$
\begin{array}{ll}
\text { trans }-\mathrm{PdCl}_{2}\left(\mathrm{PhCN}_{2}+2 \mathrm{PPh}_{3} \rightarrow \text { trans }-\mathrm{PdCl}_{2}\left(\mathrm{PPh}_{3}\right)_{2}+2 \mathrm{PhCN}\right. & \Delta \mathrm{H}=-163 \mathrm{~kJ} \mathrm{~mol}^{-1} \\
\text { trans }-\mathrm{PdCl}_{2}\left(\mathrm{PhCN}_{2}+2 \text { py } \rightarrow \text { trans }-\mathrm{PdCl}_{2}(\mathrm{py})_{2}+2 \mathrm{PhCN}\right. & \Delta \mathrm{H}=-109 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{array}
$$

From these experiments, the $\mathrm{Pd}-\mathrm{PPh}_{3}$ bond is stronger than the $\mathrm{Pd}-\mathrm{py}$ bond by 27 kJ $\mathrm{mol}^{-1}$. It is therefore reasonable to infer that the small magnitude of $\Delta \mathrm{H}$ for the $\mathrm{PdCl}_{2}\left(P, P^{\prime}-\mathrm{dmapm}\right) \rightleftharpoons \mathrm{PdCl}_{2}(P, N-\mathrm{dmapm})$ equilibrium arises because the energy cost of breaking the stronger $\mathrm{Pd}-\mathrm{P}$ bond is almost equal in magnitude to the sum of the energy recovered from the formation of the weaker $\mathrm{Pd}-\mathrm{N}$ bond and alleviation of the 4 membered ring strain. Thus, if the 5 -membered $P, N$ ring is assumed to be completely strain-free, the 4-membered ring strain energy can be estimated to be $c a .32 \mathrm{~kJ} \mathrm{~mol}^{-1}$.

Nolan and coworkers have calculated the ring strain energies associated with the binding of chelating tertiary diphosphine ligands ( $\mathrm{P}-\mathrm{P}$ ) to " $\left(\mathrm{C}_{5} \mathrm{R}_{5}\right) \mathrm{RuCl}$ " $(\mathrm{P}-\mathrm{P}=\mathrm{dppm}$,
dppb, dppe, dppp; $R=H,{ }^{41} \mathrm{Me}^{42}$ ) by comparison of the heats of reaction for the following substitution reactions in THF at $30^{\circ} \mathrm{C}$ :

$$
\begin{align*}
& \left(\mathrm{C}_{5} \mathrm{R}_{5}\right) \mathrm{RuCl}(\mathrm{cod})+\mathrm{P}-\mathrm{P} \rightarrow\left(\mathrm{C}_{5} \mathrm{R}_{5}\right) \mathrm{RuCl}(\mathrm{P}-\mathrm{P})+\operatorname{cod}  \tag{1}\\
& \left(\mathrm{C}_{5} \mathrm{R}_{5}\right) \mathrm{RuCl}(\mathrm{cod})+2 \mathrm{PPh}_{2} \mathrm{Me} \rightarrow\left(\mathrm{C}_{5} \mathrm{R}_{5}\right) \mathrm{RuCl}\left(\mathrm{PPh}_{2} \mathrm{Me}\right)_{2}+\operatorname{cod} \tag{2}
\end{align*}
$$

The ring strain energies thus calculated $\left(\Delta \mathrm{H}_{(1)}-\Delta \mathrm{H}_{(2)}\right)$ for dppm are 42 and $56 \mathrm{~kJ} \mathrm{~mol}^{-1}$ for $\mathrm{R}=\mathrm{H}$ and $\mathrm{R}=\mathrm{Me}$, respectively, in reasonable agreement with that found for $\mathrm{PdCl}_{2}\left(P, P^{\prime}-\mathrm{dmapm}\right)$.

### 3.3.3 Structure and bonding

The crystal structure of $\mathrm{PdCl}_{2}(P, N-\mathrm{dmapm})$ is shown in Figure 3.4. Relevant bond distances and angles are given in Table 3.1. The most interesting aspect is that the structure allows a direct comparison between both bound and free N - and P -atoms of equivalent type and thus permits an assessment of the relative degrees of $\sigma$ - and $\pi$ bonding between these atoms and the metal centre.


Figure 3.4 ORTEP representation of the molecular structure of $\mathrm{PdCl}_{2}(P, N$-dmapm $)$ (50 \% ellipsoids).

Table 3.1 Selected bond lengths ( $\AA$ ) and angles $\left(^{\circ}\right)$ for $\mathrm{PdCl}_{2}(P, N-\mathrm{dmapm})$ with estimated standard deviations in parentheses.

| $\mathrm{Pd}(1)-\mathrm{P}(1)$ | $2.1798(6)$ | $\mathrm{P}(2)-\mathrm{C}(18)$ | $1.847(2)$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{Pd}(1)-\mathrm{N}(1)$ | $2.132(2)$ | $\mathrm{P}(2)-\mathrm{C}(26)$ | $1.845(2)$ |
| $\mathrm{Pd}(1)-\mathrm{Cl}(1)$ | $2.3041(6)$ | $\mathrm{N}(1)-\mathrm{C}(6)$ | $1.481(3)$ |
| $\mathrm{Pd}(1)-\mathrm{Cl}(2)$ | $2.3812(6)$ | $\mathrm{N}(1)-\mathrm{C}(7)$ | $1.492(4)$ |
| $\mathrm{P}(1)-\mathrm{C}(1)$ | $1.801(2)$ | $\mathrm{N}(1)-\mathrm{C}(8)$ | $1.490(3)$ |
| $\mathrm{P}(1)-\mathrm{C}(9)$ | $1.806(2)$ | $\mathrm{N}(3)-\mathrm{C}(23)$ | $1.425(3)$ |
| $\mathrm{P}(1)-\mathrm{C}(17)$ | $1.824(2)$ | $\mathrm{N}(3)-\mathrm{C}(24)$ | $1.467(3)$ |
| $\mathrm{P}(2)-\mathrm{C}(17)$ | $1.873(2)$ | $\mathrm{N}(3)-\mathrm{C}(25)$ | $1.453(3)$ |
|  |  |  |  |
| $\mathrm{P}(1)-\mathrm{Pd}(1)-\mathrm{N}(1)$ | $86.10(6)$ | $\mathrm{P}(1)-\mathrm{Pd}(1)-\mathrm{Cl}(1)$ | $87.93(2)$ |
| $\mathrm{Cl}(1)-\mathrm{Pd}(1)-\mathrm{Cl}(2)$ | $92.63(2)$ | $\mathrm{N}(1)-\mathrm{Pd}(1)-\mathrm{Cl}(2)$ | $93.54(6)$ |
| $\mathrm{P}(1)-\mathrm{C}(17)-\mathrm{P}(2)$ | $108.4(1)$ | $\mathrm{C}-\mathrm{P}(1)-\mathrm{C}$ | $107.4(\mathrm{av})$. |
| $\mathrm{C}-\mathrm{P}(2)-\mathrm{C}$ | $100.5(\mathrm{av})$. |  |  |

The variations in P - C bond lengths on coordination of dmapm to Pd (II) can only be rationalized in light of the relatively recent hypothesis that the P-based $\pi$-acceptor orbitals (the LUMOs) are not purely 3d, but have significant 3p character and local $\sigma^{*}$ symmetry with respect to the $\mathrm{P}-\mathrm{C}$ bonds. Calculations by Xiao et al. on $\mathrm{PH}_{3}, \mathrm{PMe}_{3}$ and $\mathrm{PF}_{3}$ demonstrate that such a LUMO arises from mixing of the P -based 3d and 3p orbitals (with the 3 p component being largest for $\mathrm{PF}_{3}$ ). ${ }^{43}$ The hybrid orbital is oriented such that it is able to accept $\pi$-back donation from the metal ion. Additional calculations by Marynick even show that a qualitative understanding of $\pi$-back bonding can be attained without even including the d-orbitals in the basis set, and prove, by examination of the phase relationships between $\mathrm{P}, \mathrm{H}$ and Cr orbitals in the complex $\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{5}\left(\mathrm{PH}_{3}\right)$, that the LUMO has local $\sigma^{*}$ symmetry with respect to the $\mathrm{P}-\mathrm{H}$ bonds. ${ }^{44}$

In order to find physical evidence for these hypotheses, Orpen and Connelly have compared the $\mathrm{M}-\mathrm{P}$ and $\mathrm{P}-\mathrm{C}$ bond lengths and $\mathrm{C}-\mathrm{P}-\mathrm{C}$ bond angles for 24 structurally characterized redox-related pairs of transition metal phosphine and phosphite complexes and have demonstrated that in going from the lower to the higher oxidation state the following general trends hold true: the $\mathrm{Pd}-\mathrm{P}$ distance increases, the $\mathrm{P}-\mathrm{C}$ distance decreases and the $\mathrm{C}-\mathrm{P}-\mathrm{C}$ angle increases. ${ }^{45}$ That the $\mathrm{P}-\mathrm{C}$ distance should decrease is in accord with Marynick's assertion that the phosphine LUMO is $\sigma^{*}$ with
respect to the $\mathrm{P}-\mathrm{C}$ bonds: on oxidation, the degree of $\mathrm{M} \rightarrow \mathrm{P} \pi$-bonding is necessarily decreased because of a lowering of electron density at the metal and thus there is a depopulation of the phosphine LUMO and consequently a strengthening of the $\mathrm{P}-\mathrm{C}$ bond.

This $\pi$-back bonding explanation for the relative geometries of redox pairs does not hold for comparison of bound and free P -atoms in $\mathrm{PdCl}_{2}(P, N$-dmapm). One might expect that a direct analogy could be drawn between a bound P -atom and the P -atom(s) of any of the reduced species in Orpen's study, and between a free P -atom and the P atom(s) of any of the corresponding oxidized species. The reason for this expectation is that $\pi$-back donation is expected to be greater for a coordinated P -atom than for a free P atom, as it is for a P -atom coordinated to a reduced species than for a P -atom coordinated to an oxidized one. This assumption would lead to the prediction that $\mathrm{P}-\mathrm{C}$ bond lengths should increase upon coordination of dmapm to Pd, whereas the opposite is observed. The $\mathrm{P}-\mathrm{C}$ bond lengths involving the bound P -atom, both for $\mathrm{P}-\mathrm{C}$ (aromatic) (av. 1.804 $\AA$ ) and $\mathrm{P}-\mathrm{C}($ aliphatic ) (av. $1.824 \AA$ ) are significantly shorter than those involving the free P-atom (av. 1.846 and $1.873 \AA$, respectively).

Problems such as this are tackled in another study by Orpen's group which compares 1860 unique crystallographically characterised $\mathrm{ZPPh}_{3}$ fragments where Z may be a transition metal, main group metal or non-metal. ${ }^{46}$ The study describes the molecular orbital energy levels of $\mathrm{PPh}_{3}$ qualitatively in terms of a Walsh correlation diagram which has a trigonal plane $\left(D_{3 \mathrm{~h}}\right)$ and trigonal pyramid $\left(C_{3 \mathrm{v}}\right)$ as its extreme geometries (Figure 3.5), a model that was originally considered by Gimarc ${ }^{47}$ and Albright et al. ${ }^{48}$ Orpen and coworkers propose that when the potential for $\pi$-back bonding exists, the $\mathrm{PPh}_{3}$ ligand responds to give a lower overall energy by adopting a more pyramidal geometry, enabling better overlap between the P 3 d and $\mathrm{P}-\mathrm{C} \sigma^{*}$ orbitals which together constitute the $\pi$-acceptor LUMOs ( 2 e in Figure 3.5). This leads to a compression of the $\mathrm{C}-\mathrm{P}-\mathrm{C}$ angles and a lengthening of the $\mathrm{P}-\mathrm{C}$ bonds.

Conversely, on coordination to a strong $\sigma$-acceptor (such as $\mathrm{H}^{+}$) the tendency is for the $\mathrm{PPh}_{3}$ to assume a more planar structure with larger $\mathrm{C}-\mathrm{P}-\mathrm{C}$ angles giving better overlap for $\mathrm{P}-\mathrm{C} \sigma$-bonding and shorter $\mathrm{P}-\mathrm{C}$ bonds.


Figure 3.5 Walsh correlation diagram (adapted from Dunne et al. ${ }^{46}$ ) for the deformation of a $\mathrm{PR}_{3}$ species, showing rehybridisation of the phosphine lone pair $2 a_{1}$, and $\pi$-acceptor function $2 e$, on going from trigonal planar $\left(\mathrm{D}_{3 \mathrm{~h}}\right)$ geometry (left) to pyramidal ( $\mathrm{C}_{3 \mathrm{v}}$, right).

It is therefore more reasonable to rationalize the $\mathrm{Pd}-\mathrm{P}$ bonding in $\mathrm{PdCl}_{2}(P, N-$ dmapm) in terms of a dominant $\mathrm{P} \rightarrow \mathrm{M} \sigma$-contribution. This view of the bonding conforms to Orpen's observation that the relative importance of $\pi$-bonding with respect to $\sigma$ bonding decreases on going from left to right across the transition series (due to metal d-
electrons becoming increasingly tightly bound). ${ }^{46}$ Indeed, in addition to having a significantly shorter average $\mathrm{P}-\mathrm{C}$ bond length, the bound P -atom of $\mathrm{PdCl}_{2}(P, N$-dmapm $)$ also has an average $\mathrm{C}-\mathrm{P}-\mathrm{C}$ angle $\left(107.4^{\circ}\right)$ which is much larger than that found at the free atom (100.5 ${ }^{\circ}$.

In addition, the $\mathrm{N}-\mathrm{C}$ bonds, both for $\mathrm{N}-\mathrm{C}($ aromatic) (av. $1.481 \AA$ ) and $\mathrm{N}-$ C (aliphatic) (av. $1.491 \AA$ ) involving the bound N -atom are significantly longer than those involving the free (av. 1.430 and $1.463 \AA$, respectively). Nitrogen does not have dorbitals available for bonding and therefore the observed increase in $\mathrm{N}-\mathrm{C}$ bond lengths upon coordination points to the fact that the N-based "lone pair", typically thought to be an $\mathrm{sp}^{3}$ orbital, is not entirely non-bonding but has significant $\mathrm{N}-\mathrm{C} \sigma$ character. Depopulation of this orbital on coordination would induce a lengthening of the $\mathrm{N}-\mathrm{C}$ bonds.

Other aspects of the structure are also worthy of mention:
(1) The $\mathrm{Pd}(1)-\mathrm{Cl}(1)$ bond is shorter than the $\mathrm{Pd}(1)-\mathrm{Cl}(2)$ bond because of the higher trans influence of P with respect to $\mathrm{N} .{ }^{49}$
(2) The $\mathrm{Pd}(1)-\mathrm{P}(1)$ bond $(2.1798 \AA)$ is unusually short. As a comparison, the mean $\mathrm{Pd}-\mathrm{P}$ distances for $\mathrm{PMe}_{3}, \mathrm{PPh}_{3}, \mathrm{PPhMe}_{2}$, dppe and dppm complexes calculated by Orpen et al. are $2.287,2.308,2.253,2.260$ and $2.258 \AA$, respectively. ${ }^{50}$
(3) The $\mathrm{P}(1)-\mathrm{C}(17)-\mathrm{P}(2)$ angle is a relaxed $107.4^{\circ}$, intermediate between the compressed $\mathrm{P}-\mathrm{C}-\mathrm{P}$ angles commonly found in 4-membered $P, P^{\prime}$-metallacycles $\left(93.0^{\circ}\right.$ for $\left.\mathrm{PdCl}_{2}(\mathrm{dppm})^{51}\right)$ and those found in complexes containing $\eta^{1}$ - $\mathrm{dppm}\left(118.9^{\circ}\right.$ for trans$\mathrm{Ru}\left(\eta^{1} \text {-dppm }\right)_{2}(\mathrm{~N}, \mathrm{O} \text {-quin })_{2}$, quin $=2$-quinaldinate anion ${ }^{52}$ ).
(4) The $\mathrm{P}(1)-\mathrm{Pd}(1)-\mathrm{N}(1)$ "bite" angle is $86.1^{\circ}$. This similar to the corresponding angles found in Ru complexes of PMA. These have been determined for both 5- and 6-coordinate $\mathrm{Ru}(\mathrm{II})$ complexes to lie in the range 80-83 ${ }^{\circ} .53,54$

The average $\mathrm{P}-\mathrm{C}$ and $\mathrm{N}-\mathrm{C}$ bond lengths for the crystallographically characterised anilinyldiphosphine ligands and complexes discussed in this dissertation are collected in Table 3.2.

Table 3.2 Average $\mathrm{P}-\mathrm{C}$ and $\mathrm{N}-\mathrm{C}$ bond distances $(\AA)$ for the crystallographically characterised anilinyldiphosphine ligands and their complexes. ${ }^{\text {a }}$

| $\begin{aligned} & \ddot{0} \\ & \text { Bn } \end{aligned}$ | $\begin{aligned} & \stackrel{0}{\tilde{G}} \\ & \stackrel{\rightharpoonup}{\square} \end{aligned}$ | $\begin{aligned} & \text { O} \\ & \text { O. } \\ & \text { 퉁 } \end{aligned}$ |  |  | $\stackrel{+}{\stackrel{+}{\sim}}$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P}_{\mathrm{f}}-\mathrm{C}_{\text {al }}$ | 1.854 [2] | 1.881 [2] | - | - | - | 1.873 [1] | - |
| $\mathrm{P}_{\mathrm{f}}-\mathrm{C}_{\text {ar }}$ | 1.849 [2] | 1.842 [4] | - | - | - | 1.846 [2] | - |
| $\mathrm{P}_{\mathrm{b}}-\mathrm{C}_{\mathrm{al}}$ | - | - | 1.826 [2] | 1.835 [2] | 1.840 [1] ${ }^{\text {b }}$ | 1.824 [1] | 1.839 [2] |
|  |  |  |  |  | $1.820[1]^{\text {c }}$ |  |  |
| $\mathrm{P}_{\mathrm{b}}-\mathrm{C}_{\text {ar }}$ | - | - | 1.821 [4] | 1.811 [4] | $1.810{ }^{\text {[2] }}{ }^{\text {b }}$ | 1.804 [2] | 1.819 [4] |
|  |  |  |  |  | 1.813 [2] ${ }^{\text {c }}$ |  |  |
| $\mathrm{N}_{\mathrm{f}}-\mathrm{C}_{\text {al }}$ | 1.457 [8] | 1.460 [8] | 1.462 [8] | 1.472 [6] | 1.470 [4] | 1.463 [6] | 1.454 [4] |
| $\mathrm{N}_{\mathrm{f}}-\mathrm{C}_{\text {ar }}$ | 1.427 [4] | 1.434 [4] | 1.433 [4] | 1.438 [3] | 1.438 [2] | 1.430 [3] | 1.440 [2] |
| $\mathrm{N}_{\mathrm{b}}-\mathrm{C}_{\mathrm{al}}$ | - | - | - | 1.493 [2] | 1.495 [2] | 1.491 [2] | 1.493 [4] |
| $\mathrm{N}_{\mathrm{b}}-\mathrm{C}_{\mathrm{ar}}$ | - | - | - | 1.481 [1] | 1.483 [1] | 1.481 [1] | 1.458 [2] |

${ }^{\mathrm{a}}$ The number of each type of observation appears in square brackets. $\mathrm{f}=$ free, $\mathrm{b}=$ bound, ar $=$ aromatic, al $=$ aliphatic; data are excerpted from Sections 2.3.3, 2.4.1.1, 2.4.2.2, 2.6.1.1, 3.3.3 and 3.4.5.1.
${ }^{\mathrm{b}} \mathrm{P}$-atom coordinated to Pd .
${ }^{\mathrm{c}} \mathrm{P}$-atom bound to O .

The entries in Table 3.2 suggest that the conclusions drawn about the bonding in $\mathrm{PdCl}_{2}(P, N$-dmapm $)$ can perhaps be extended to encompass the bonding of the anilinyldiphosphines to late transition metals and non-metals generally. From the table, it is evident that:
(1) In all cases, whether the "metal" is $\mathrm{Pd}^{11}, \mathrm{Pt}^{I I}, \mathrm{Pd}^{1}$ or " O ", the $\mathrm{P}_{\mathrm{b}}-\mathrm{C}_{\mathrm{ar}}$ and $\mathrm{P}_{\mathrm{b}}-\mathrm{C}_{\mathrm{al}}$ bond lengths are shorter than the corresponding lengths involving the free P atoms. This implies that the $\sigma$-contribution to the bonding is more significant than the $\pi$-contribution.
(2) In all cases, the $N_{b}-C_{a l}$ and $N_{b}-C_{a r}$ are longer than the corresponding lengths involving free N -atoms implying that the N "lone pair" is not purely non-bonding but has a significant $\mathrm{N}-\mathrm{C} \sigma$ component.

### 3.3.4 Reactions with halide and cyanide

$\mathrm{PdCl}_{2}$ (dmapm) reacts with an excess of NaBr (Section 3.9.2) or NaI (Section 3.9.3) in acetone/water or acetone to give the bromo or iodo analogue. Like the parent chloro compound, both exist as an equilibrium mixture of the $P, P$ - and $P, N$-isomers in $\mathrm{CDCl}_{3}$ solution. The $\operatorname{PdX}_{2}\left(P, P^{\prime}-d m a p m\right) \rightleftharpoons \mathrm{PdX}_{2}\left(P, N^{\prime}-\mathrm{dmapm}\right)$ equilibrium constants at 250 K for the series are 4.1, 4.8 and 6.3 for $\mathrm{X}=\mathrm{Cl}, \mathrm{Br}$ and I , respectively.

Pringle and Shaw discovered that $\mathrm{PdCl}_{2}(\mathrm{dppm})$ reacts with NaCN to give the dppm-bridged dimers $\left[\text { trans }-\mathrm{Pd}(\mathrm{CN})_{2}(\mu \text {-dppm })\right]_{2} .{ }^{55}$ In contrast, $\mathrm{PdCl}_{2}(\mathrm{dmapm})$ reacts with 2 equiv. of KCN to give exclusively the monometallic compound, $\operatorname{Pd}(\mathrm{CN})_{2}(P, N-$ dmapm) (Section 3.9.4), i.e., because the $P, P^{\prime}$-isomer is present in $\mathrm{CDCl}_{3}$ solution at a concentration lower than the limit of detection by NMR spectroscopy, $\mathrm{K}>100$; however, $\mathrm{PtCl}_{2}\left(P, P^{\prime}-\mathrm{dmapm}\right)$ reacts to give both $\operatorname{Pt}(\mathrm{CN})_{2}\left(P, P^{\prime}-\mathrm{dmapm}\right)$ and $\mathrm{Pt}(\mathrm{CN})_{2}(P, N-\mathrm{dmapm})$ (Section 3.9.10). This result is in accord with the reaction of dmapm with $\mathrm{PtCl}_{2}(\operatorname{cod})$ which generates $\mathrm{PtCl}_{2}\left(P, P^{\prime}-\mathrm{dmapm}\right)$ exclusively, showing that Pt has a higher affinity than Pd for P .

Thus, the magnitude of K for the $\operatorname{PdX}_{2}\left(P, P^{\prime}-\mathrm{dmapm}\right) \rightleftharpoons \mathrm{PdX}_{2}\left(P, N^{\prime}-\mathrm{dmapm}\right)$ equilibrium correlates with the position of X in the trans effect series $(\mathrm{Cl}<\mathrm{Br}<\mathrm{I} \ll$ $\mathrm{CN})$. Because P -donors also show a strong trans effect, $\mathrm{PdX}_{2}(P, N$-dmapm) should be progressively more stable than $\operatorname{PdX}_{2}\left(P, P^{\prime}\right.$-dmapm) as the trans effect of X increases.

### 3.3.5 Reactions with peroxide and $S_{8}$

$\mathrm{PdCl}_{2}$ (dmapm) reacts with cumene hydroperoxide in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ or $\mathrm{H}_{2} \mathrm{O}_{2}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{H}_{2} \mathrm{O}$ at r.t., and with $\mathrm{S}_{8}$ in $\mathrm{CH}_{2} \mathrm{ClCH}_{2} \mathrm{Cl}$ heated to reflux, to give $\mathrm{PdCl}_{2}(P, N-\mathrm{dmapmO})$ (Section 3.9.6; the molecular structure of the analogous $\mathrm{PtI}_{2}(P, N-\mathrm{dmapmO})$ is given in Figure 3.18 , p. 132) and $[\mathrm{PdCl}(P, N, S$-dmapmS $)] \mathrm{Cl}($ Section 3.9 .8$)$ respectively (Chart $3.2, \mathrm{Ar}=$ ${ }_{o}-\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{NMe}_{2}$ ). The S -atom of the $\mathrm{P}=\mathrm{S}$ fragment being a "soft" donor is a sufficiently good ligand to displace $\mathrm{Cl}^{-}$from the metal coordination sphere, whereas the "harder" O atom of the $\mathrm{P}=\mathrm{O}$ fragment is not. $\mathrm{PdCl}_{2}\left(P, N\right.$-dmapmO) is a non-electrolyte in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution $\left(\Lambda_{\mathrm{M}}<1 \mathrm{~cm}^{2} \mathrm{ohm}^{-1} \mathrm{~mol}^{-1}\right)$ and does not dissolve in $\mathrm{H}_{2} \mathrm{O}$, while $[\operatorname{PdCl}(P, N, S$ dmapmS $)] \mathrm{Cl}$ dissolves in $\mathrm{H}_{2} \mathrm{O}$ as a $1: 1$ electrolyte $\left(\Lambda_{\mathrm{M}}=99 \mathrm{~cm}^{2} \mathrm{ohm}^{-1} \mathrm{~mol}^{-1}\right)$, ${ }^{56}$ and the $\mathrm{Cl}^{-}$counterion is easily exchanged for $\mathrm{PF}_{6}{ }^{-}$by reaction with $\mathrm{KPF}_{6}$ (Section 3.9.7).

## Chart 3.2




### 3.3.6 $\quad \mathbf{P d C l}(\mathrm{Me})(P, N$-dmapm $)$

In contrast to $\mathrm{PdCl}_{2}$ (dmapm) which exists as an equilibrium mixture of $P, P^{\prime}$ - and $P, N$ isomers in $\mathrm{CDCl}_{3}$ solution, the title complex (Section 3.9.5) exists solely as a $P, N$-isomer (Chart 3.3; $\mathrm{Ar}=o-\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{NMe}_{2}$ ). This is easily ascertained from the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum which shows the presence of both bound and free P-atoms ( $\delta 24.0$ (d), -39.3 (d), $\left.{ }^{2} J_{\mathrm{PP}}=130 \mathrm{~Hz}\right)$, the large ${ }^{2} J_{\mathrm{PP}}$ value being reminiscent of that of $\mathrm{PdCl}_{2}(P, N$-dmapm $)$ $(108 \mathrm{~Hz})$. The $P, N$ bonding mode can be ascribed not only to the need for 4 -membered ring strain ( $c a .32 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ) to be overcome in order for the $P, P^{\prime}$ isomer to form, but also to the fact that a trans arrangement of the strong field ligands $P$ and Me is highly disfavoured. In fact, even if 4-membered ring strain is eliminated, e.g., in the reaction between $\mathrm{PdCl}(\mathrm{Me})(\mathrm{cod})$ and dmape (which contains two C -atoms in its "bridge"), a mixture of the $P, N$ - and $P, P^{\prime}$ - isomers is produced $\left({ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}\right.$ NMR: $\operatorname{PdCl}(\mathrm{Me})\left(P, P^{\prime}-\right.$ dmape) $\delta 28.2$ (d), 30.2 (d), ${ }^{2} J_{\mathrm{PP}}=63 \mathrm{~Hz} . \operatorname{PdCl}(\mathrm{Me})(P, N$-dmape) $\delta 28.0$ (d), -27.9 (d), ${ }^{3} J_{\mathrm{PP}}=38 \mathrm{~Hz}$.

## Chart 3.3



### 3.4 Complexes Containing Two Metal Centres

### 3.4.1 Reactions with trans- $\mathbf{P d C l}_{\mathbf{2}}(\mathbf{P h C N})_{2}$ and $\mathbf{K}_{2} \mathbf{P t C l}_{4}$

The synthesis of homo- and heterobimetallic complexes containing bridging dmapm depends both upon the presence in the monometallic precursor of a "dangling" P-atom and the on existence of the $P, P^{\prime} \rightleftharpoons P, N$ equilibrium. Thus, $\mathrm{PdCl}_{2}(\mathrm{dmapm})$ reacts with trans $-\mathrm{PdCl}_{2}(\mathrm{PhCN})_{2}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at r.t. (Section 3.9.11) or with $\mathrm{K}_{2} \mathrm{PtCl}_{4}$ in $\mathrm{EtOH} / \mathrm{H}_{2} \mathrm{O}$ at $70^{\circ} \mathrm{C}$ (Section 3.9.13) to form $\mathrm{Pd}_{2} \mathrm{Cl}_{4}(\mathrm{dmapm})$ or $\mathrm{PtPdCl}_{4}(\mathrm{dmapm})$, respectively (Chart 3.4; $\mathrm{Ar}=0-\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{NMe}_{2}, \mathrm{M}=\mathrm{Pd}$, Pt. The molecular structure of the iodo analogue $\mathrm{PtPdI}_{4}(\mathrm{dmapm})$ is given in Figure 3.17, p.132)

## Chart 3.4



Were it not for the requisite equilibrium, such reactions would result in a less than quantitative yield of the bimetallic product as a significant proportion of the precursor would remain unreacted. The mixed metal compound $\mathrm{PtPdCl}_{4}(\mathrm{dmapm})$ could not be made by reaction of $\mathrm{PdCl}_{2}(\mathrm{dmapm})$ with either of cis $-\mathrm{PtCl}_{2}(\mathrm{MeCN})_{2}$ or $\mathrm{PtCl}_{2}$ (cod). In addition, $\mathrm{PtPdCl}_{4}(\mathrm{dmapm})$ could not be made from $\mathrm{PtCl}_{2}\left(P, P^{\prime}-\mathrm{dmapm}\right)$ and trans-
$\mathrm{PdCl}_{2}(\mathrm{PhCN})_{2}$ because of the absence in the monometallic precursor of a dangling P atom. This means that under these conditions, it is not possible to make homobimetallic dmapm-bridged $\mathrm{Pt}^{\mathrm{II}}$ complexes. However, analysis of the off-white product mixture from the reaction between $\mathrm{Pt}(\mathrm{CN})_{2}(\mathrm{dmapm})$ and $\mathrm{K}_{2} \mathrm{PtCl}_{4}$ in $\mathrm{EtOH} / \mathrm{H}_{2} \mathrm{O}$ at $70{ }^{\circ} \mathrm{C}$ by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy revealed that $\mathrm{Pt}_{2} \mathrm{Cl}_{2}(\mathrm{CN})_{2}$ (dmapm) was generated in low yield $\left({ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}\right.$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta 12.9\left(\mathrm{~s},{ }^{1} J_{\mathrm{PPt}}=2730 \mathrm{~Hz}, \mathrm{P}\right.$ trans to CN$), 7.3$ ( $\mathrm{s},{ }^{1} J_{\mathrm{PPt}}=4070 \mathrm{~Hz}, \mathrm{P}$ trans to Cl$)$ ). This route was not pursued as it was felt that CN containing complexes would generally not make for good catalysts.

Single crystals of $\mathrm{Pd}_{2} \mathrm{Cl}_{4}$ (dmapm) were grown on two occasions and analysed by X-ray crystallography. Unfortunately, the molecular structure could not be refined to acceptable quality because of a twinning problem. Nevertheless, the analysis established the essential geometry of the complex to be analogous to that given in the PLUTO representation of $\mathrm{PtPdI}_{4}(\mathrm{dmapm})$ (Figure 3.17, p. 132).

In contrast to the large coupling between inequivalent P -atoms in $\mathrm{PdCl}_{2}\left(P, N^{\prime}-\right.$ dmapm) ( 108 Hz ), no 2-bond PP coupling is observed in the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra of $\mathrm{Pd}_{2} \mathrm{Cl}_{4}$ (dmapm) and $\mathrm{PtPdCl}_{4}$ (dmapm). In addition, although both of the P -atoms in the bimetallic complexes are chiral, no diastereomers are observed in either the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ or ${ }^{1} \mathrm{H}$ NMR spectra. The $\mathrm{NCH}_{3}$ region of the ${ }^{1} \mathrm{H}$ NMR spectrum of e.g. $\mathrm{PtPdCl}_{4}(\mathrm{dmapm})$ contains 8 distinct peaks, each corresponding to 3 protons (Figure 3.6). These represent diastereotopic methyl groups associated with both the bound and free N -atoms on the Pt and Pd "sides" of the molecule. The peak shapes suggest that there is either slow or no exchange of coordinated and free anilinyl N -atoms, and imply thereby that diastereomers should be apparent.


Figure 3.6 The $\mathrm{NCH}_{3}$ region of the ${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right)$ spectrum of $\mathrm{PtPdCl}_{4}$ (dmapm).

The assignment of the peaks in Figure 3.6 is based on chemical shift, integration and shape (see below), and is illustrated in Chart 3.5 ( Cl -atoms have been omitted for clarity).

## Chart 3.5



A ${ }^{1} \mathrm{H}$ 2D EXSY measurement of $\mathrm{PtPdCl}_{4}$ (dmapm) revealed that the free and bound N -atoms are in fact in chemical exchange. The spectrum demonstrates that the methyl group $a$ is in exchange with $c, b$ with $d$, e with $h$ and $f$ with $g$. Furthermore, the spectrum shows that there is no exchange between the N -atoms associated with opposite "sides" of the molecule, i.e., between groups a-d and e-h. The fact that no diastereomers of this compound or its dipalladium analogue are observed may be due to the fact that the exchange occurs in a concerted way that generates enantiomers only. If so, the rate of exchange at Pt and Pd must be equal, in contradiction to the well established greater
lability of $\mathrm{Pd}^{\mathrm{II}}$. In addition, peaks e-h appear broader than a-d implying that the protons they represent are in a fluxional process which occurs faster than it does in the former group. The broader peaks are likely to be due to the $\mathrm{NCH}_{3}$ protons associated with the Pd "side" of the molecule.

### 3.4.2 Reaction with $\mathrm{NH}_{4} \mathrm{PF}_{6}$

In addition to dmapm-bridged bimetallic complexes, the chloride-bridged dimer $[\operatorname{Pd}(\mu-$ $\left.\mathrm{Cl})\left(P, P^{\prime}-\mathrm{dmapm}\right)\right]_{2}\left[\mathrm{PF}_{6}\right]_{2}$ was also synthesised (Section 3.9.14). In an attempt to make a $\mathrm{Pd}(\mathrm{II})-\mathrm{Rh}(\mathrm{I})$ dimer, $\mathrm{PdCl}_{2}$ (dmapm) was stirred with $[\mathrm{Rh}(\mu-\mathrm{Cl})(\operatorname{cod})]_{2}$ in the presence of $\mathrm{KPF}_{6}$ in a two-phase $\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{H}_{2} \mathrm{O}$ mixture, a standard methodology for making $\mathrm{Rh}(\mathrm{I})$ phosphine complexes. ${ }^{57}$ However, no new Rh-containing species were produced and the Pd complex was cleanly converted to a species whose ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum consisted of a singlet at $\delta-52.0$ and a septet at $\delta-145.0\left(\mathrm{PF}_{6}{ }^{-}\right)$and whose elemental analysis was consistent with the formulation " $\mathrm{PdCl}(\mathrm{dmapm})\left(\mathrm{PF}_{6}\right)$ ". In addition, the ${ }^{1} \mathrm{H}$ NMR spectrum demonstrated the chemical equivalence of all 24 NMe protons by the existence of only one singlet ( $\delta 2.56$ ) in the appropriate region. The upfield ${ }^{31} \mathrm{P}$ singlet is indicative of chemically equivalent P -atoms involved in a 4-membered metallacycle, and the ${ }^{1} \mathrm{H}$ singlet at $\delta 2.56$ shows that none of the N -atoms are coordinated. This compound was also made successfully in a rational manner via the reaction of $\mathrm{PdCl}_{2}$ (dmapm) and $\mathrm{NH}_{4} \mathrm{PF}_{6}$ in acetone and was shown by its conductivity in $\mathrm{CH}_{3} \mathrm{NO}_{2}$ to be a $2: 1$ electrolyte $\left(\Lambda_{\mathrm{M}}=213 \mathrm{~cm}^{2} \mathrm{ohm}^{-1} \mathrm{~mol}^{-1}\right) .{ }^{56}$

### 3.4.3 Reaction with $\left[\mathrm{Rh}(\mu-\mathrm{Cl})(\mathrm{CO})_{2}\right]_{2}$

Although it does not react with $[\mathrm{Rh}(\mu-\mathrm{Cl})(\operatorname{cod})]_{2}$ under the conditions tested, $\mathrm{PdCl}_{2}(\mathrm{dmapm})$ reacts rapidly with $\left[\mathrm{Rh}(\mu-\mathrm{Cl})(\mathrm{CO})_{2}\right]_{2}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution at r.t. (Section 3.9.15) to give a complex whose elemental analysis is consistent with the formulation $\mathrm{PdRhCl}_{3}(\mathrm{CO})$ (dmapm). This compound is proposed, on the basis of $\mathbb{R}$ and NMR data, to have the structure illustrated in Chart $3.6\left(\mathrm{Ar}=o-\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{NMe}_{2}\right)$. Its ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum comprises a singlet at $\delta 28.1$ due to the P -atom bound to Pd , and a doublet centred at $\delta 41.7$ due to the P-atom bound to $\mathrm{Rh}\left({ }^{1} J_{\mathrm{PRh}}=179 \mathrm{~Hz}\right)$. As in the case of
$\mathrm{PtPdCl}_{4}(\mathrm{dmapm})$, neither 2-bond PP coupling nor diastereomers were observed in the NMR spectra.

## Chart 3.6



The solid-state IR spectrum of $\mathrm{PdRhCl}_{3}(\mathrm{CO})(\mathrm{dmapm})$ reveals a terminal carbonyl $\left(v_{\mathrm{CO}}=1975 \mathrm{~cm}^{-1}\right.$ ), assumed still to be bound to Rh as Pd has a well-established low affinity for CO , especially when it is terminal. In addition, this arrangement alleviates the necessity for ligand reorganisation on Pd during the synthesis of the compound. Finally, the CO ligand is presumably trans to N because this configuration lowers competition for electron density between the strong-field ligands P and CO .
$\mathrm{PdRhCl}_{3}(\mathrm{CO})(\mathrm{dmapm})$ dissolves in boiling water to give a compound whose molar conductivity is $363 \mathrm{~cm}^{2} \mathrm{ohm}^{-1} \mathrm{~mol}^{-1}$ (once the water has been cooled to $25^{\circ} \mathrm{C}$ ), consistent with the formulation $\left[\mathrm{PdRh}\left(\mathrm{OH}_{2}\right)_{3}(\mathrm{CO})(\mathrm{dmapm})\right] \mathrm{Cl}_{3}$. The neutral complex is a non-electrolyte in $\mathrm{CH}_{3} \mathrm{NO}_{2}$ solution, and does not react with 1 atm $\mathrm{H}_{2}$ in $\mathrm{CDCl}_{3}$ solution.

### 3.4.4 $\left.\quad \mathbf{R h}_{2} \mathbf{C l}_{2} \mathbf{( C O}\right)_{2}$ (dmapm)

The ligand dmapm reacts cleanly and briskly with $\left[\mathrm{Rh}(\mathrm{CO})_{2}(\mu-\mathrm{Cl})\right]_{2}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution at r.t. to give $\mathrm{Rh}_{2} \mathrm{Cl}_{2}(\mathrm{CO})_{2}$ (dmapm) (Section 3.9.16). The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of this complex is given in Figure 3.7.

$\begin{array}{lllllll}\text { Figure 3.7 } & \text { The } \quad{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} & \mathrm{NMR} & (162 \mathrm{MHz}, & \mathrm{CDCl}_{3}, & 300 \mathrm{~K}) & \text { spectrum } \\ & \left.\mathrm{Rh}_{2} \mathrm{Cl}_{2}(\mathrm{CO})\right)_{2}(\mathrm{dmapm}) .\end{array}$

Budzelaar et al. have reported the crystal structure of $\mathrm{Rh}_{2} \mathrm{Cl}_{2}(\mathrm{CO})_{2}\left(\mathrm{pyPhPCH}{ }_{2} \mathrm{PPhpy}\right)$ (py $=2$-pyridyl), the anilinyl analogue of which is depicted in Chart 3.7 (centre). ${ }^{58}$ The NMR coupling constants for this compound are: ${ }^{1} J_{\mathrm{PRh}}=101,{ }^{2} J_{\mathrm{PP}}=67,{ }^{3} J_{\mathrm{PRh}}=9 \mathrm{~Hz}$. The complex pattern is a result of magnetic inequivalence of the P -atoms. The corresponding values for $\mathrm{Rh}_{2} \mathrm{Cl}_{2}(\mathrm{CO})_{2}$ (dmapm) are 180,22 and 1 Hz , respectively, the last having been determined by simulation. ${ }^{59}$

The ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathrm{Rh}_{2} \mathrm{Cl}_{2}(\mathrm{CO})_{2}(\mathrm{dmapm})$ at 300 K is broad and uninformative. At 220 K , the $\mathrm{NCH}_{3}$ region of the spectrum consists of 4 singlets of equal intensity which signify 2 bound and 2 free N -atoms. These data are consistent with all of the structures depicted in Chart 3.7.

## Chart 3.7





### 3.4.5 Complexes containing $\mathbf{M}-\mathbf{M}$ bonds

### 3.4.5.1 Reaction of $\mathbf{P d C l}_{\mathbf{2}}$ (dmapm) with $\left.\mathbf{P d}_{\mathbf{2}} \mathbf{( d b a}\right)_{3}$

Reaction of $\mathrm{PdCl}_{2}(\mathrm{dmapm})$ with 0.5 equiv. of $\mathrm{Pd}_{2}(\mathrm{dba})_{3} \cdot \mathrm{CHCl}_{3}$ in refluxing $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ generates the $\mathrm{Pd}^{1}$ dimer $\mathrm{Pd}_{2} \mathrm{Cl}_{2}(\mathrm{dmapm})$ in $70-80 \%$ isolated yield (Section 3.9.17). This represents a minor modification to the now widely-adopted general method of Balch and Benner ${ }^{60}$ for the preparation of phosphine-bridged $\mathrm{Pd}^{1}$ dimers such as $\mathrm{Pd}_{2} \mathrm{Cl}_{2}(\mu \text {-dppm })_{2} ;{ }^{61}$ the procedure is a significant improvement over the original synthesis involving reaction of $[\mathrm{Pd}(\mathrm{CO}) \mathrm{Cl}]_{\mathrm{n}}$ and dppm ${ }^{62}$ which has been reported to give variable yields. ${ }^{61}$

Prior to the determination of the crystal structure of $\mathrm{Pd}_{2} \mathrm{Cl}_{2}(\mathrm{dmapm})$, its geometry could be inferred from ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ and ${ }^{1} \mathrm{H}$ NMR spectra and from known structures of analogous complexes. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ singlet at $\delta-29.9$ indicates 2 chemically equivalent P-atoms in the product. The $\mathrm{NCH}_{3}{ }^{1} \mathrm{H}$ peaks appear as singlets at $\delta 2.44,2.89$ and 3.07 with relative integrations of $2: 1: 1$, respectively, i.e., 12:6:6 protons. By analogy to $\mathrm{PdCl}_{2}(P, N$-dmapm), the two downfield singlets correspond to two diastereotopic sets of methyl protons associated with bound N -atoms (sets a and b in Chart 3.8) and the more upfield singlet is due to the methyl groups attached to the free N -atoms (set c in Chart 3.8). The chemically equivalent $\mathrm{CH}_{2}$ protons appear as a triplet at $\delta 3.72$ because of coupling to 2 identical P -atoms.

The crystal structure of the related complex $\mathrm{Pd}_{2} \mathrm{Br}_{2}(\mathrm{dppm})_{2}$ has been determined, and consists of 2 interpenetrating square planes mutually twisted by $39^{\circ} .63$ This structure
maintains the chemical equivalence not only of the 4 P -atoms, but also of the $4 \mathrm{CH}_{2}$ protons (by virtue of a $C_{2}$-axis which bisects the $\mathrm{Pd}-\mathrm{Pd}$ bond and contains the methylene C -atoms). A similar motif seemed very likely in the structure of $\mathrm{Pd}_{2} \mathrm{Cl}_{2}$ (dmapm), and indeed an X-ray crystallographic study confirmed the structure to be that shown in cartoon form in Chart 3.8.

## Chart 3.8



Molecular structure of $\mathrm{Pd}_{2} \mathrm{Cl}_{2}$ (dmapm)
Slow evaporation of a $\mathrm{CDCl}_{3}$ solution of the complex in an NMR tube resulted in the deposition of orange, irregular crystals of $\mathrm{Pd}_{2} \mathrm{Cl}_{2}(\mathrm{dmapm}) \cdot 2 \mathrm{CDCl}_{3}$. The molecular structure is given in Figure 3.8, and selected bond distances and angles appear in Table 3.3.


Figure 3.8 ORTEP representation of the molecular structure of $\mathrm{Pd}_{2} \mathrm{Cl}_{2}(\mathrm{dmapm})(50 \%$ ellipsoids). H -atoms have been omitted for clarity.

Table 3.3 Selected bond distances $(\AA)$ and angles $\left({ }^{\circ}\right)$ for $\mathrm{Pd}_{2} \mathrm{Cl}_{2}(\mathrm{dmapm}) \cdot 2 \mathrm{CDCl}_{3}$ with estimated standard deviations in parentheses.

| $\mathrm{Pd}(1)-\mathrm{Pd}(2)$ | $2.527(1)$ | $\mathrm{Pd}(1)-\mathrm{Cl}(1)$ | $2.384(4)$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{Pd}(1)-\mathrm{P}(1)$ | $2.153(4)$ | $\mathrm{Pd}(1)-\mathrm{N}(1)$ | $2.23(1)$ |
| $\mathrm{Pd}(2)-\mathrm{Cl}(2)$ | $2.364(3)$ | $\mathrm{Pd}(2)-\mathrm{Cl}(2)$ | $2.184(3)$ |
| $\mathrm{Pd}(2)-\mathrm{N}(3)$ | $2.26(1)$ | $\mathrm{P}(1)-\mathrm{Pd}(1)-\mathrm{N}(1)$ | $85.8(3)$ |
| $\mathrm{N}(1)-\mathrm{Pd}(1)-\mathrm{Pd}(2)$ | $164.4(3)$ | $\mathrm{P}(2)-\mathrm{Pd}(2)-\mathrm{N}(3)$ | $86.3(3)$ |
| $\mathrm{N}(3)-\mathrm{Pd}(2)-\mathrm{Pd}(1)$ | $165.5(3)$ | $\mathrm{P}(1)-\mathrm{Pd}(1)-\mathrm{Pd}(2)$ | $78.7(1)$ |
| $\mathrm{P}(2)-\mathrm{Pd}(2)-\mathrm{Pd}(1)$ | $86.99(9)$ | $\mathrm{Cl}(1)-\mathrm{Pd}(1)-\mathrm{Pd}(2)$ | $98.86(9)$ |
| $\mathrm{Cl}(2)-\mathrm{Pd}(2)-\mathrm{Pd}(1)$ | $92.12(9)$ | $\mathrm{P}(1)-\mathrm{C}(17)-\mathrm{P}(2)$ | $102.9(6)$ |

At the core of $\mathrm{Pd}_{2} \mathrm{Cl}_{2}$ (dmapm) lie two interpenetrating Pd square planes mutually canted by $59.9^{\circ}$; Figure 3.9 shows perpendicular views of the metal coordination spheres. This structural motif has been described previously as "T-over-square" and is most perfectly exemplified by the homoleptic $\mathrm{Pd}^{1}$ dimer $\left[\mathrm{Pd}_{2}(\mathrm{NCMe})_{6}\right]^{2+}$, first prepared by Eisenberg and coworkers, ${ }^{64,65}$ in which the dihedral angle between the planes is $90^{\circ}$. The $\mathrm{Pd}-\mathrm{Pd}$ bond length in $\mathrm{Pd}_{2} \mathrm{Cl}_{2}$ (dmapm) is $2.527(1) \AA$, the shortest observed for a neutral $\mathrm{Pd}^{\mathrm{I}}$ dimer and the second shortest ever after $\left[\mathrm{Pd}_{2}\left(o-\mathrm{Ph}_{2} \mathrm{PC}_{6} \mathrm{H}_{4} \mathrm{CH}_{2} \mathrm{O}\left(\mathrm{CH}_{2}\right)_{3}\right.\right.$-opy $\left.)_{2}\right]\left[\mathrm{BF}_{4}\right]_{2} \cdot 4 \mathrm{H}_{2} \mathrm{O}(2.500(1) \AA),{ }^{66}$. Structurally characterised $\mathrm{Pd}^{1}$ dimers supported by tridentate ligands are relatively rare. The other example is $\left[\mathrm{Pd}_{2}\left(\mathrm{Ph}_{2} \mathrm{PC}_{2} \mathrm{H}_{4} \mathrm{P}(\mathrm{Ph}) \mathrm{C}_{2} \mathrm{H}_{4} \mathrm{PPh}_{2}\right)_{2}\right]\left[\mathrm{BF}_{4}\right]_{2}$ which has a Pd — Pd length of $2.617(1) \AA .{ }^{67}$ $\mathrm{Pd}_{2} \mathrm{Cl}_{2}$ (dmapm) represents, to this author's knowledge, the first example of a bimetallic $\mathrm{Pd}^{1}$ complex supported by a tetradentate ligand.


Figure 3.9 The coordination environments of the Pd centres in $\mathrm{Pd}_{2} \mathrm{Cl}_{2}$ (dmapm) viewed along (left) and perpendicularly to (right) the $\mathrm{Pd}-\mathrm{Pd}$ axis.

Figure 3.9 (left) clearly demonstrates that the Pd-N bonds are not collinear with the $\mathrm{Pd} — \mathrm{Pd}$ bond but are "bent back" by $c a .15^{\circ}$ from this axis. In addition, the $\mathrm{P} — \mathrm{Pd}-$ Pd angles are both less than $90^{\circ}$; one $\left(78.7^{\circ}\right)$ is substantially smaller than the other $\left(86.99^{\circ}\right)$ which gives rise to unexpected asymmetry in the molecule. This tilting of the $\mathrm{Pd}-\mathrm{P}$ bonds towards each other is indicative of compressive strain within the $\mathrm{PCH}_{2} \mathrm{P}$ "backbone" of the dmapm ligand. Indeed, the $\mathrm{P}-\mathrm{C}-\mathrm{P}$ angle found for $\mathrm{PdCl}_{2}(P, N$ dmapm) which is assumed to represent the "strain free" state $\left(108.4^{\circ}\right)$ is larger than that found in $\mathrm{Pd}_{2} \mathrm{Cl}_{2}(\mathrm{dmapm})\left(102.9^{\circ}\right)$.

The steric bulk presented by dmapm in this complex rests largely behind the Pd Pd bond which, protected only by the chloride ligands, is exposed to electrophilic attack (Figure 3.10). This structural characteristic is atypical of diphosphine-bridged $\mathrm{Pd}^{1}$ dimers which usually bear two of the bridging ligands and whose metal-metal bonds are much more sterically inaccessible. This feature should give rise to differences in reactivity, e.g. with small molecules, between this complex (see Section 3.4.5.3) and the more typical $\mathrm{Pd}_{2} \mathrm{X}_{2}(\mathrm{P}-\mathrm{P})_{2}{ }^{61,68-70}$ or $\mathrm{Pd}_{2} \mathrm{X}_{2}(\mathrm{P}-\mathrm{N})_{2}{ }^{71,72}$ compounds.


Figure 3.10 Space-filling representation of $\mathrm{Pd}_{2} \mathrm{Cl}_{2}(\mathrm{dmapm})$ showing the lopsided distribution of steric bulk about the $\mathrm{Pd}-\mathrm{Pd}$ bond. All visible, unlabelled atoms are C -atoms.

The $\mathrm{P}-\mathrm{N}$ "bite" angle found for $\mathrm{Pd}_{2} \mathrm{Cl}_{2}$ (dmapm) is approximately $86^{\circ}$, the same as that found for $\mathrm{PdCl}_{2}(P, N-\mathrm{dmapm})$. The $\mathrm{Pd}-\mathrm{Cl}$ bond lengths found for the two complexes are the same within error for Cl trans to P ; the $\mathrm{Pd}-\mathrm{N}$ bond lengths are significantly longer in the former ( $2.25 \AA$ ) than in the latter ( $2.132 \AA$ ) possibly due to the high trans influence of the metal-metal bond. In the case of the $\mathrm{Pd}-\mathrm{P}$ bond lengths, one
of those found for $\mathrm{Pd}_{2} \mathrm{Cl}_{2}(\mathrm{dmapm})(\mathrm{Pd}(2)-\mathrm{P}(2), 2.184(3) \AA)$ is essentially the same as that found for $\mathrm{PdCl}_{2}(P, N$-dmapm $)(2.1798(6) \AA)$ while the other $(\operatorname{Pd}(1)-\mathrm{P}(1)$, $2.153(4) \AA$ ) is significantly shorter. As in the case of discrepancy between the P—PdPd angles, there is no obvious reason for the asymmetry within the $\mathrm{Pd}_{2} \mathrm{Cl}_{2}$ (dmapm) molecule, but crystal packing effects can be invoked.

The absolute configurations of the P -atoms in the ORTEP shown in Figure 3.8 are $R, R$. Because the space group of the crystal ( $C 2 / \mathrm{c}$ ) contains a glide plane, the opposite enantiomer must also be present in equal abundance in the unit cell. The diastereomeric $R, S$ form is not present, however. In addition, the $300 \mathrm{~K}{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of this compound consists of a lone singlet which indicates that there is either rapid exchange between diastereomers, or the molecule is formed stereoselectively. In order to shed light on this question, two NMR experiments were conducted. In the first, ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra were acquired at successively lower temperatures in order to "freeze out" the putative diastereomeric exchange; no splitting of the singlet was observed. This indicates either that the exchange between diastereomers is facile and occurs rapidly even at 220 K , or that there is no exchange. Because the mechanism of diastereomeric switching must proceed through exchange of free and coordinated N -atoms, a $2 \mathrm{D}{ }^{1} \mathrm{H}$ EXSY experiment was also carried out at 300 K . The resulting spectrum shows no cross peaks between the $\mathrm{NCH}_{3}$ groups of the bound and the free N -atoms. This evidence definitively rules out diastereomeric exchange and proves that the $\mathrm{Pd}_{2} \mathrm{Cl}_{2}(\mathrm{dmapm})$ molecule is formed stereoselectively.

These results are very different from those obtained by Xie et al. for the complex $\mathrm{Pd}_{2} \mathrm{Cl}_{2}\left(\mu-\mathrm{PN}_{2}\right)_{2} .{ }^{73}$ This compound exhibits a broad singlet in its r.t. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ spectrum which transforms into two closely separated sharp singlets at 253 K indicating the presence of diastereomers. In addition, the lack of exchange between free and coordinated N -atoms in $\mathrm{Pd}_{2} \mathrm{Cl}_{2}$ (dmapm) contrasts with the opposite behaviour observed for the monometallic $\mathrm{Pd}^{\mathrm{II}}$ compound, $\mathrm{PdCl}_{2}$ (dmapm) (Section 3.3.1, Scheme 3.2).

### 3.4.5.2 Two-electron reductions of bimetallic M(II) complexes

In contrast to the reaction between $\mathrm{PdCl}_{2}(\mathrm{dmapm})$ and $\mathrm{Pd}_{2}(\mathrm{dba})_{3} \cdot \mathrm{CHCl}_{3}, \mathrm{PdCl}_{2}(\mathrm{dmapm})$ does not react under the conditions tested with the analogous $\mathrm{Pt}(0)$ starting material
$\mathrm{Pt}(\mathrm{dba})_{2}$. Instead, the only viable route to the mixed metal $\mathrm{Pt}^{1}-\mathrm{Pd}^{1}$ dimer was via a loweryielding 2-electron reduction of the $\mathrm{Pt}^{\mathrm{II}}-\mathrm{Pd}^{\mathrm{II}}$ dimer $\mathrm{PtPdCl}_{4}(\mathrm{dmapm})$ using hot ethanolic KOH (Scheme 3.3. Section 3.9.18).

## Scheme 3.3

$$
\begin{gathered}
\mathrm{PtPdCl}_{4}(\mathrm{dmapm})+\mathrm{KOH}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH} \rightarrow \\
\mathrm{PtPdCl}_{2}(\mathrm{dmapm})+\mathrm{KCl}+\mathrm{HCl}+\mathrm{CH}_{3} \mathrm{CHO}+\mathrm{H}_{2} \mathrm{O}
\end{gathered}
$$

Although several reducing agents have been used in attempts to uncover convenient and reliable syntheses of $\mathrm{M}^{1}$ dimers, conproportionation reactions between the appropriate $\mathrm{M}^{\mathrm{II}}$ and $\mathrm{M}^{0}$ complexes in the presence of the bridging ligand give the best results. Pringle and Shaw tested zinc dust, formic acid, hydrazine and sodium borohydride in the synthesis of $\mathrm{Pd}_{2} \mathrm{Cl}_{2}(\mathrm{dppm})_{2}$ and the results were generally unsatisfactory. ${ }^{74}$ Overall yields were typically in the range of $40 \%$ and the desired product was often contaminated with $\mathrm{PdCl}_{2}\left(P, P^{\prime}-\mathrm{dppm}\right)$ which was difficult to remove.

The mixed metal dimer $\mathrm{PtPdCl}_{2}(\mathrm{dppm})_{2}$, first reported by Pringle and Shaw in 1982, ${ }^{75}$ was made in high yield by addition of the labile $\mathrm{Pt}^{11}$ precursor $\mathrm{PtCl}_{2}\left(\mathrm{NC}^{t} \mathrm{Bu}\right)_{2}$ and dppm to the red solution resulting from the reaction between $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}$ and dppm. Mixed metal PtPd complexes containing bridging $\mathrm{PN}_{n}$ ligands have also been made by the conproportionation route. ${ }^{39,72}$

Reduction of platinum metal(II) salts by ethanolic KOH is not new (and, for example, is the standard route by which $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{4}$ is synthesised from $\mathrm{K}_{2} \mathrm{PtCl}_{4}{ }^{76}$ ) but to this author's knowledge this is the first occasion in which the method has been used to make a $\mathrm{M}^{\mathrm{I}}-\mathrm{M}^{\mathrm{L}}$ complex from the corresponding $\mathrm{M}^{\mathrm{II}}{ }_{2}$ compound.

The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of $\mathrm{PtPdCl}_{2}(\mathrm{dmapm})$ and its proposed structure are shown in Figure 3.11. The spectrum is typical for a phosphine-bridged PtPd bimetallic compound. ${ }^{39,74,75}$ The P -atoms are chemically inequivalent and give rise to doublets $\left({ }^{2} J_{\mathrm{PaPb}}=21.9 \mathrm{~Hz}\right.$ ), while $\mathrm{P}_{\mathrm{a}}$ shows a large one-bond coupling to ${ }^{195} \mathrm{Pt}\left({ }^{1} J_{\mathrm{PaPt}}=4200 \mathrm{~Hz}\right)$ and $\mathrm{P}_{\mathrm{b}}$ shows a small two-bond coupling ( ${ }^{2} \int_{\mathrm{PbPt}}=260 \mathrm{~Hz}$ ).


Figure 3.11 The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ) spectrum and proposed structure of $\mathrm{PtPdCl}_{2}$ (dmapm). The small peak at $\delta-30$ is due to trace $\mathrm{Pd}_{2} \mathrm{Cl}_{2}$ (dmapm) impurity. $\left(\mathrm{Ar}=o-\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{NMe}_{2}\right.$.)

As for $\mathrm{Pd}_{2} \mathrm{Cl}_{2}$ (dmapm), the mixed metal complex does not exhibit a "doubling" of NMR spectral peaks which would indicate the presence of diastereomers and, by analogy to the former complex, is most probably formed stereoselectively. The ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathrm{PtPdCl}_{2}$ (dmapm) is consistent with the proposed structure. The $\mathrm{NCH}_{3}$ region shows six sharp peaks in a $1: 1: 1: 1: 2: 2$ ratio at $\delta 3.19,3.07,3.02,2.78,2.45$ and 2.36 . By virtue of their similar positions in the spectrum of $\mathrm{Pd}_{2} \mathrm{Cl}_{2}(\mathrm{dmapm})$, the singlets at 3.07 and 2.78, and 2.45 can be assigned to the two diastereotopic $\mathrm{NCH}_{3}$ groups of the Pd -bound N -atom and the two chemically equivalent $\mathrm{NCH}_{3}$ groups of the free N -atom associated with the Pd -bound P -atom, respectively. The remaining peaks at $\delta 3.19,3.02$ and 2.36 correspond to the analogous peaks on the Pt "side" of the molecule.

### 3.4.5.3 Reactions of bimetallic $M^{1}$ complexes

Like the well known $P, P^{\prime}$ - and $P, N$-bridged $\mathrm{Pd}^{\mathrm{I}}$ dimers, $\mathrm{Pd}_{2} \mathrm{Cl}_{2}$ (dmapm) contains a reactive $\mathrm{Pd}-\mathrm{Pd}$ bond. Although $\mathrm{Pd}^{1}$ dimers of this type typically undergo insertion reactions with small molecules such as $\mathrm{CO},{ }^{61,68,72,77} \mathrm{CNMe},{ }^{61,77} \mathrm{SO}_{2},{ }^{78} \mathrm{CS}_{2},{ }^{79}$ $\mathrm{H}_{2} \mathrm{~S},{ }^{69,70,80} \mathrm{H}_{2} \mathrm{Se}^{81}$ etc (Chart 3.9, (a); Y = small molecule), there are ligand-dependent
differences in their reactivities. For example, whereas the $P, P^{\prime}$ '-bridged complexes react with CO to form insertion products of the type $\mathrm{Pd}_{2} \mathrm{X}_{2}(\mu-\mathrm{CO})(\mu-\mathrm{P}-\mathrm{P})_{2}(\mathrm{X}=$ halide $),{ }^{61}$ the $P, N$-bridged complexes such as $\mathrm{Pd}_{2} \mathrm{Cl}_{2}\left(\mu-\mathrm{PN}_{1}\right)_{2}\left(\mathrm{PN}_{1}=2\right.$-diphenylphosphinopyridine $)$ react via displacement of the pyridyl groups to form $\mathrm{Pd}_{2} \mathrm{Cl}_{2}(\mathrm{CO})_{2}\left(\mathrm{PN}_{1}\right)_{2}$ which contains terminal CO ligands and an unsupported metal-metal bond. ${ }^{72}$ This difference in reactivity is probably due to rigidity in the bridging ligand. As another example, $\operatorname{Pd}_{2} \mathrm{X}_{2}(\mu-$ dppm $)_{2}$ is unreactive toward $\mathrm{CS}_{2} 82$ but $\mathrm{Pd}_{2} \mathrm{X}_{2}(\mu-\mathrm{dmpm})_{2}$ reacts rapidly to give $\mathrm{Pd}_{2} \mathrm{X}_{2}(\mu-$ $\left.\mathrm{CS}_{2}\right)(\mu-\mathrm{dmpm})_{2}{ }^{79}$
$\mathrm{Pd}_{2} \mathrm{Cl}_{2}$ (dmapm) and $\mathrm{PtPdCl}_{2}$ (dmapm) differ fundamentally from the majority of diphosphine-bridged $M^{1}$ dimers in that they bear only one diphosphine ligand which has potentially dissociable anilinyl "arms". The doubly-bridged $\mathrm{M}^{1}$ complexes give "Aframe" insertion products with small molecules (Chart 3.9, (a)). Because of the putative lability of the N -atoms, $\mathrm{MM}^{\prime} \mathrm{Cl}_{2}$ (dmapm) complexes should be able to form not only the analogous "A-frame" complexes (Chart 3.9, (c)), but also double insertion products (Chart 3.9, (b)). By analogy to the reaction of CO with $\mathrm{Pd}_{2} \mathrm{Cl}_{2}\left(\mu-\mathrm{PN}_{1}\right)_{2},{ }^{72}$ another possible reaction pathway is displacement of the anilinyl groups without disruption of the M-M' bond (Chart 3.9, (d)).

## Chart 3.9

(a)

(c)

(b)

(d)


In addition, as noted above, the geometries of $\mathrm{Pd}_{2} \mathrm{Cl}_{2}$ (dmapm) and $\operatorname{PtPdCl}_{2}$ (dmapm) leave the $\mathrm{M}-\mathrm{M}$ ' bond significantly more exposed than in the case of $\mathrm{MM}^{\prime} \mathrm{Cl}_{2}(\mu-\mathrm{P}-\mathrm{P})_{2}$ (Figure 3.10). Finally, the chloride ligands in the dmapm complexes are trans to P , whereas they are trans to the $\mathrm{M}-\mathrm{M}$ ' bond in the "more typical" dimers. It was therefore of interest to examine the reactivity of the new bimetallic $M^{1}$ complexes with small molecules.

## $\mathrm{Pd}_{2} \mathrm{Cl}_{2}$ (dmapm): Reaction with CO .

Exposure of an orange $\mathrm{CDCl}_{3}$ solution containing $\mathrm{Pd}_{2} \mathrm{Cl}_{2}(\mathrm{dmapm})$ to $\mathrm{CO}(1 \mathrm{~atm})$ resulted in a rapid colour change to intense purple. The in situ ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum consists of a singlet at $\delta 43.0$ and an upfield singlet corresponding to unreacted $\mathrm{Pd}_{2} \mathrm{Cl}_{2}(\mathrm{dmapm})$ in a ratio of $c a .6: 1$. The ${ }^{1} \mathrm{H}$ NMR spectrum indicates that all $24 \mathrm{NCH}_{3}$ protons of the COcontaining product are equivalent. From this one can conclude that the two coordinated N -atoms in the starting material are displaced by CO. Conducting 3 freeze-pump-thaw cycles on this solution is sufficient to regenerate quantitatively the starting material. A purple solid whose elemental analysis is consistent with the formulation $\mathrm{Pd}_{2} \mathrm{Cl}_{2}(\mathrm{CO})_{2}$ (dmapm) could be isolated from a $\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{Et}_{2} \mathrm{O}$ slurry containing $\mathrm{Pd}_{2} \mathrm{Cl}_{2}$ (dmapm) which had been exposed to CO (1 atm) overnight (Section 3.9.19). The IR spectrum of this solid showed a single strong $v_{\mathrm{CO}}$ at $1798 \mathrm{~cm}^{-1}$ which corresponds to a bridging carbonyl. In contrast, $\mathrm{Pd}_{2} \mathrm{Cl}_{2}(\mathrm{CO})_{2}\left(\mathrm{PN}_{1}\right)_{2}$ has $v_{\mathrm{CO}}$ bands at 2019 and $1994 \mathrm{~cm}^{-1}$, clearly indicating terminal CO ligands. Thus, the IR and elemental analysis findings lead to the conclusion that the product contains two bridging CO ligands opposite one-another (Chart 3.10). In this arrangement, the symmetric CO stretch is $\mathbb{R}$ invisible and only one CO band is observed. A Pd—Pd bond is included to ensure that each metal centre retains the requisite 16 electrons.

Chart 3.10


## $\mathrm{PdCl}_{2}$ (dmapm): Reaction with diethylacetylenedicarboxylate (DEAD).

Interest in acetylene complexes has been fuelled by the search for hydrogenation and cyclotrimerisation catalysts. ${ }^{83}$ For bimetallic complexes, two acetylene coordination modes are known. In the first, prevalent in carbonyl complexes of the first row transition metals, the acetylene sits perpendicular to the metal-metal axis with the acetylene C atoms bridging (Chart 3.11 , left). ${ }^{84-86}$ In the second, most commonly observed for phosphine complexes of the second and third row transition metals, the acetylene lies parallel to the metal-metal axis and each $\mathrm{C} \equiv \mathrm{C} \mathrm{C}$-atom binds one metal atom (Chart 3.11, right). ${ }^{87-89}$ The crystal structure of $H, T-\mathrm{Pd}_{2} \mathrm{Cl}_{2}(\mu-\mathrm{DMAD})\left(\mu-\mathrm{PN}_{3}\right)_{2}$ shows the acetylene to adopt the second "parallel" coordination mode. ${ }^{73}$ In addition, the kinetic aspects of the reaction of DMAD with $H, T-\mathrm{Pt}_{2} \mathrm{I}_{2}\left(\mu-\mathrm{PN}_{3}\right)_{2}$ have been examined. ${ }^{71}$

It should be noted that whereas the "perpendicular" mode is not possible (without either dissociation of diphosphine or invocation of 5-coordinate Pd ) for the reaction between acetylenes and $\mathrm{Pd}_{2} \mathrm{Cl}_{2}(\mu-\mathrm{P}-\mathrm{P})_{2}$, the ability of the N "arms" to dissociate makes this mode a possibility in the analogous reaction with $\mathrm{Pd}_{2} \mathrm{Cl}_{2}$ (dmapm).

## Chart 3.11




The $\mathrm{Pd}(\mathrm{I})$ dimer $\mathrm{Pd}_{2} \mathrm{Cl}_{2}$ (dmapm) reacts with DEAD to give the compound $\mathrm{Pd}_{2} \mathrm{Cl}_{2}$ (DEAD)(dmapm) as a monohydrate (Section 3.9.20). This compound is fluxional in $\mathrm{CDCl}_{3}$ solution, the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra at 325 and 220 K being given in Figure 3.12.


Figure 3.12 The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) spectra of $\mathrm{Pd}_{2} \mathrm{Cl}_{2}(\mathrm{DEAD})(\mathrm{dmapm})$ at 325 (top) and 220 K (bottom).

One possible interpretation of the NMR spectra is according to the process illustrated in Scheme $3.4(\mathrm{R}=\mathrm{C}(\mathrm{O}) \mathrm{OEt})$. At higher temperatures, the P -atoms are rendered chemically equivalent by rapid exchange. Coordination of a "dangling" N -atom of dmapm causes the acetylene moiety to be shuttled from one Pd centre to the other with concomitant displacement of the recipient Pd centre's bound N -atom. The two extremes represented in the scheme are, of course, identical and should therefore give rise to identical spectra should the motion be frozen. In the "frozen" state, for example at 220 K , when the shuttling mechanism is slow on the NMR time-scale, the two P -atoms become inequivalent. A 2D ${ }^{31} \mathrm{P}$ EXSY measurement at 220 K confirmed that the P -atoms of $\mathrm{Pd}_{2} \mathrm{Cl}_{2}(\mathrm{DEAD})(\mathrm{dmapm})$ are in chemical exchange.

## Scheme 3.4



## PtPdCl $2_{2}$ (dmapm)

In contrast to the reactions of CO and DEAD with $\mathrm{Pd}_{2} \mathrm{Cl}_{2}$ (dmapm), the analogous reactions with $\mathrm{PtPdCl}_{2}$ (dmapm) at r.t. resulted in disproportionation to $\mathrm{PtCl}_{2}\left(P, P^{\prime}\right.$ dmapm) and Pd metal; this reaction was followed by low temperature ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy, after 1 atm of CO was admitted to an NMR tube containing a $\mathrm{CDCl}_{3}$ solution of $\mathrm{PtPdCl}_{2}$ (dmapm) at $c a .230 \mathrm{~K}$. The tube was then allowed to warm in the spectrometer probe to 300 K over 2.5 h with measurements taken at 10 K intervals. A typical spectrum is given in Figure 3.13.


Figure 3.13 The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \quad \mathrm{NMR} \quad\left(162 \mathrm{MHz}, \quad \mathrm{CDCl}_{3}, \quad 253 \mathrm{~K}\right)$ spectrum of $\mathrm{PtPdCl}_{2}$ (dmapm) under $\mathrm{CO}, 90 \mathrm{~min}$ after admitting the gas. $*$ denotes PtPdCl 2 (dmapm) and \# signifies a small $\mathrm{Pd}_{2} \mathrm{Cl}_{2}$ (dmapm) impurity. Other assignments are discussed in the text.

Whereas meaningful data can be extracted from the ${ }^{3!} \mathrm{P}$ spectra, peaks in the corresponding ${ }^{1} \mathrm{H}$ spectra at this temperature are broad and uninformative. The following analysis is tentative.

The spectrum in Figure 3.13 clearly demonstrates the presence of two new species, both containing Pt and Pd bridged by dmapm and most probably a $\mathrm{Pt}-\mathrm{Pd}$ bond. The first (a) has the following spectral data: $\delta-18.4\left(\mathrm{~d},{ }^{1} J_{\mathrm{PPt}}=3060,{ }^{2} J_{\mathrm{PP}}=23.3 \mathrm{~Hz}, \mathrm{P}\right.$ bonded to Pt), -8.3 ( $\mathrm{d},{ }^{2} J_{\mathrm{PPt}}=300,{ }^{2} J_{\mathrm{PPP}}=23.3 \mathrm{~Hz}, \mathrm{P}$ bonded to Pd ). By comparison to the ${ }^{31} \mathrm{P}$ singlet of $\mathrm{Pd}_{2} \mathrm{Cl}_{2}(\mu-\mathrm{CO})_{2}(\mathrm{dmapm})(\delta 43.0)$, which shows a downfield shift from that of $\mathrm{Pd}_{2} \mathrm{Cl}_{2}$ (dmapm) ( $\delta-29.0$ ), species a, not manifesting such a dramatic shift from that of the starting $\mathrm{PtPdCl}_{2}(\mathrm{dmapm})(\delta-31.7,-23.0)$, may contain only one bridging CO ligand (Chart 3.12, left; $\mathrm{Ar}=o-\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{NMe}_{2}$ ), although this would necessitate breaking the Pt Pd bond, if the anilinyl N -atoms were to remain bound, and a quenching of the 2 -bond P Pt coupling would presumably result. Or, a may contain CO bound terminally, most probably to Pt (Chart 3.12, middle), which would maintain the 2-bond $\mathrm{P}-\mathrm{Pt}$ coupling.

The second major new species (b) gives the following values: $\delta 25.6\left(\mathrm{~d},{ }^{1} J_{\mathrm{PPt}}=\right.$ $5120,{ }^{2} J_{\mathrm{PP}}=173 \mathrm{~Hz}, \mathrm{P}$ bonded to Pt), 46.9 (d, ${ }^{2} J_{\mathrm{PPt}}=1270,{ }^{2} J_{\mathrm{PP}}=173 \mathrm{~Hz}, \mathrm{P}$ bonded to $\mathrm{Pd})$. The large downfield shift of peaks due to $\mathbf{b}$ relative to those of $\mathrm{PtPdCl}_{2}$ (dmapm) suggest a structure analogous to that of $\mathrm{Pd}_{2} \mathrm{Cl}_{2}(\mathrm{CO})_{2}(\mathrm{dmapm})$. Of note, all the coupling constants observed for $\mathbf{b}$ are very much larger than those of $\mathrm{PtPdCl}_{2}(\mathrm{dmapm})\left({ }^{1} J_{\mathrm{PPt}}=\right.$ $4200,{ }^{2} J_{\mathrm{PPt}}=260,{ }^{2} J_{\mathrm{PP}}=21.9 \mathrm{~Hz}$.

## Chart 3.12


a

a

b

The intermediates $\mathbf{a}$ and $\mathbf{b}$ began to appear after 30 min at 233 K . At 243 K , their concentrations increased markedly and that of $\mathrm{PtPdCl}_{2}$ (dmapm) decreased accordingly. This trend continued as the probe was warmed over the next 60 min to 263 K , when the peak due to $\mathrm{PtCl}_{2}$ (dmapm) ( $\delta-65.2$ ) began to appear. At 283 K , all of the starting material disappeared but a and $\mathbf{b}$ persisted. At 300 K , a vanished and $\mathbf{b}$ persisted for a brief period (ca. 10 min ) before it, too, decomposed and the ${ }^{31} \mathrm{P}$ NMR spectrum indicated $\mathrm{PtCl}_{2}$ (dmapm) to be the sole P-containing product.

### 3.5 A General Introduction to Cluster Catalysis

A cluster catalyst is a complex containing two or more identical or different metal centres supported by one or more metal-metal bonds which, in addition to operating homogeneously, satisfies at the minimum the most basic criterion in an hierarchical set of conditions outlined by Rosenberg and Laine. ${ }^{90}$ In order of decreasing precedence these are: (1) the catalyst must facilitate multi-site activation of organic substrates, (2) if activation occurs at only one site on the intact cluster, the system must give different product distributions from the same reaction mediated by complexes containing a single metal centre, (3) if (1) and (2) are not met, and if the cluster fragments giving a monometallic active catalyst, the intact cluster must at least be a part of the catalytic cycle.

### 3.5.1 Homogeneous vs. heterogeneous

Compared to monometallic complexes, clusters have a greater tendency to fragment and reaggregate in solution after loss of one or more ligands, and this leads to metal particle formation driven by metal-metal bonding. ${ }^{91,92}$ One effective test for the homogeneity of a reaction (especially those catalysed by complexes of group 10 metals which are known to form amalgams) is the addition of metallic Hg to the reaction mixture. ${ }^{93}$ This is a reasonably certain way to eliminate metal particles and therefore their heterogeneous contribution to the catalysis. In the opposite sense, addition of the rigid, tub-shaped dibenzocyclooctatetraene, which binds homogeneous catalysts irreversibly, will inhibit
the homogeneous component. ${ }^{94}$ A combination of Hg tolerance and inhibition by the tetraene is a good indicator therefore of the homogeneous nature of a reaction.

### 3.5.2 Multi-site activation

In heterogeneously catalysed organic reactions, more than one metal centre on the surface is required to effect the transformation of reactant into product. By analogy, cluster catalysis in the strictest sense requires multi-site activation of the substrate. Only in catalysts where this criterion is fulfilled can true cooperative effects occur. However, the cluster may contain only a single active site, or multiple non-interacting sites, and these possibilities must be allowed for in a less rigid definition of cluster catalysis. In the case of a single active site, inactive metal centres and their associated ligand scaffold are conceptually equivalent to the $\mathrm{L}_{n}$ portion of the monometallic catalyst, $\mathrm{ML}_{n}$. Where there are $m$ non-interacting active sites, the catalyst operates as the kinetic equivalent of $m \mathrm{ML}_{n}$.

### 3.5.3 Product distribution in single-site cluster catalysis

If the product distributions given by a monometallic and a single-active-site polymetallic catalyst differ, cluster catalysis is indicated. The ring-opening cyclooligomerisation of thietane represents a good example of a reaction which is mediated both by one centre of the cluster $\mathrm{Os}_{4}(\mathrm{CO})_{11}\left[\mathrm{~S}\left(-\mathrm{CH}_{2}-\right)_{3}\right](\mu-\mathrm{H})_{4}{ }^{95}$ and by the monometallic complex $\mathrm{W}(\mathrm{CO})_{5}[\mathrm{~S}(-$ $\left.\left.\mathrm{CH}_{2}-\right)_{3}\right] .{ }^{96}$ However, the product distributions resulting from the two catalysts differ significantly, with the cluster producing predominantly small crown thioethers because of steric effects resulting from the extended metal-CO scaffold.

### 3.5.4 Cluster fragmentation

Metal cluster catalysis often involves fragmentation either into smaller clusters or monometallic species, ${ }^{97}$ and the latter may be the active component. This possibility is accommodated in the least strict definition of cluster catalysis which necessitates that the intact cluster must form part of the catalytic cycle. This is the case for the $\mathrm{Ru}_{3}(\mathrm{CO})_{12^{-}}$ catalysed reduction of CO to ethylene glycol 98,99 in which the carbonyl is converted to $\left[\mathrm{HRu}_{3}(\mathrm{CO})_{11}\right]^{-}$and $\left[\mathrm{RuI}_{3}(\mathrm{CO})_{3}\right]^{-}$in the presence of $\mathrm{H}_{2}, \mathrm{CO}$ and $\mathrm{I}^{-}$. The hydride donor is proposed to be $\left[\mathrm{HRu}(\mathrm{CO})_{4}\right]^{-}$formed from $\left[\mathrm{HRu}_{3}(\mathrm{CO})_{11}\right]^{-}$and CO . Although the latter Ru
compound is not the active species, it is regenerated during the cycle. In contrast, the synthesis of acetic acid mediated by $\mathrm{Ru}_{3}(\mathrm{CO})_{12} / \mathrm{CoI}_{2}$ involves only monometallic species generated by fragmentation. ${ }^{100}$

### 3.5.5 Indications

Fulfillment of one or more of the following criteria indicates cluster catalysis: 90
(1) The turnover frequency (TOF) increases with increasing catalyst concentration.
(2) Product distributions obtained using cluster catalysts differ significantly from those obtained using monometallic precursors, or products cannot be explained using reasonable mechanisms occurring at a single metal centre (as mentioned above).
(3) The use of a cluster or cluster precursor containing two or more different metals significantly enhances the reaction rate, or changes the product selectivity of a reaction catalysed by one of the metals, or allows catalysis by a metal which is normally inactive.
(4) Reaction conditions are such that metal-metal bond formation is promoted.
(5) A chiral metal framework results in catalytic asymmetric induction.

### 3.6 The Heck Reaction

### 3.6.1 General

The Heck reaction represents the Pd-catalysed $\mathrm{C}-\mathrm{C}$ bond forming reaction between an alkene and an aryl- or alkenylhalide in the presence of a base (Scheme 3.5; B = base).

## Scheme 3.5



The most widely accepted mechanism ${ }^{2}$ involves the oxidative addition of the aryl- or alkenylhalide to $\mathrm{Pd}^{0}$ (most commonly generated in situ from $\mathrm{Pd}^{\text {ll }}$ ), coordination of the alkene and insertion into the $\mathrm{Pd}-\mathrm{C}$ bond, $\beta$-hydride elimination to give the coupled product, and finally deprotonation by base to regenerate $\mathrm{Pd}^{0}$. An alternative mechanism involves a $\mathrm{Pd}^{\mathrm{II}} / \mathrm{Pd}^{\mathrm{IV}}$ cycle, although this is usually invoked only in the case of electronrich Pd centres. ${ }^{4}$

### 3.6.2 Heck coupling of iodobenzene and styrene using anilinylphosphine complexes

### 3.6.2.1 Compounds tested

The complexes tested as catalyst precursors for the production of cis- and trans-stilbene by Heck coupling of iodobenzene and styrene at $100^{\circ} \mathrm{C}$ in $\mathrm{DMF} / \mathrm{H}_{2} \mathrm{O}$ with $\mathrm{K}_{2} \mathrm{CO}_{3}$ as base (Section 3.9.23) are shown in Chart $3.13\left(\mathrm{M}=\mathrm{Pt}, \mathrm{Pd} ; \mathrm{Ar}=o-\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{NMe}_{2}\right)$. Also tested were $\mathrm{MCl}_{2}$. Catalyst loadings were on the order of $0.05-0.1 \mathrm{~mol} \%$.

## Chart 3.13



The monometallic compounds $\mathrm{MCl}_{2}(\mathrm{PMA})^{101}\left(\mathrm{PMA}=\mathrm{Ph}_{2} \mathrm{P}-o-\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{NMe}_{2}\right)$ were chosen so that their steric and electronic properties would mimic closely the "halves" of the bimetallic complexes; to assess whether cooperative effects were a factor during the bimetal-catalysed reactions, a baseline activity for each of the metals was needed. This approach has been adopted previously by Stanley and coworkers in the analysis of hydroformylations catalysed by dirhodium complexes. ${ }^{29}$

### 3.6.2.2 Results

$\mathrm{PdCl}_{2}(\mathrm{PMA})$ and $\mathrm{PdMCl}_{4}(\mathrm{dmapm})(\mathrm{M}=\mathrm{Pt}, \mathrm{Pd})$ were effective catalyst precursors for the Heck coupling of PhI and styrene under the conditions described in Section 3.9.23 $\left(100{ }^{\circ} \mathrm{C}\right.$, DMF/ $\mathrm{H}_{2} \mathrm{O}$ solvent (3:2 by vol.), $\mathrm{K}_{2} \mathrm{CO}_{3}$ base). Although DMF and $\mathrm{H}_{2} \mathrm{O}$ are miscible in all proportions, the reaction mixture consists of 2 phases at r.t. because of the presence of significant quantities of the reactants. However, at the operating temperature of $100^{\circ} \mathrm{C}$, the phases are miscible and the solution is homogeneous by visual inspection (see Homogeneity below).

A typical plot of [PhI] vs. time for the coupling reaction is given in Figure 3.14.


Figure 3.14 The variation of [ PhI$]$ with time for the Heck coupling of PhI and styrene using $\mathrm{Pd}_{2} \mathrm{Cl}_{4}$ (dmapm) $\left(4.4 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1}\right)$ as catalyst precursor $\left(100^{\circ} \mathrm{C}\right.$, DMF/ $\mathrm{H}_{2} \mathrm{O}$ solvent (3:2 by vol.), $\mathrm{K}_{2} \mathrm{CO}_{3}$ base). The inset shows a plot of $\ln \left([\mathrm{PhI}] /[\mathrm{PhI}]_{0}\right)$ vs. time where $[\mathrm{PhI}]_{0}$ is the initial PhI concentration.

Figure 3.14 shows first-order loss of PhI (see inset), consistent with one step in the catalytic cycle involving oxidative addition of the aryl halide. However, Figure 3.14 is also consistent with the reaction being first-order in styrene and zero-order in PhI with the first-order decay of $[\mathrm{PhI}]$ resulting from the stoichiometry; further experiments in
which the [PhI]:[styrene] ratio is varied need to be done in order to rule out this possibility. Loss of styrene could not be followed accurately because the GC peak corresponding to the alkene overlapped with that of the DMF solvent.

The stilbene product could be recovered pure simply by allowing the reaction mixture to cool: this resulted in precipitation of trans-stilbene. Cis-stilbene, which is a liquid at r.t., is only produced to the extent of about $1 \%$ under these conditions and remains in solution.

The initial rates and turnover frequencies (TOFs) for mono- and bimetal-catalysed Heck coupling reactions between PhI and styrene are given in Table 3.4. $(\mathrm{TOF}=\mathrm{mol}$ product per mol catalyst per s.)

Table 3.4 Initial rates and TOFs for the Heck coupling of $\mathrm{PhI}\left(0.4 \mathrm{~mol} \mathrm{~L}^{-1}\right)$ and styrene ( $0.4 \mathrm{~mol} \mathrm{~L} \mathrm{~L}^{-1}$ ) at $100^{\circ} \mathrm{C}$ in DMF/ $\mathrm{H}_{2} \mathrm{O}$ (3:2 by vol.) with $\mathrm{K}_{2} \mathrm{CO}_{3}$ ( $0.4 \mathrm{~mol} \mathrm{~L}^{-1}$ ) as base.

| Catalyst | Concentration <br> $\left(\mathrm{mol} \mathrm{L}^{-1}, \times 10^{4}\right)$ | Initial rate <br> $\left(\mathrm{mol} \mathrm{L}^{-1} \mathrm{~s}^{-1}, \times 10^{5}\right)$ | Initial TOF <br> $\left(\mathrm{s}^{-1}\right)$ |
| :--- | :---: | :---: | :---: |
| $\mathrm{PtCl}_{2}$ (PMA) | 7.00 | 0.00 | 0.000 |
| $\mathrm{PdCl}_{2}$ (PMA) | 7.41 | 11.9 | 0.161 |
| $\mathrm{Pd}_{2} \mathrm{Cl}_{4}(\mathrm{dmapm})$ | 1.15 | 5.87 | 0.510 |
| $\mathrm{PtPdCl}_{4}$ (dmapm) | 2.14 | 4.85 | 0.227 |
|  | 3.80 | 10.1 | 0.266 |
|  |  |  | $\mathrm{Av} .=0.247$ |

The initial TOFs imply both that the bimetallic catalysts are more active than would be predicted from the sum of the activities of their corresponding "halves" and that the catalysis is mediated by Pd only given that (i) $\mathrm{Pd}_{2} \mathrm{Cl}_{4}$ (dmapm) is almost exactly twice as active as $\mathrm{PtPdCl}_{4}(\mathrm{dmapm})$ and (ii) $\mathrm{PtCl}_{2}$ (PMA) is completely inactive. Comparing TOFs in this concentration regime is valid because catalyst loading studies (see below) show the reaction to be first-order in Pd up to $c a .5 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1}$.

## Catalyst Loading

The variation of initial rate of the Heck coupling of PhI and styrene catalysed by $\mathrm{PdMCl}_{4}(\mathrm{dmapm})(\mathrm{M}=\mathrm{Pd}, \mathrm{Pt})$ and $\mathrm{PdCl}_{2}(\mathrm{PMA})$ with total Pd concentration is given in Figure 3.15.


Figure 3.15 Variation of initial rate of the Heck coupling of PhI and styrene with total Pd concentration for reactions catalysed by $\mathrm{PdMCl}_{4}(\mathrm{dmapm})(\mathrm{M}=\mathrm{Pd}, \mathrm{Pt})$ and $\mathrm{PdCl}_{2}$ (PMA) under the conditions outlined in Section 3.9.23.

If, during catalysis, the bimetallic $\mathrm{PdMCl}_{4}$ (dmapm) fragments completely or if no fragmentation at all occurs, then the rate should show a first-order dependence on the catalyst concentration. If, however, an equilibrium between bimetallic and monometallic species is established and, if the reaction is catalysed by one or both of the smaller fragments, then the rate should show a first-order dependence on catalyst concentration in the lower concentration regime (in which the bimetallic complex is almost completely fragmented into its constituent pieces) and a half-order dependence in the higher concentration regime (in which it is almost completely undissociated). ${ }^{90}$

When $\mathrm{PdCl}_{2}$ (PMA) is used as the catalyst, the initial rate shows a first-order dependence on total $[\mathrm{Pd}]$ to a concentration of at least $1.6 \times 10^{-3} \mathrm{~mol} \mathrm{~L}^{-1}$; at higher concentrations, Pd metal precipitates immediately on addition of $\mathrm{K}_{2} \mathrm{CO}_{3}$, and the initial rate shows a corresponding non-linear dependence on catalyst loading.

The dependence of the initial rate of the bimetal-catalysed reactions on total [Pd] is first-order to a limit of $c a .5 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1}$. In this concentration range, the bimetallic
catalysts are slightly more active than $\mathrm{PdCl}_{2}$ (PMA) while being very similar to each other in activity. These observations suggest that both homo- and heterobimetallic catalyst precursors give rise to the same active species.

The initial rates of both bimetal-catalysed reactions show almost identical nonlinear dependence on total [Pd] above the $5 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1}$ limit. For example, when the concentration of $\mathrm{PtPdCl}_{4}(\mathrm{dmapm})$ is approximately doubled from $5.38 \times 10^{-4}$ to $1.16 \times$ $10^{-3} \mathrm{~mol} \mathrm{~L}^{-1}$, the initial rate increases from 1.10 to $1.56 \times 10^{-4} \mathrm{~mol} \mathrm{~L} \mathrm{~s}{ }^{-1}$, i.e., by a factor of 1.42 , or approximately the square root of 2 . At higher concentrations still, this halforder dependence is lost, pointing to catalyst degradation. (It should be noted, however, that in no reactions catalysed by bimetallic complexes was metal precipitation observed.)

In addition, above the $5 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1}$ concentration limit, the bimetallic catalysts are substantially less active than $\mathrm{PdCl}_{2}$ (PMA), pointing to a dearth of monometallic active species in solution at high total [Pd].

Shown in Figure 3.16 is a plot of $\ln ($ Initial rate $)$ vs. $\ln ($ Total [Pd]) for the Heck coupling of PhI and styrene catalysed by the bimetallic complexes $\mathrm{PdMCl}_{4}(\mathrm{dmapm})(\mathrm{M}=$ $\mathrm{Pd}, \mathrm{Pt})$. The plot is broken into low and high [Pd] regimes; linear regression analysis of these shows a rough first- to half-order transition. The point corresponding to the highest total [Pd] has been omitted from this analysis.


Figure 3.16 Plot of $\ln$ (Initial rate) vs. $\ln ($ Total [Pd]) for the Heck coupling of PhI and styrene catalysed by the bimetallic complexes $\mathrm{PdMCl}_{4}(\mathrm{dmapm})(\mathrm{M}=\mathrm{Pd}$, Pt).

These observations suggest that an equilibrium between bi- and monometallic species is established and that the catalysis is due mainly to monometallic species. For the heterobimetallic complex, $\mathrm{PtPdCl}_{4}$ (dmapm), the two possible equilibria are shown in Scheme $3.6\left(\mathrm{PdCl}_{2}\right.$ (dmapm) represents an equilibrium mixture of the $P, P^{\prime}-$ and $P, N$ bonded forms).

## Scheme 3.6

$$
\begin{aligned}
\operatorname{PtPdCl}_{4}(\mathrm{dmapm}) & \rightleftharpoons \mathrm{PdCl}_{2}(\mathrm{dmapm})+\mathrm{PtCl}_{2} \\
\mathrm{PtPdCl}_{4}(\mathrm{dmapm}) & \rightleftharpoons \mathrm{PtCl}_{2}\left(P, P^{\prime}-\mathrm{dmapm}\right)+\mathrm{PdCl}_{2}
\end{aligned}
$$

In order to assess which of the two equilibria predominates, $\mathrm{PdCl}_{2}(\mathrm{dmapm})$ was used as a catalyst precursor for the Heck reaction at a concentration of $4.0 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1}$. This gave an initial rate of $2.2 \times 10^{-5} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}$ which is about 10 times less than predicted by extrapolation of the curve due to $\mathrm{PdMCl}_{4}(\mathrm{dmapm})(\mathrm{M}=\mathrm{Pt}, \mathrm{Pd})$ in Figure 3.15 (ca. $2 \times 10^{-4} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}$ ). This is consistent with equilibrium II being dominant and with the catalysis proceeding via a simple derivative of $\mathrm{PdCl}_{2}$.

The following experiment suggests perhaps that equilibrium II dominates but that I is also operative. A mixture of DMF $(1 \mathrm{~mL})$ and $\mathrm{H}_{2} \mathrm{O}(1 \mathrm{~mL})$ containing equimolar $\mathrm{PtPdCl}_{4}(\mathrm{dmapm})$ and dppe was heated to $100^{\circ} \mathrm{C}$ under air for 4.5 h . The solvent was removed in vacuo and the residue analysed by NMR spectroscopy. The most abundant product was $\mathrm{PdCl}_{2}$ (dppe); if it is assumed that dppe reacts preferentially with $\mathrm{MCl}_{2}$, this result reflects the predominance of equilibrium II. In order of decreasing abundance, the other products were: $\mathrm{PtCl}_{2}$ (dppe) which is accessed presumably by equilibrium $\mathbf{I}$, unreacted $\mathrm{PtPdCl}_{4}(\mathrm{dmapm}),\left[\mathrm{Pt}(\mathrm{dppe})_{2}\right] \mathrm{Cl}_{2}, \mathrm{dmapm}$ and $\mathrm{PtCl}_{2}\left(P, P^{\prime}-\mathrm{dmapm}\right)$.

Given that equilibrium II is likely to predominate and, assuming that $\mathrm{PtCl}_{2}\left(P, P^{\prime}-\right.$ dmapm) does not contribute to the catalysis (a likely prediction in light of inactivity of $\mathrm{PtCl}_{2}(\mathrm{PMA})$ and $\mathrm{PtCl}_{2}$ ), the overall catalysis is most probably mainly due to $\mathrm{PdCl}_{2}$ (which may be complexed by any of DMF, $\mathrm{H}_{2} \mathrm{O}$ or styrene). Of note, the Heck coupling of iodobenzene derivatives and styrene has been shown to occur in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}$ without any added ancillary ligands in predominantly aqueous medium. ${ }^{102}$

The initial TOF for a $\mathrm{PdCl}_{2}$-catalysed Heck reaction between PhI and styrene under the conditions used in this work was $4.86 \times 10^{-2} \mathrm{~s}^{-1}$, significantly lower than would be expected from inspection of Table 3.4 - especially if a simple derivative of $\mathrm{PdCl}_{2}$ is the active species in the bimetal-catalysed reactions. In this experiment, $\mathrm{PdCl}_{2}$ was dissolved in the reaction mixture at $100^{\circ} \mathrm{C}$ prior to addition of aqueous $\mathrm{K}_{2} \mathrm{CO}_{3}$. Metallic Pd deposited during the course of the reaction from the resulting blood red solution, pointing to the fact that the catalytic cycles involving the homo- and heterobimetallic complexes $\mathrm{PdMCl}_{4}(\mathrm{dmapm})$ and that involving $\mathrm{PdCl}_{2}$ differ. The former is homogeneous while in the latter significant precipitation of Pd metal occurs. In addition, the bimetallic catalytic precursors are more active than simple monometallic derivatives of $\mathrm{PdCl}_{2}$, perhaps because of the possibility for cluster recombination during the cycle which prevents the precipitation of metal.

## Homogeneity

The "Hg test" was used to determine whether the Heck reaction is truly homogeneous under the conditions outlined in Section 3.9.23. Thus, 0.05 mL of Hg was added to a reaction run under the standard conditions and catalysed by $\mathrm{PtPdCl}_{4}(\mathrm{dmapm})\left(1.0 \times 10^{-3}\right.$ $\mathrm{mol} \mathrm{L}^{-1}$ ) after the reaction had already been in progress for 30 min . GC analysis of the reaction mixture over the subsequent 30 min showed that addition of Hg had not affected the rate, indicating that the catalysis is homogeneous.

### 3.6.2.3 Oxidative degradation

Subsequent to an unsuccessful attempt to follow the $\mathrm{PtPdCl}_{4}(\mathrm{dmapm})$-catalysed reaction by NMR spectroscopy, orange-brown crystals deposited from a mixture of $\mathrm{DMF} / \mathrm{D}_{2} \mathrm{O}$ containing PhI and styrene which had been heated to $80^{\circ} \mathrm{C}$ for 0.5 h in air and then left for 2 d at r.t. These were submitted for X-ray crystallographic analysis but unfortunately the structure did not refine sufficiently for publication standards. However, the molecular structures of two constituent complexes were established unequivocally. Present in the unit cell were the compounds $\mathrm{PtPdl}_{4}\left(\mathrm{dmapm}^{2}\right)$ (Figure 3.17) and $\mathrm{PtI}_{2}(P, N-\mathrm{dmapmO})$ (Figure 3.18), and one solvate molecule of both DMF and $\mathrm{D}_{2} \mathrm{O}$. In these complexes,
chloride has been substituted by iodide (which is produced stoichiometrically as a byproduct of the Heck reaction; see Scheme 3.5).


Figure 3.17 PLUTO representation of the molecular structure of $\mathrm{PtPdI}_{4}$ (dmapm). Hatoms are omitted for clarity.


Figure 3.18 PLUTO representation of the molecular structure of $\mathrm{PtI}_{2}(P, N$-dmapmO $)$. H -atoms are omitted for clarity.

The crystallographic results show that the bimetallic catalyst can also decompose via a redox route. Discounting equilibrium I, the paths outlined in Scheme 3.7 are plausible ( X is Cl or I ). In the first, $\mathrm{PtPdCl}_{4}(\mathrm{dmapm}$ ) (or its iodo-derivative) is attacked by $\mathrm{OH}^{-}$to give a mono-oxide derivative of dmapm bound to Pt in a $P, N$ fashion, i.e., $\mathrm{PtX}_{2}\left(P, N-\mathrm{dmapmO}\right.$ ), and $\mathrm{Pd}^{0}$ (which may contribute to the catalysis). The generation of $\mathrm{Pd}^{0}$ from $\mathrm{Pd}^{\mathrm{II}}$-phosphine complexes during catalytic transformations of arylhalides is well documented. ${ }^{103,104}$ In the second, less likely and more speculative path, $\mathrm{PtCl}_{2}\left(P, P^{\prime}-\right.$ dmapm), generated by equilibrium II, reacts with $\mathrm{OH}^{-}$to give an intermediate such á " $\mathrm{Pt}(\mathrm{dmapmO})$ " which is transformed in a subsequent step(s) to give $\mathrm{PtX}_{2}(P, N-\mathrm{dmapmO})$ (e.g., by double oxidative addition of PhI followed by reductive elimination of biphenyl). It is important to note that even under the high temperature, strong base conditions of the reaction, a significant proportion of the catalyst survived intact (based on the composition of the isolated crystals).

## Scheme 3.7



### 3.6.2.4 Attempted isolation and identification of Heck catalytic intermediates

Section 3.9.21 outlines an attempt to isolate an intermediate from the Heck reaction catalysed by $\mathrm{PtPdCl}_{4}(\mathrm{dmapm})$. The orange powder thus obtained gave the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum shown in Figure 3.19; the spectrum is obviously due to a mixture of complexes. The species considered most likely to be present were: $\operatorname{PtPdI}_{4}(\mathrm{dmapm}), \mathrm{PtI}_{2}(P, N$ -
dmapmO), $\mathrm{PdI}_{2}\left(P, N\right.$-dmapmO) and $\mathrm{PtPdI}_{2}(\mathrm{dmapm})$. True organometallic intermediates are also possible. Not surprisingly, neither the parent complex $\mathrm{PtPdCl}_{4}(\mathrm{dmapm})$ nor its 2electron reduced product, $\mathrm{PtPdCl}_{2}(\mathrm{dmapm})$ is present because of the stoichiometric iodide produced and the known degradation pathways. Three P-containing compounds (1, 2 and $\mathbf{3}$ ) can be detected (Table 3.5), and in an attempt to identify them, the following experiments were performed.


Figure 3.19 The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ) spectrum of the orange powder isolated from the Heck reaction catalysed by $\mathrm{PtPdCl}_{4}(\mathrm{dmapm})$.

Table 3.5 The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}, 300 \mathrm{~K}$ ) spectral data for compounds 1,2 and 3.

| Species | $\delta_{\mathrm{Pa}}$ | $\delta_{\mathrm{Pb}}$ | ${ }^{2} J_{\mathrm{PaPb}}(\mathrm{Hz})$ | ${ }_{J_{\mathrm{PaPt}}}(\mathrm{Hz})$ |
| :--- | :--- | :--- | :--- | :--- |
| $\mathbf{1}$ | -3.5 | 24.3 | Not observed | 3680 |
| $\mathbf{2}$ | -4.0 | 24.3 | Not observed | 3560 |
| $\mathbf{3}$ | 48.5 | 65.6 | 11.3 | 3370 |

$\mathrm{PtPdI}_{4}(\mathrm{dmapm})$ was synthesised in situ by reaction of $\mathrm{PtPdCl}_{4}(\mathrm{dmapm})$ with an excess of NaI in a mixture of acetone $-\mathrm{d}_{6}$ and $\mathrm{CDCl}_{3}$, and was characterised by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy: $\delta_{\mathrm{Pa}} 12.1, \delta_{\mathrm{Pb}} 23.6 ; 2$-bond PP coupling was again not observed, while ${ }^{1} J_{\text {Papt }}$ could not be determined because of the very low solubility of the complex in this medium.

The synthetic strategy given in Scheme 3.8 was employed in order to synthesise $\mathrm{Pt}_{2}(P, N$-dmapmO $)$; experimental details are given in Section 3.9.22. Although the
procedure did not give either $\mathrm{PtCl}_{2}\left(P, N\right.$-dmapmO) or $\mathrm{PtI}_{2}(P, N$-dmapmO) pure, these compounds could be identified spectroscopically. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.$, $300 \mathrm{~K})$ data are as follows: $\mathrm{PtCl}_{2}\left(P, N\right.$-dmapmO) $\delta_{\mathrm{Pa}}-3.4, \delta_{\mathrm{Pb}} 26.1,{ }^{2} J_{\mathrm{PaPb}}$ not observed, ${ }^{1} J_{\mathrm{PaPt}}=4110 \mathrm{~Hz} . \mathrm{PtI}_{2}(P, N$-dmapmO $) \delta_{\mathrm{Pa}}-5.4, \delta_{\mathrm{Pb}} 26.9,{ }^{2} J_{\mathrm{PaPb}}$ not observed, ${ }^{1} J_{\mathrm{PaPt}}=$ 3850 Hz . Because of the similarity between these data and those given in Table 3.5, complexes 1 and 2 probably contain dmapmO P,N-bound to Pt. In addition, the downfield resonances due to 3 , cannot be rationalised.

Scheme 3.8


### 3.6.2.5 Summary of the catalysis

The major observations of the catalysis study are summarised below:
(1) The homo- and heterobimetallic complexes are more active catalysts than their monometallic "halves", and they also outstrip both $\mathrm{PtCl}_{2}$ and $\mathrm{PdCl}_{2}$.
(2) The catalyst does not remain intact during the reaction but is degraded by fragmentation and oxidation.

A general scheme which accounts for these observations remains elusive. Whereas the kinetic data suggest the equilibria given in Scheme 3.6, examination of the post-reaction
residue does not conclusively reveal any of these species. In addition, although a simple derivative of $\mathrm{PdCl}_{2}$ is suggested as the most active species, reactions catalysed by $\mathrm{PdCl}_{2}$ do not proceed as quickly as those catalysed by the bimetallic complexes. Finally, phosphine oxidation by base precludes the equilibria I and II as they are written because it prevents recombination to give bimetallic complexes of the original type; however, $P, N$-bridged as opposed to $P, P^{\prime}$-bridged compounds remain possible, resulting in equilibria of the type III shown in $\left(M, M^{\prime}=P t, P d\right)$.

## Scheme 3.9

$\mathrm{MM}^{\prime} \mathrm{X}_{4}\left(\right.$ dmapmO-к- $\left.P, N-\mu-P, N^{\prime}\right) \rightleftharpoons \mathrm{MX}_{2}($ dmapmO-к- $P, N)+\mathrm{M}^{\prime} \mathrm{X}_{2}$

### 3.6.3 A cooperativity index proposal

Because bi- and polymetallic catalysis research has received renewed attention and that cooperative mechanisms have been suggested and in some cases proven, I now propose a general index for the degree of cooperativity between metal centres in a polymetallic assembly. This index serves as a kinetic complement to the well-established Hill coefficient ${ }^{105}$ for thermodynamic cooperativity.

Assuming no inter-metallic interactions, the predicted total activity, $A_{P}$, of a polymetallic catalyst of $n$ metal centres is given by equation (1), where $A_{i}$ is the measured activity of the monometallic complex which most closely mimics the steric and electronic attributes of the $i$ th metal centre in the polymetallic assembly. By activity, any reasonable observable should suffice, e.g., initial rate, TOF or $\%$ conversion in a given time.

$$
\begin{equation*}
A_{P}=\sum_{i=1}^{n} A_{i} \tag{1}
\end{equation*}
$$

The average activity, $\bar{A}$, is then given by equation (2).

$$
\begin{equation*}
\bar{A}=\frac{A_{P}}{n} \tag{2}
\end{equation*}
$$

If the observed activity of the polymetallic complex is $A_{O}$, then equation (3) defines one possibility for an index of cooperativity, $a$.

$$
\begin{equation*}
a=\frac{A_{O}-A_{P}}{\bar{A}} \tag{3}
\end{equation*}
$$

This index aligns with common sense in that impeding effects result in $a$ values less than zero while completely non-interacting centres give $a=0$, and cooperative effects yield positive $a$ values. If $a=0$, cluster catalysis is not ruled out. In this case, catalysis may proceed at only one centre in the complex, or at multiple non-interacting centres (Section 3.5.2). Conversely, the cluster may be fragmenting.

In general, the index corresponds to a number of "virtual" metal centres, i.e., the number of centres of average catalytic activity the polymetallic complex appears to possess beyond its real number, $n$.

Of note, Jacobsen and coworkers have been able to distinguish kinetically between inter- and intramolecular pathways in the catalytic asymmetric ring-opening of cyclopentene oxide by Cr (salen)-type dimers linked by tethers of varying lengths, and for each of these an effective reactive concentration of the two salen units has been determined by the ratio of $k_{\text {intra }} / k_{\text {inter }}{ }^{35}$ This method is akin to the cooperativity index now proposed and is an exact treatment for reactions which necessarily involve two metal centres, even if they are not held in proximity by a bridging ligand. The $a$ index is appropriate for reactions which occur readily at one active site and which may or may not benefit by the juxtaposition of other sites.

The $a$ values for the bimetallic catalysts used here are calculated from initial TOFs. The observed activities $\left(A_{O}\right)$ for $\mathrm{PdMCl}_{4}(\mathrm{dmapm})(\mathrm{M}=\mathrm{Pt}, \mathrm{Pd})$ are taken to be the initial TOFs given in Table 3.4; the calculations of $a$ for each of the bimetallic complexes are outlined in Table 3.6. $A_{P}$ values are determined by summing the appropriate initial TOFs of reactions catalysed by $\mathrm{MCl}_{2}$ (PMA).

Table 3.6 Calculation of cooperativity indices for $\mathrm{PdMCl}_{4}(\mathrm{dmapm})$ catalysts.

|  | $\left.\mathbf{P d}_{\mathbf{2}} \mathbf{C l}_{\mathbf{4}} \mathbf{( d m a p m}\right)$ | $\left.\mathbf{P t P d C l}_{\mathbf{4}} \mathbf{( d m a p m}\right)$ |
| :--- | :---: | :---: |
| $A_{O}$ | 0.510 | 0.247 |
| $A_{P}$ | 0.322 | 0.161 |
| $\bar{A}=A_{P} / 2$ | 0.161 | 0.081 |
| $a=\left(A_{O}-A_{P}\right) / \bar{A}$ | 1.17 | 1.06 |

The $a$ indices imply that each of the bimetallic catalysts acts as if it possessed an additional metal centre of average catalytic activity.

As a comparison, the $a$ values for Stanley's bimetallic Rh hydroformylation catalysts $\left[\mathrm{Rh}_{2}(\mathrm{nbd})_{2}(\mathrm{rac}\right.$-et, $\left.\mathrm{ph}-\mathrm{P} 4)\right]\left[\mathrm{BF}_{4}\right]_{2}$ and $\left[\mathrm{Rh}_{2}(\mathrm{nbd})_{2}(\right.$ meso-et, $\left.\mathrm{ph}-\mathrm{P} 4)\right]\left[\mathrm{BF}_{4}\right]_{2}$ are 422 and 34 , respectively (see Chart 3.14, p. 140). ${ }^{29}$

It should be noted that the index $a$ is based solely on kinetic data at a single catalyst concentration (i.e., it assumes that the reaction is first-order in catalyst) and may lead to the conclusion that a cooperative mechanism is at work whereas studies of the rate dependence on catalyst loading may prove otherwise. Notwithstanding the fact that the Heck reaction studied here may be catalysed mainly by a simple derivative of $\mathrm{PdCl}_{2}$ and not by a bimetallic assembly, I feel that the $a$ index outlined above will be of general utility.

### 3.7 Conclusions

The dmapm ligand gives access to a wide variety of platinum metal complexes because of its ability both to bridge $\left(P, P^{\prime}\right)$ and chelate ( $P, P^{\prime}$ and $P, N$ ). In monometallic $\mathrm{Pd}^{\mathrm{II}}$ complexes, the ligand is in equilibrium between its $P, P^{\prime}$ - and $P, N$-chelated forms, the exchange mechanism probably involving 5-coordinate intermediates of the $P, P^{\prime}, N$ - and $P, N, N^{\prime}$ - variety. The ligand binds to $\mathrm{Pd}^{11}$ via P predominantly through $\sigma$-donation. The higher affinity of $\mathrm{Pt}^{\text {II }}$ than $\mathrm{Pd}^{\text {II }}$ for P is illustrated by the fact that in monometallic halo complexes of $\mathrm{Pt}^{\mathrm{II}}$, only the $P, P^{\prime}$-chelated ligand is observed; this necessitates the surmounting of an approximately $32 \mathrm{~kJ} \mathrm{~mol}^{-1} 4$-membered ring strain.

Homo- and heterobimetallic complexes supported by dmapm can be synthesised, where the ligand adopts a $P, P^{\prime}$-bridging, $P, N$-chelate coordination mode. In the $I I, I I$ complexes $\mathrm{MM}^{\prime} \mathrm{Cl}_{4}(\mathrm{dmapm})\left(\mathrm{M}=\mathrm{Pd} ; \mathrm{M}^{\prime}=\mathrm{Pt}, \mathrm{Pd}\right)$, the bound and free N -atoms are in chemical exchange, whereas in the I,I species $\mathrm{MM}^{\prime} \mathrm{Cl}_{2}$ (dmapm), which can be accessed either through conproportionation of $\mathrm{M}^{0}$ and $\mathrm{M}^{\text {II }}$ or via reduction of the appropriate II,II compound, there is no exchange.

The $\mathrm{MM}^{\prime} \mathrm{Cl}_{2}$ (dmapm) complexes, having a very different structure from most other diphosphine-bridged $\mathrm{M}^{\mathrm{I}}$ complexes, show unique reactivity with EtSH and $\mathrm{CS}_{2}$ (see Section 3.8.3, p. 141). The possibility for the formation of doubly-bridged adducts with small molecules via displacement of the anilinyl "arms" exists. Fluxional compounds can also result, and the high affinity of Pt for P can lead to disproportionation in the case of the mixed-metal complexes.

The homo- and heterobimetallic II,II compounds serve as useful catalytic precursors for the Heck reaction in aqueous media. These compounds do not survive intact under catalytic conditions but are degraded both by phosphine oxidation and by fragmentation. The latter process generates $\mathrm{PdCl}_{2}$, a simple derivative of which likely being the predominantly active species in the catalysis.

A generally applicable index of cooperativity is proposed. This corresponds to the number of virtual centres of average activity a complex appears to have beyond its real number.

### 3.8 Recommendations for Future Work

### 3.8.1 More accurate determination of ring strain energy

The 4-membered dmapm ring strain energy has been calculated based on the relative bond strengths of $\mathrm{Pd}-\mathrm{PPh}_{3}$ and $\mathrm{Pd}-$ py which serves as the approximate energy difference between the $\mathrm{Pd}-\mathrm{P}$ and $\mathrm{Pd}-\mathrm{N}$ bonds in $\mathrm{PdCl}_{2}$ (dmapm) (Section 3.3.2). A better value for this difference may be determined from the $\operatorname{PdCl}(\mathrm{Me})(P, P-$ $\mathrm{dmape}) \rightleftharpoons \mathrm{PdCl}(\mathrm{Me})(P, N$-dmape $)$ equilibrium. The difference in enthalpy between this and the analogous equilibrium involving $\mathrm{PdCl}_{2}$ (dmapm) should give a reasonably
accurate value for the 4-membered ring strain energy, with the caveat that non-identical ligand sets are being compared.

### 3.8.2 Assessment of cooperative effects in other types of homogeneous catalysis

### 3.8.2.1 Hydroformylation

Stanley and coworkers have demonstrated cooperative effects in dirhodium catalysed hydroformylations. Their highly active, regioselective catalysts are based on the electronrich tetraphosphine ligand rac-et,ph-P4 (Chart 3.14, left) which forms complexes of the type $\left[\mathrm{Rh}_{2}(\mathrm{nbd})_{2}(\mathrm{rac}\right.$-et,ph-P4)$]\left[\mathrm{BF}_{4}\right]_{2}$ (Chart 3.14, right).

## Chart 3.14




Given that $\mathrm{P}, \mathrm{N}$-chelate ligands have been shown to enhance the rate of hydroformylation of styrene, ${ }^{106}$ it would be of interest to compare the rate and regioselectivity of Stanley's catalyst to those of $\left[\mathrm{Rh}_{2}(\mathrm{nbd})_{2}(\mathrm{dmapm})\right]\left[\mathrm{BF}_{4}\right]_{2}$ which should be accessible.

### 3.8.2.2 Imine/CO copolymerisation

The catalytic copolymerisation of imines and CO to form polypeptides is an attractive goal. Imine insertion into Pd-acyl bonds has been observed ${ }^{107-110}$ but, unlike in ethylene/CO copolymerisations, ${ }^{111}$ subsequent coordination and insertion of CO to continue chain growth are hampered by the resulting formation of a stable 5 -membered palladacycle (Chart 3.15 , left). ${ }^{107}$ If the amide carbonyl could be tethered to a sacrificial metal centre in a bimetallic complex, for example in one supported by dmapm (Chart 3.15, right; $\mathrm{Ar}=o-\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{NMe}_{2}, \mathrm{X}=$ halide), CO coordination would then be possible at the other centre and chain propagation could proceed. Cationic organometallic
derivatives of dipalladium dmapm complexes warrant investigation for such an application.

## Chart 3.15




### 3.8.3 Exploration of the reactivity of $\mathbf{M M}^{\prime} \mathbf{X}_{\mathbf{2}}$ (dmapm) complexes

For the geometrical reasons outlined in Section 3.4.5.3, $\mathrm{MM}^{\prime} \mathrm{Cl}_{2}$ (dmapm) complexes are fundamentally different from the "typical" bimetallic diphosphine-bridged $\mathrm{M}^{1}$ complexes $\mathrm{M}_{2} \mathrm{Cl}_{2}(\mathrm{P}-\mathrm{P})_{2}$. During the course of this work, preliminary investigations into the reactivity of these complexes with small molecules like $\mathrm{H}_{2} \mathrm{~S}$, EtSH, and $\mathrm{CS}_{2}$ were conducted, and some in situ characterisation data are summarised in Table 3.7. None of the products of these reactions has been isolated.

Table 3.7 $\quad{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}, 300 \mathrm{~K}\right)$ data for the in situ reactions between small molecules and $\mathrm{MM}^{\prime} \mathrm{Cl}_{2}$ (dmapm). ${ }^{\text {a }}$

| Molecule | MM' | Spectral data |
| :---: | :--- | :--- |
| $\mathrm{H}_{2} \mathrm{~S}$ | PtPd | $\delta 21.2(\mathrm{~d}), 46.8(\mathrm{~d}),{ }^{2} J_{\mathrm{PP}}=47.5 \mathrm{~Hz}$ |
| $\mathrm{H}_{2} \mathrm{~S}$ | PdPd | $\delta 47.4(\mathrm{~s})$ and broad, ill defined peaks between $\delta 25-35$ |
| EtSH | PdPd | $\delta 48.4(\mathrm{~s})$ |
| $\mathrm{CS}_{2}{ }^{\mathrm{b}}$ | PdPd | $\delta 9.9\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=70.1 \mathrm{~Hz}\right), 16.4\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=55.7 \mathrm{~Hz}\right)$, |
|  |  | $19.0\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=65.7 \mathrm{~Hz}\right), 20.7(\mathrm{~s}), 26.9\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=63.9 \mathrm{~Hz}\right)$, |
|  | $33.8\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=57.6 \mathrm{~Hz}\right), 40.3\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=61.4 \mathrm{~Hz}\right)$, |  |
|  | $41.1\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=55.5 \mathrm{~Hz}\right)$ |  |
|  |  |  |
| ${ }^{\text {a }}$ Spectra recorded at 121 MHz unless otherwise indicated. |  |  |
| ${ }^{\mathrm{b}}$ Recorded at 162 MHz. |  |  |

In the reactions with $\mathrm{H}_{2} \mathrm{~S}, \mathrm{H}_{2}$ was identified as a product in the ${ }^{1} \mathrm{H}$ NMR spectra ( $\delta$ 4.6). Moreover, significant effervescence occurred on introduction of $\mathrm{H}_{2} \mathrm{~S}$ to $\mathrm{CDCl}_{3}$ solutions containing $\mathrm{MM}^{\prime} \mathrm{Cl}_{2}(\mathrm{dmapm})$. This suggests that, like $\mathrm{M}_{2} \mathrm{X}_{2}(\mathrm{P}-\mathrm{P})_{2},{ }^{80}$ $\mathrm{MM}^{\prime} \mathrm{Cl}_{2}$ (dmapm) mediates the conversion of $\mathrm{H}_{2} \mathrm{~S}$ to $\mathrm{H}_{2}$ and ' S ,' with the metal complex product probably being a bridged sulphide species like $\mathrm{MM}^{\prime} \mathrm{Cl}_{2}(\mu-\mathrm{S})(\mathrm{dmapm})$ or $\mathrm{MM}^{\prime} \mathrm{Cl}_{2}(\mu-\mathrm{S})_{2}$ (dmapm). In the $\mathrm{H}_{2} \mathrm{~S}$ reaction with $\mathrm{Pd}_{2} \mathrm{Cl}_{2}$ (dmapm), the broad $\delta 25-35$ region is not resolved at 220 K , perhaps indicating fluxionality involving the anilinyl "arms" of the complex. Peaks in the ${ }^{1} \mathrm{H}$ NMR spectra both at 220 and 300 K are broad and uninformative.

In the ${ }^{1} \mathrm{H}$ NMR spectrum of the in situ reaction with EtSH, no hydride was detected to $\delta-4$. The $\mathrm{CH}_{2}$ protons in the ligand backbone gave a triplet at $\delta 4.75$ and the NMe protons appeared to be equivalent, giving rise to a broad singlet at $\delta 2.9$. These data are consistent with a $C_{2}$-symmetrical product resulting from substitution of the bound N atoms of $\mathrm{Pd}_{2} \mathrm{Cl}_{2}$ (dmapm) by EtSH. Alternatively, the similarity in the spectra of this and that of the reaction with $\mathrm{H}_{2} \mathrm{~S}$ is consistent with a bridging-sulphide or -thiolate species. It should be noted that $\mathrm{M}_{2} \mathrm{X}_{2}(\mathrm{P}-\mathrm{P})_{2}$ species do not react with EtSH. ${ }^{112}$

The reaction of $\mathrm{CS}_{2}$ with $\mathrm{Pd}_{2} \mathrm{Cl}_{2}(\mathrm{dmapm})$ gives a range of products which remain unidentified. This finding is in contrast to that of the analogous reaction with $\mathrm{Pd}_{2} \mathrm{Cl}_{2}(\mathrm{dmpm})_{2}$ which yields $\mathrm{PdCl}_{2}\left(\mu-\mathrm{CS}_{2}\right)(\mathrm{dmpm})_{2} .{ }^{79}$ Clearly, further work is necessary to elucidate the nature of the products of the reactions outlined in Table 3.7, and to rationalise the results in terms of the structural features of the $\mathrm{MM}^{\prime} \mathrm{Cl}_{2}(\mathrm{dmapm})$ complexes.

### 3.9 Experimental

### 3.9.1 $\operatorname{PdCl}_{2}\left(P, P P^{\prime}\right.$-dmapm $)$ and $\mathrm{PdCl}_{2}(P, N$-dmapm $)$.

To a combination of trans $-\mathrm{PdCl}_{2}\left(\mathrm{PhCN}_{2}\right)_{2}(31 \mathrm{mg}, 0.081 \mathrm{mmol})$ and dmapm ( 48 mg , 0.086 mmol ) was added $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$. The initially orange solution turned yellow within a few seconds. After the solution was stirred for 5 min , the volume was reduced in
vacuo to ca. 1 mL and $\mathrm{Et}_{2} \mathrm{O}(20 \mathrm{~mL})$ was added to give a yellow powder. This was isolated by filtration, washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 3 \mathrm{~mL})$ and dried under vacuum. Yield: 54 mg ( 92 \%). Anal. Calcd for $\mathrm{C}_{33} \mathrm{H}_{42} \mathrm{~N}_{4} \mathrm{Cl}_{2} \mathrm{P}_{2} \mathrm{Pd}$ : C, 54.0; H, 5.8; N, 7.6. Found: C, 53.8; H, 5.9; N, 7.4. UV-vis $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right): 360$ [3870]. $\mathbf{P d C l}_{2}$ ( $\boldsymbol{P}, \boldsymbol{P}{ }^{\prime}$-dmapm): ${ }^{1} \mathrm{H}$ NMR ( 300 MHz , $\left.\mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta 2.35\left(\mathrm{~s}, 24 \mathrm{H}, \mathrm{NCH}_{3}\right), 5.31\left(\mathrm{t}, 2 \mathrm{H}, \mathrm{CH}_{2},{ }^{2} J_{\mathrm{HP}}=12.1\right)$. The aromatic proton resonances of this and $\mathrm{PdCl}_{2}(P, N-\mathrm{dmapm})$ overlap ( $\delta 6.4-8.2$ ) and could not be resolved. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta-56.8$ (s). $\mathbf{P d C l}_{\mathbf{2}}$ ( $\boldsymbol{P}, \boldsymbol{N}$-dmapm): ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 215 \mathrm{~K}$ ): $\delta 1.61\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.43\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.87(\mathrm{pt}, 1 \mathrm{H}$, $\mathrm{CH}_{2}$ ), $2.91\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.97\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{NCH}_{3}\right), 3.46\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right), 3.79\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right)$, 4.01 (pt, 1H, CH2). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \operatorname{NMR}\left(121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 215 \mathrm{~K}\right): \delta-39.8\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{PP}}=88.9\right.$ ), 35.4 (d, ${ }^{2} J_{\mathrm{PP}}=88.9$ ). Crystals of $\mathrm{PdCl}_{2}(P, N$-dmapm) suitable for analysis by X-ray diffraction were grown by slow evaporation of a $\mathrm{CDCl}_{3}$ solution.

### 3.9.2 $\operatorname{PdBr}_{2}\left(P, P P^{\prime}\right.$-dmapm $)$ and $\operatorname{PdBr}_{2}(P, N$-dmapm $)$.

To a combination of $\mathrm{PdCl}_{2}$ (dmapm) ( $77 \mathrm{mg}, 0.10 \mathrm{mmol}$ ) and $\mathrm{NaBr}(170 \mathrm{mg}, 1.7 \mathrm{mmol})$ was added acetone ( 10 mL ) and $\mathrm{H}_{2} \mathrm{O}(2 \mathrm{~mL})$. The yellow slurry was stirred for 2 h before reduction to dryness at the pump. The residue was taken up in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$ and filtered through Celite 545. The volume of the filtrate was reduced in vacuo to ca. 1 mL and $E t_{2} \mathrm{O}(20 \mathrm{~mL})$ was added to give a yellow powder which was isolated by filtration, washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 3 \mathrm{~mL})$ and dried under vacuum. Yield: $55 \mathrm{mg}(64 \%)$. Anal. Calcd for $\mathrm{C}_{33} \mathrm{H}_{42} \mathrm{~N}_{4} \mathrm{Br}_{2} \mathrm{P}_{2} \mathrm{Pd}$ : C, 48.2; H, 5.1; N, 6.8. Found: C, 48.1; H, 5.1; N, 6.6. UV-vis $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right): 378$ [4310]. $\mathbf{P d B r}_{2}$ ( $\boldsymbol{P}, \boldsymbol{P}{ }^{\prime}$-dmapm): ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 250 \mathrm{~K}$ ): $\delta 2.30$ (br s, $24 \mathrm{H}, \mathrm{NCH}_{3}$ ), $5.41\left(\mathrm{t}, 2 \mathrm{H}, \mathrm{CH}_{2},{ }^{2} J_{\mathrm{HP}}=12.0\right.$ ). The aromatic proton resonances of the two isomers overlap ( $\delta 6.3-7.9$ ) and could not be resolved. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 162 MHz , $\mathrm{CDCl}_{3}, 250 \mathrm{~K}$ ) : $\delta$-58.5 (s). $\mathbf{P d B r}_{2}$ ( $\boldsymbol{P}, \mathbf{N}$-dmapm): ${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 250 \mathrm{~K}\right.$ ): $\delta 1.61\left(\mathrm{br} \mathrm{s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.45\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.92\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{NCH}_{3}\right), 3.01\left(\mathrm{pt}, 1 \mathrm{H}, \mathrm{CH}_{2}\right)$, $3.51\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right), 3.82\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right), 3.97\left(\mathrm{pt}, 1 \mathrm{H}, \mathrm{CH}_{2}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 162 MHz , $\left.\mathrm{CDCl}_{3}, 250 \mathrm{~K}\right): \delta-40.4\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=112\right), 33.3\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=112\right)$.

### 3.9.3 $\operatorname{PdI}_{2}(P, P$-dmapm $)$ and $\operatorname{PdI}_{2}(P, N$-dmapm $)$.

To a combination of $\mathrm{PdCl}_{2}(\mathrm{PhCN})_{2}(91 \mathrm{mg}, 0.24 \mathrm{mmol})$, dmapm ( $130 \mathrm{mg}, 0.23 \mathrm{mmol}$ ) and $\mathrm{NaI}(190 \mathrm{mg}, 1.3 \mathrm{mmol})$ was added $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ followed after 5 min by acetone $(10 \mathrm{~mL})$ which caused an almost immediate colour change from yellow to deep orange. The slurry was stirred for 2 h at r.t. before reduction to dryness in vacuo. The work-up was the same as that for $\mathrm{PdBr}_{2}$ (dmapm). Yield: $180 \mathrm{mg}(83 \%)$. Anal. Calcd for $\mathrm{C}_{33} \mathrm{H}_{42} \mathrm{~N}_{4} \mathrm{I}_{2} \mathrm{P}_{2} \mathrm{Pd}$ : C, $43.2 ; \mathrm{H}, 4.6 ; \mathrm{N}, 6.1$. Found: C, $43.4 ; \mathrm{H}, 4.7 ; \mathrm{N}, 6.0$. UV-vis $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$ : 304 [16100], 430 [4010]. $\mathbf{P d I}_{2}\left(\boldsymbol{P}, \boldsymbol{P}{ }^{\prime}\right.$-dmapm): ${ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 250 \mathrm{~K}\right): \delta$ 2.26 (br s, $24 \mathrm{H}, \mathrm{NCH}_{3}$ ), $5.58\left(\mathrm{t}, 2 \mathrm{H}, \mathrm{CH}_{2},{ }^{2} J_{\mathrm{HP}}=12.4\right.$ ). The aromatic proton resonances of the two isomers overlap ( $\delta 6.3-8.0$ ) and could not be resolved. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}(121 \mathrm{MHz}$, $\mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta-65.6$ (s). $\mathbf{P d I}_{\mathbf{2}}$ (P,N-dmapm): ${ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 250 \mathrm{~K}\right): \delta$ $1.55\left(\mathrm{br} \mathrm{s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.46\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.80\left(\mathrm{br} \mathrm{s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.88\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{NCH}_{3}\right)$, 3.22 (pt, $1 \mathrm{H}, \mathrm{CH}_{2}$ ), 3.55 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{NCH}_{3}$ ), 3.84 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{NCH}_{3}$ ), 3.93 (pt, $1 \mathrm{H}, \mathrm{CH}_{2}$ ). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta-40.8\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=98\right), 27.3\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=98\right)$.

### 3.9.4 $\operatorname{Pd}(C N)_{2}(P, N$-dmapm $)$.

To a yellow slurry of $\mathrm{PdCl}_{2}$ (dmapm) $(46 \mathrm{mg}, 0.063 \mathrm{mmol})$ and $\mathrm{KCN}(8.3 \mathrm{mg}$, $0.013 \mathrm{mmol})$ in $\mathrm{EtOH}(5 \mathrm{~mL})$ was added $\mathrm{H}_{2} \mathrm{O}(2 \mathrm{~mL})$ whereupon a colourless solution formed. The solvent was removed in vacuo after 10 min and the residue was taken up in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$. This was filtered through a mixture of Celite 545 and $\mathrm{MgSO}_{4}$ and reduced to $c a .1 \mathrm{~mL}$. Addition of $\mathrm{Et}_{2} \mathrm{O}(10 \mathrm{~mL})$ gave the product as a white powder that was isolated by filtration, washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 3 \mathrm{~mL})$ and dried under vacuum. Yield: 24 mg ( $54 \%$ ). Anal. Calcd for $\mathrm{C}_{35} \mathrm{H}_{42} \mathrm{~N}_{6} \mathrm{P}_{2} \mathrm{Pd}$ : C, 58.8; H, 5.9; N, 11.8. Found: C, 58.9; $\mathrm{H}, 6.0$; $\mathrm{N}, 11.5 .{ }^{\mathrm{I}} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 233 \mathrm{~K}$ ): $\delta 1.57\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.33(\mathrm{~s}, 6 \mathrm{H}$, $\mathrm{NCH}_{3}$ ), $2.74\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.96\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{NCH}_{3}\right), 3.11\left(\mathrm{pt}, 1 \mathrm{H}, \mathrm{CH}_{2}\right), 3.41\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right)$, $3.61\left(\mathrm{pt}, 1 \mathrm{H}, \mathrm{CH}_{2}\right), 3.77\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right), 6.39(\mathrm{pt}, 1 \mathrm{H}, \mathrm{Ar}), 6.66(\mathrm{~m}, 2 \mathrm{H}, \mathrm{Ar}), 6.96(\mathrm{~m}, 3 \mathrm{H}$, Ar), $7.15(\mathrm{pt}, 1 \mathrm{H}, \mathrm{Ar}), 7.22(\mathrm{pt}, 1 \mathrm{H}, \mathrm{Ar}), 6.39(\mathrm{pt}, 1 \mathrm{H}, \mathrm{Ar}), 7.32(\mathrm{~m}, 5 \mathrm{H}, \mathrm{Ar}), 7.48(\mathrm{~m}, 2 \mathrm{H}$, Ar), 7.72 (pt, 1H, Ar). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \operatorname{NMR}\left(121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 233 \mathrm{~K}\right): \delta 21.1\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=130\right)$, $41.6\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{PP}}=130\right)$.

### 3.9.5 $\quad \mathbf{P d C l}(\mathrm{Me})(\boldsymbol{P}, N$-dmapm).

This compound was made in the same manner as for $\mathrm{PdCl}_{2}$ (dmapm). Thus, reaction of $\mathrm{PdCl}(\mathrm{Me})(\mathrm{cod})(60 \mathrm{mg}, 0.23 \mathrm{mmol})$ and dmapm ( $130 \mathrm{mg}, 0.23 \mathrm{mmol}$ ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$ gave $86 \mathrm{mg}(53 \%)$ of a yellow powder. ${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta 0.19(\mathrm{~d}$, $\left.3 \mathrm{H}, \mathrm{Pd}-\mathrm{CH}_{3},{ }^{3} J_{\mathrm{HP}}=2.84\right), 2.16\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.41\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.41\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{NCH}_{3}\right)$, $2.78\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.85\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{CH}_{2}\right), c a .3 .1\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{CH}_{2}\right.$, obscured), $3.14(\mathrm{~s}, 3 \mathrm{H}$, $\left.\mathrm{NCH}_{3}\right), 3.31\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right), 6.6-7.6(\mathrm{~m}, 14 \mathrm{H}, \mathrm{Ar}), 7.80(\mathrm{~m}, 2 \mathrm{H}, \mathrm{Ar}) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 24.0\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=130\right),-39.3\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=130\right)$.

### 3.9.6 $\quad \mathbf{P d C l}_{2}(P, N$-dmapmO $)$.

This complex could be prepared either in a single phase using cumene hydroperoxide as oxidant, or in a two-phase mixture using $\mathrm{H}_{2} \mathrm{O}_{2}$.
(a) Cumene hydroperoxide. The precursor $\mathrm{PdCl}_{2}$ (dmapm) was prepared in situ by the reaction of dmapm $(140 \mathrm{mg}, 0.25 \mathrm{mmol})$ and trans $-\mathrm{PdCl}_{2}(\mathrm{PhCN})_{2}$ ( 94 mg , 0.25 mmol ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$, and to the yellow solution was added cumene hydroperoxide ( $75 \mu \mathrm{~L}, 0.41 \mathrm{mmol}$ ). The solution was stirred over night and then reduced in vacuo to ca. 2 mL , whereupon $\mathrm{Et}_{2} \mathrm{O}(20 \mathrm{~mL})$ was added to give the product as a yellow precipitate. This was isolated by filtration, washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 3 \mathrm{~mL})$ and dried under vacuum. Yield: 155 mg ( $84 \%$ ).
(b) $\mathrm{H}_{2} \mathrm{O}_{2}$. To a $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution ( 5 mL ) containing $\mathrm{PdCl}_{2}$ (dmapm) $(28 \mathrm{mg}$, $0.038 \mathrm{mmol})$ was added a $3 \% \mathrm{H}_{2} \mathrm{O}_{2}(2 \mathrm{~mL})$ solution. The two-phase mixture was stirred for 1 h and the aqueous phase was removed. The volume of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ was reduced in vacuo to $c a .1 \mathrm{~mL}$, and $\mathrm{Et}_{2} \mathrm{O}(10 \mathrm{~mL})$ was added to give the product as a yellow precipitate. Yield: 25 mg ( $88 \%$ ).

Anal. Calcd for $\mathrm{C}_{33} \mathrm{H}_{42} \mathrm{~N}_{4} \mathrm{Cl}_{2} \mathrm{OP}_{2} \mathrm{Pd}$ : C, $52.9 ; \mathrm{H}, 5.6 ; \mathrm{N}, 7.5$. Found: C, $53.0 ; \mathrm{H}$, 6.0; N, 7.0. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 1.7-3.3\left(\mathrm{br}, 12 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.35(\mathrm{~s}, \mathrm{H}$, $\mathrm{NCH}_{3}$ ), $2.51\left(\mathrm{~s}, \mathrm{H}, \mathrm{NCH}_{3}\right), 3.47\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right), 3.70\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right), 4.27\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{CH}_{2}\right)$, $4.81(\mathrm{~m}, 1 \mathrm{H}, \mathrm{CH} 2), 6.8-7.9$ (br m, 16H, Ar). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta$ $26.2\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=7.0\right), 26.5\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=7.0\right) . v_{\mathrm{PO}}: 1185(\mathrm{~m}) . \Lambda_{\mathrm{M}}\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}, 298 \mathrm{~K}\right):<1$.

### 3.9.7 $[\mathrm{PdCl}(P, N, S$-dmapmS $)]\left[\mathrm{PF}_{6}\right]$.

To a mixture of $\mathrm{PdCl}_{2}$ (dmapm) ( $44 \mathrm{mg}, 0.060 \mathrm{mmol}$ ) and $\mathrm{S}_{8}(13 \mathrm{mg}, 0.42 \mathrm{mmol})$ was added $\mathrm{CH}_{2} \mathrm{ClCH}_{2} \mathrm{Cl}(5 \mathrm{~mL})$ and the resulting yellow solution heated to reflux for 3.5 h . The solvent was removed in vacuo and the residue dissolved in warm $\mathrm{H}_{2} \mathrm{O}(20 \mathrm{~mL})$. After filtration through Celite 545 to remove the excess $\mathrm{S}_{8}$ and unreacted $\mathrm{PdCl}_{2}$ (dmapm), an aqueous solution ( 5 mL ) containing $\mathrm{KPF}_{6}(90 \mathrm{mg}, 0.49 \mathrm{mmol})$ was added. This immediately gave a yellow-orange precipitate that was isolated by filtration and washed with $\mathrm{H}_{2} \mathrm{O}(10 \mathrm{~mL})$. Yield: $30 \mathrm{mg}(56 \%)$. Anal. Calcd for $\mathrm{C}_{33} \mathrm{H}_{42} \mathrm{~N}_{4} \mathrm{ClF}_{6} \mathrm{P}_{3} \mathrm{PdS}: \mathrm{C}, 45.3$; H, 4.8; N, 6.4. Found: C, 45.2; H, 5.0; N, 6.2. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 2.15$ (s, $\mathrm{H}, \mathrm{NCH}_{3}$ ), $2.86\left(\mathrm{~s}, \mathrm{H}, \mathrm{NCH}_{3}\right), 4.50\left(\mathrm{br} \mathrm{m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 7.30(\mathrm{~m}, 4 \mathrm{H}, \mathrm{Ar}), 7.46(\mathrm{~m}, 4 \mathrm{H}$, Ar), $7.57(\mathrm{~m}, 4 \mathrm{H}, \mathrm{Ar}), 7.87(\mathrm{~m}, 2 \mathrm{H}, \mathrm{Ar}), 8.50\left(\mathrm{dd}, 2 \mathrm{H}, \mathrm{Ar},{ }^{2} J_{\mathrm{HH}}=7.39,{ }^{4} J_{\mathrm{HP}}=15.3\right)$. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta 37.0\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=33.6\right), 48.6\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=33.6\right),-$ $144\left(\mathrm{spt},{ }^{1} J_{\mathrm{PF}}=710, \mathrm{PF}_{6}{ }^{-}\right.$).

### 3.9.8 $\quad[\mathrm{PdCl}(P, N, S$-dmapmS $)] \mathrm{Cl}$.

This compound was made in the same manner as for $[\mathrm{PdCl}(P, N, S$-dmapmS $)]\left[\mathrm{PF}_{6}\right]$ except that after the reaction of $\mathrm{PdCl}_{2}$ (dmapm) ( $130 \mathrm{mg}, 0.18 \mathrm{mmol}$ ) and $\mathrm{S}_{8}(45 \mathrm{mg}, 1.4 \mathrm{mmol})$, the orange solution was allowed to cool to r.t. and was then filtered through Celite 545. The volume of the yellow filtrate was reduced in vacuo to $c a .1 \mathrm{~mL}$ and $\mathrm{Et}_{2} \mathrm{O}(20 \mathrm{~mL})$ was added to give the product as a beige precipitate. Yield: $100 \mathrm{mg}(71 \%)$. The NMR spectroscopic data for this complex are the same as for $[\mathrm{PdCl}(P, N, S$-dmapmS $)]\left[\mathrm{PF}_{6}\right]$ except for the absence of peaks due to $\mathrm{PF}_{6}^{-} \cdot \Lambda_{\mathrm{M}}\left(\mathrm{H}_{2} \mathrm{O}, 298 \mathrm{~K}\right): 99$.

### 3.9.9 $\quad \mathrm{PtCl}_{2}\left(\boldsymbol{P}, P^{\prime}{ }^{\prime}\right.$-dmapm $)$.

The synthesis of this compound was identical in principle to that of $\mathrm{PdCl}_{2}(\mathrm{dmapm})$. Thus, $\mathrm{PtCl}_{2}(\mathrm{cod})(58 \mathrm{mg}, 0.15 \mathrm{mmol})$ and dmapm ( $86 \mathrm{mg}, 0.16 \mathrm{mmol}$ ) gave $83 \mathrm{mg}(66 \%)$ of an off-white powder. Anal. Calcd for $\mathrm{C}_{33} \mathrm{H}_{42} \mathrm{~N}_{4} \mathrm{Cl}_{2} \mathrm{P}_{2} \mathrm{Pt}$ : C, $48.2 ; \mathrm{H}, 5.2 ; \mathrm{N}, 6.8$. Found: C, 48.5; H, 5.4; N, 6.7. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 2.24\left(\mathrm{~s}, 24 \mathrm{H}, \mathrm{NCH}_{3}\right), 5.77(\mathrm{t}$, $2 \mathrm{H}, \mathrm{CH}_{2},{ }^{2} J_{\mathrm{HP}}=12.9,{ }^{3} J_{\mathrm{HPt}}=60$ ), 7.17 (pt, $\left.4 \mathrm{H}, \mathrm{Ar}\right), 7.25(\mathrm{pd}, 4 \mathrm{H}, \mathrm{Ar}), 7.44(\mathrm{pt}, 4 \mathrm{H}, \mathrm{Ar})$, 7.17 (br m, 4H, Ar). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta-65.6\left(\mathrm{~s},{ }^{1} \mathrm{~J}_{\mathrm{PPt}}=3084\right)$.

### 3.9.10 $\operatorname{Pt}(\mathrm{CN})_{2}(P, P \prime-d m a p m)$ and $\operatorname{Pt}(\mathbf{C N})_{2}(P, N$-dmapm $)$.

To a slurry of $\mathrm{PtCl}_{2}\left(P, P^{\prime}-\mathrm{dmapm}\right)(190 \mathrm{mg}, 0.23 \mathrm{mmol})$ in $\mathrm{EtOH}(10 \mathrm{~mL})$ was added solid $\mathrm{KCN}(30 \mathrm{mg}, 0.47 \mathrm{mmol})$ followed by $\mathrm{H}_{2} \mathrm{O}(2 \mathrm{~mL})$. The mixture was warmed to $50^{\circ} \mathrm{C}$ for 0.5 h before all the solvent was removed at the pump. The work-up was identical to that for $\operatorname{Pd}(\mathrm{CN})_{2}(P, N$-dmapm $)$. Yield: $140 \mathrm{mg}(74 \%)$. Anal. Calcd for $\mathrm{C}_{35} \mathrm{H}_{42} \mathrm{~N}_{6} \mathrm{P}_{2} \mathrm{Pt}: \mathrm{C}, 52.3 ; \mathrm{H}, 5.3 ; \mathrm{N}, 10.5$. Found: C, $51.5 ; \mathrm{H}, 5.3 ; \mathrm{N}, 10.0 . \operatorname{Pt}(\mathbf{C N})_{2}\left(\boldsymbol{P}, \boldsymbol{P}^{\prime}-\right.$ dmapm): ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 2.34$ (s, $24 \mathrm{H}, \mathrm{NCH}_{3}$ ), $5.46\left(\mathrm{t}, 2 \mathrm{H}, \mathrm{CH}_{2}\right.$, ${ }^{2} J_{\mathrm{HP}}=12.3,{ }^{3} J_{\mathrm{HPt}}=38.3$ ). The aromatic proton resonances of the two isomers overlap ( $\delta$ 6.5-7.9) and could not be resolved. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right.$ ): $\delta-60.7$ (s, $\left.{ }^{1} J_{\mathrm{PPt}}=2230\right) . \mathbf{P t}(\mathbf{C N})_{\mathbf{2}}\left(\boldsymbol{P}, \mathbf{N}\right.$-dmapm) : ${ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta 2.38(\mathrm{~s}, 6 \mathrm{H}$, $\mathrm{NCH}_{3}$ ), $2.88\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{NCH}_{3}\right), 3.19\left(\mathrm{pt}, 1 \mathrm{H}, \mathrm{CH}_{2}\right), 3.59\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{NCH}_{3}\right.$ and $\mathrm{CH}_{2}$ (obscured), $\left.{ }^{3} J_{\mathrm{HPt}}=22.5\right), 3.84\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3},{ }^{3} J_{\mathrm{HPt}}=22.5\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right):$ $\delta-41.5\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=125\right), 11.6\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=125,{ }^{1} J_{\mathrm{PPt}}=2760\right)$.

### 3.9.11 $\mathbf{P d}_{2} \mathbf{C l}_{4}$ (dmapm).

This compound was made in the same fashion as $\mathrm{PdCl}_{2}$ (dmapm), but a $2: 1 \mathrm{~mol}$ ratio of Pd:dmapm was used. Thus, trans $-\mathrm{PdCl}_{2}(\mathrm{PhCN})_{2}(110 \mathrm{mg}, 0.29 \mathrm{mmol})$ and dmapm $(82 \mathrm{mg}, 0.15 \mathrm{mmol})$ gave 110 mg ( $78 \%$ ) of a yellow powder. Anal. Calcd for $\mathrm{C}_{33} \mathrm{H}_{42} \mathrm{~N}_{4} \mathrm{Cl}_{4} \mathrm{P}_{2} \mathrm{Pd}_{2}$ : C, 43.5; H, 4.7; N, 6.2. Found: C, 43.8; H, 4.6; N, 6.0. UV-vis $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right): 354$ [3050]. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 2.31\left(\mathrm{~s}, 12 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.78$ $\left(\mathrm{s}, 6 \mathrm{H}, \mathrm{NCH}_{3}\right), 3.28\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{NCH}_{3}\right), 4.97\left(\mathrm{t}, 2 \mathrm{H}, \mathrm{CH}_{2},{ }^{2} J_{\mathrm{HP}}=17.1\right), 7.40(\mathrm{br} \mathrm{m}, 6 \mathrm{H}, \mathrm{Ar})$, 7.65 (br m, 4H, Ar), 7.80 (br m, 2H, Ar), 8.52 (br m, 2H, Ar), 8.74 (br m, 2H, Ar). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 34.8$ (s).

### 3.9.12 $\mathbf{P d}_{2} \mathbf{I}_{\mathbf{4}}(\mathrm{dmapm})$.

The synthesis of this compound was the same in principle as that of $\mathrm{PdBr}_{2}$ (dmapm), except that $\mathrm{H}_{2} \mathrm{O}$ was not used. Thus, a combination of $\mathrm{Pd}_{2} \mathrm{Cl}_{4}$ (dmapm) ( 42 mg , 0.046 mmol ) and $\mathrm{NaI}(140 \mathrm{mg}, 0.95 \mathrm{mmol})$ in acetone gave $20 \mathrm{mg}(34 \%)$ of a red powder. Anal. Calcd for $\mathrm{C}_{33} \mathrm{H}_{42} \mathrm{~N}_{4} \mathrm{I}_{4} \mathrm{P}_{2} \mathrm{Pd}_{2}$ : C, 31.0; H, 3.3; N, 4.4. Found: C, 31.0; H, 3.4; $\mathrm{N}, 4.2 .{ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 300 \mathrm{~K}\right): \delta 1.83$ (br s, $6 \mathrm{H}, \mathrm{NCH}_{3}$ ), 2.37 (br s, 6 H , $\mathrm{NCH}_{3}$ ), $2.76\left(\mathrm{br} \mathrm{s}, 6 \mathrm{H}, \mathrm{NCH}_{3}\right), 3.46\left(\mathrm{br} \mathrm{s}, 6 \mathrm{H}, \mathrm{NCH}_{3}\right), 3.52\left(\mathrm{t}, 2 \mathrm{H}, \mathrm{CH}_{2},{ }^{2} J_{\mathrm{HP}}=16\right), 7.55$
(br m, 14H, Ar), 8.12 (br m, 2H, Ar). ${ }^{31} \mathrm{P}\left\{{ }^{\mathrm{l}} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 300 \mathrm{~K}$ ): $\delta 22.3$ (s).

### 3.9.13 $\mathrm{PtPdCl}_{4}$ (dmapm).

A mixture of EtOH $(10 \mathrm{~mL})$ and $\mathrm{H}_{2} \mathrm{O}(4 \mathrm{~mL})$ containing $\mathrm{K}_{2} \mathrm{PtCl}_{4}(25 \mathrm{mg}, 0.060 \mathrm{mmol})$ and $\mathrm{PdCl}_{2}$ (dmapm) $(42 \mathrm{mg}, 0.057 \mathrm{mmol})$ was heated to $70^{\circ} \mathrm{C}$ for 1.5 h during which a beige precipitate formed. The solvent was removed in vacuo and the residue was dried thoroughly before being taken up in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$. The slurry was filtered through a mixture of Celite 545 and $\mathrm{MgSO}_{4}$ and reduced to $c a .1 \mathrm{~mL}$. Addition of $\mathrm{Et}_{2} \mathrm{O}(10 \mathrm{~mL})$ gave the product as a beige powder which was collected by filtration, washed with $\mathrm{Et}_{2} \mathrm{O}$ ( $3 \times 3 \mathrm{~mL}$ ) and dried under vacuum. Yield: 39 mg ( $69 \%$ ). Anal. Calcd for $\mathrm{C}_{33} \mathrm{H}_{42} \mathrm{~N}_{4} \mathrm{Cl}_{4} \mathrm{P}_{2} \mathrm{PdPt}: \mathrm{C}, 39.6 ; \mathrm{H}, 4.2$; $\mathrm{N}, 5.6$. Found: C, 39.9; H, 4.3; N, 5.4. UV-vis $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right): 352$ [2000]. ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta 2.10\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.23$ $\left(\mathrm{s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.56\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.69\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.70\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.85(\mathrm{~s}, 3 \mathrm{H}$, $\left.\mathrm{NCH}_{3}\right), 3.30\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right), 3.44\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right), 4.74\left(\mathrm{dt}, 1 \mathrm{H}, \mathrm{CH}_{2},{ }^{2} J_{\mathrm{HH}}=19.2,{ }^{2} J_{\mathrm{HP}}=\right.$ 27.7), $5.27\left(\mathrm{dt}, 1 \mathrm{H}, \mathrm{CH}_{2},{ }^{2} J_{\mathrm{HH}}=19.2,{ }^{2} J_{\mathrm{HP}}=26.6\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(121 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.$, 300 K ): $\delta 11.8\left(\mathrm{~s},{ }^{1} J_{\mathrm{PPt}}=3980\right), 30.7(\mathrm{~s})$. Not observed were the two-bond PP coupling or the three-bond HPt coupling with either the $\mathrm{CH}_{2}$ or $\mathrm{NCH}_{3}$ protons.

### 3.9.14 $\left[\mathbf{P d}(\mu-\mathrm{Cl})\left(\boldsymbol{P}, \boldsymbol{P}^{\prime} \text {-dmapm }\right)\right]_{2}\left[\mathrm{PF}_{6}\right]_{2}$.

To a $\mathrm{CH}_{2} \mathrm{Cl}_{2}(4 \mathrm{~mL})$ solution containing $\mathrm{PdCl}_{2}$ (dmapm) $(110 \mathrm{mg}, 0.15 \mathrm{mmol})$ was added acetone ( 6 mL ) followed by $\mathrm{NH}_{4} \mathrm{PF}_{6}(220 \mathrm{mg}, 1.3 \mathrm{mmol})$. The resulting orange slurry was stirred at r.t. for 3 h and then reduced to dryness in vacuo. The residue was taken up in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and filtered through Celite 545 . The orange filtrate was reduced to $c a .1 \mathrm{~mL}$ under vacuum, and $\mathrm{EtOH}(10 \mathrm{~mL})$ was added to give the product as an orange precipitate. Addition of $\mathrm{Et}_{2} \mathrm{O}(10 \mathrm{~mL})$ gave more of the product that was isolated by filtration, washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 3 \mathrm{~mL})$ and dried in vacuo. Yield: $77 \mathrm{mg}(61 \%)$. Anal. Calcd for $\mathrm{C}_{66} \mathrm{H}_{84} \mathrm{~N}_{8} \mathrm{Cl}_{2} \mathrm{P}_{6} \mathrm{~F}_{12} \mathrm{Pd}_{2}$ : C, 47.0; H, 5.0; N, 6.6. Found: C, 47.1; H, 5.0; N, 6.6. UV-vis $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right): 360$ [14600]. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 2.56\left(\mathrm{~s}, 24 \mathrm{H}, \mathrm{NCH}_{3}\right), 4.91$ $\left(\mathrm{t}, 2 \mathrm{H}, \mathrm{CH}_{2},{ }^{2} J_{\mathrm{HP}}=12.3 \mathrm{~Hz}\right.$ ), $7.32(\mathrm{~m}, 8 \mathrm{H}, \mathrm{Ar}), 7.57(\mathrm{pt}, 4 \mathrm{H}, \mathrm{Ar}), 7.97(\mathrm{~m}, 4 \mathrm{H}, \mathrm{Ar})$.
${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta-52.0(\mathrm{~s}),-145.0\left(\mathrm{spt}, \mathrm{PF}_{6}{ }^{-},{ }^{1} J_{\mathrm{PF}}=710\right) . \Lambda_{\mathrm{M}}$ $\left(\mathrm{CH}_{3} \mathrm{NO}_{2}, 298 \mathrm{~K}\right): 213$.

### 3.9.15 $\mathrm{PdRhCl}_{3}(\mathrm{CO})$ (dmapm).

To a $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ solution containing $\mathrm{PdCl}_{2}$ (dmapm) $(230 \mathrm{mg}, 0.31 \mathrm{mmol})$ was added $\left[\mathrm{Rh}(\mu-\mathrm{Cl})(\mathrm{CO})_{2}\right]_{2}(61 \mathrm{mg}, 0.32 \mathrm{mmol})$, and this resulted in a brisk effervescence. The volume of the solution was reduced at the pump to $c a .1 \mathrm{~mL}$ and $\mathrm{Et}_{2} \mathrm{O}(10 \mathrm{~mL})$ was added to give the product as a beige precipitate. Yield: 250 mg ( $90 \%$ ). Anal. Calcd for $\mathrm{C}_{34} \mathrm{H}_{42} \mathrm{~N}_{4} \mathrm{Cl}_{3} \mathrm{OP}_{2} \mathrm{PdRh}: \mathrm{C}, 45.4 ; \mathrm{H}, 4.7 ; \mathrm{N}, 6.2$. Found: C, $45.5 ; \mathrm{H}, 4.7 ; \mathrm{N}, 6.0$. UV-vis $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right): 358$ [5520]. ${ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta 2.62\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.72$ (s, $18 \mathrm{H}, \mathrm{NCH}_{3}$ ), $3.31\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right), 4.25\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{CH}_{2}\right), 4.51\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{CH}_{2}\right), 6.93(\mathrm{~m}, 1 \mathrm{H}$, $\mathrm{Ar}), 7.09(\mathrm{~m}, 1 \mathrm{H}, \mathrm{Ar}), 7.44(\mathrm{~m}, 7 \mathrm{H}, \mathrm{Ar}), 7.65(\mathrm{~m}, 4 \mathrm{H}, \mathrm{Ar}), 7.85(\mathrm{pt}, 1 \mathrm{H}, \mathrm{Ar}), 8.08(\mathrm{~m}, 1 \mathrm{H}$, Ar), $8.68(\mathrm{pt}, 1 \mathrm{H}, \mathrm{Ar}) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta 28.1(\mathrm{~s}), 41.7\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{PRh}}\right.$ $=179) . \Lambda_{\mathrm{M}}(298 \mathrm{~K}): 363\left(\mathrm{H}_{2} \mathrm{O}\right), 12\left(\mathrm{CH}_{3} \mathrm{NO}_{2}\right) . v_{\mathrm{CO}}: 1975[\mathrm{~s}]$.

### 3.9.16 $\mathbf{R h}_{2} \mathbf{C l}_{2}(\mathbf{C O})_{2}$ (dmapm).

To a combination of $\left[\mathrm{Rh}(\mathrm{CO})_{2}(\mu-\mathrm{Cl})\right]_{2}(46 \mathrm{mg}, 0.12 \mathrm{mmol})$ and dmapm $(67 \mathrm{mg}$, $0.12 \mathrm{mmol})$ was added $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$. Over the course of 2 min , the solution changed from orange to yellow and there was a brisk effervescence due to release of CO. The solution was stirred for 5 min before all but 1 mL of the solvent was removed in vacuo. Addition of $\mathrm{Et}_{2} \mathrm{O}(10 \mathrm{~mL})$ gave the product as a canary yellow powder that was isolated by filtration, washed with $\mathrm{Et}_{2} \mathrm{O}(4 \times 2 \mathrm{~mL})$ and dried under vacuum. Yield: 100 mg (95 \%). Anal. Calcd for $\mathrm{C}_{35} \mathrm{H}_{42} \mathrm{~N}_{4} \mathrm{Cl}_{2} \mathrm{O}_{2} \mathrm{P}_{2} \mathrm{Rh}_{2}$ : C, 47.3; H, 4.8; N, 6.3. Found: C, 46.7; H, 4.9; N, 6.1. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 220 \mathrm{~K}$ ): $\delta 2.31$ ( $\mathrm{s}, 6 \mathrm{H}, \mathrm{NCH}_{3}$ ), 2.73 ( $\mathrm{s}, 6 \mathrm{H}$, $\mathrm{NCH}_{3}$ ), $2.95\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{NCH}_{3}\right.$ ), 3.77 ( $\mathrm{s}, 6 \mathrm{H}, \mathrm{NCH}_{3}$ ), 4.64 (br m, $2 \mathrm{H}, \mathrm{CH}_{2}$ ), 6.87 (br m, 2 H , Ar), 7.08 (br m, $2 \mathrm{H}, \mathrm{Ar}$ ), $7.35-7.85$ (br m, $12 \mathrm{H}, \mathrm{Ar}$ ). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(162 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.$, $300 \mathrm{~K}): \delta 40.4\left(\mathrm{~m},{ }^{1} J_{\mathrm{PRh}}=180,{ }^{2} J_{\mathrm{PP}}=22,{ }^{3} J_{\mathrm{PRh}}=1\right) . \mathrm{v}_{\mathrm{CO}}: 2000[\mathrm{~s}]$.

### 3.9.17 $\mathbf{P d}_{2} \mathbf{C l}_{2}$ (dmapm)

To a Schlenk tube containing trans $-\mathrm{PdCl}_{2}(\mathrm{PhCN})_{2}(32 \mathrm{mg}, 0.083 \mathrm{mmol})$ and dmapm ( $47 \mathrm{mg}, 0.084 \mathrm{mmol}$ ) was added $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$, and the resulting yellow solution was
stirred for 15 min . Solid $\mathrm{Pd}_{2}(\mathrm{dba})_{3} \cdot \mathrm{CHCl}_{3}(44 \mathrm{mg}, 0.043 \mathrm{mmol})$ was then added and the resulting purple solution was warmed to reflux for 3 h during which it became orange. All but 1 mL of solvent was removed in vacuo, and $\mathrm{Et}_{2} \mathrm{O}(20 \mathrm{~mL})$ was added to give the product as an orange powder that was isolated by filtration, washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 5 \mathrm{~mL})$ and dried under vacuum. Yield: 54 mg ( $76 \%$ ). Anal. Calcd for $\mathrm{C}_{33} \mathrm{H}_{42} \mathrm{~N}_{4} \mathrm{Cl}_{2} \mathrm{P}_{2} \mathrm{Pd}_{2}$ : C, 47.2; H, 5.0; N, 6.7. Found: C, 47.5; H, 5.1; N, 6.6. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ) : $\delta 2.44\left(\mathrm{~s}, 12 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.89\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{NCH}_{3}\right), 3.07\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{NCH}_{3}\right), 3.72\left(\mathrm{t}, 2 \mathrm{H}, \mathrm{CH}_{2},{ }^{2} J_{\mathrm{HP}}=\right.$ 11.3 Hz ), 6.99 (pt, $2 \mathrm{H}, \mathrm{Ar}$ ), 7.22 (m, $6 \mathrm{H}, \mathrm{Ar}$ ), 7.45 (m, 4H, Ar), $7.60(\mathrm{~m}, 4 \mathrm{H}, \mathrm{Ar})$. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta-29.9$ (s).

### 3.9.18 $\mathrm{PtPdCl}_{2}$ (dmapm)

To a combination of trans $-\mathrm{PdCl}_{2}(\mathrm{PhCN})_{2}(130 \mathrm{mg}, 0.33 \mathrm{mmol})$ and dmapm $(190 \mathrm{mg}$, 0.33 mmol ) in a Schlenk tube was added $\mathrm{CH}_{2} \mathrm{Cl}_{2}(7 \mathrm{~mL})$. The initially orange solution turned yellow within a few seconds. The solvent was removed at the pump and EtOH ( 10 mL ) was added followed by an aqueous solution ( 5 mL ) containing $\mathrm{K}_{2} \mathrm{PtCl}_{4}$ ( 140 mg , 0.33 mmol ). The orange slurry was heated to $70^{\circ} \mathrm{C}$ for 1 h when it turned yellow. An ethanolic solution containing $\mathrm{KOH}\left(13 \mathrm{~mL}, 70 \mathrm{mmol} \mathrm{L}^{-1}\right)$ was added over 3 min and the resulting brown solution stirred at $70^{\circ} \mathrm{C}$ for an additional 0.5 h . The solvents were then removed in vacuo and the residue dried thoroughly overnight. The residue was partially dissolved in warm $\mathrm{C}_{6} \mathrm{H}_{6}(30 \mathrm{~mL})$ and then the mixture was filtered through a plug of Celite $545 / \mathrm{MgSO}_{4}$. The brown filtrate was shown by NMR to contain a combination of unreacted $\mathrm{PtPdCl}_{4}(\mathrm{dmapm})$ and the desired $\mathrm{Pt}^{\mathrm{I}} \mathrm{Pd}^{1}$ dimer. The solid trapped on the Celite plug was then washed through with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$ and the brown-red filtrate was concentrated to $c a .1 \mathrm{~mL}$ at the pump. Addition of $\mathrm{Et}_{2} \mathrm{O}(25 \mathrm{~mL})$ gave the product as a green-brown precipitate that was isolated by filtration, washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 3 \mathrm{~mL})$ and dried in vacuo. Yield: $99 \mathrm{mg}(32 \%)$. Anal. Calcd for $\mathrm{C}_{33} \mathrm{H}_{42} \mathrm{~N}_{4} \mathrm{Cl}_{2} \mathrm{P}_{2}$ PdPt: C, 42.7; H, 4.6; N, 6.0. Found: C, 41.5; H, 4.6; N, 5.7. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 2.36(\mathrm{~s}, 6 \mathrm{H}$, $\left.\mathrm{NCH}_{3}\right), 2.45\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.78\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right), 3.02\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right), 3.07\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NCH}_{3}\right)$, 3.19 (s, $3 \mathrm{H}, \mathrm{NCH}_{3}$ ), 3.54 (ddd, $1 \mathrm{H}, \mathrm{CH}_{2},{ }^{2} J_{\mathrm{HH}}=15.9 \mathrm{~Hz},{ }^{2} J_{\mathrm{HP}}=7.77$ ), 3.93 (ddd, 1 H , $\left.\mathrm{CH}_{2},{ }^{2} J_{\mathrm{HH}}=15.9 \mathrm{~Hz},{ }^{2} J_{\mathrm{HP}}=7.77\right), 6.94\left(\mathrm{ddd}, 1 \mathrm{H}, \mathrm{Ar},{ }^{3} J_{\mathrm{HH}}=6.4 \mathrm{~Hz},{ }^{3} J_{\mathrm{HP}}=8.0 \mathrm{~Hz},{ }^{4} J_{\mathrm{HP}}=\right.$ 1.3 Hz ), 7.01 (pt, 1H, Ar), 7.13 (pt, 1H, Ar), 7.24 (m, 4H, Ar), 7.41 (m, 4H, Ar), 7.53 (m,
$4 \mathrm{H}, \mathrm{Ar}), 8.18\left(\mathrm{dd}, 1 \mathrm{H}, \mathrm{Ar},{ }^{3} J_{\mathrm{HH}}=7.5 \mathrm{~Hz},{ }^{3} J_{\mathrm{HP}}=14.2 \mathrm{~Hz}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}(121 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta-23.0\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=21.9 \mathrm{~Hz},{ }^{2} J_{\mathrm{PPt}}=260 \mathrm{~Hz}, \mathrm{P}\right.$ bound to Pd$),-31.7\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}\right.$ $=21.9 \mathrm{~Hz},{ }^{1} J_{\mathrm{PPt}}=4200 \mathrm{~Hz}, \mathrm{P}$ bound to Pt).

### 3.9.19 $\mathbf{P d}_{2} \mathrm{Cl}_{\mathbf{2}}(\mathbf{C O})_{2}($ dmapm $)$

To a Schlenk tube containing $\mathrm{Pd}_{2} \mathrm{Cl}_{2}$ (dmapm) ( $31 \mathrm{mg}, 0.037 \mathrm{mmol}$ ) was admitted CO ( 1 atm ) followed by $\mathrm{Et}_{2} \mathrm{O}(10 \mathrm{~mL})$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \mathrm{~mL})$. The orange slurry was stirred overnight when it became blue-purple. The solid was removed by filtration, washed with $\mathrm{Et}_{2} \mathrm{O}$ and dried in vacuo. Yield: 21 mg ( $64 \%$ ). Anal. Calcd for $\mathrm{C}_{35} \mathrm{H}_{42} \mathrm{~N}_{4} \mathrm{Cl}_{2} \mathrm{O}_{2} \mathrm{P}_{2} \mathrm{Pd}_{2}$ : C, 46.9; H, 4.7; N, 6.2. Found: C, 46.4; H, 4.8; N, 6.3. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}, 1$ $\operatorname{atm} \mathrm{CO}): \delta 2.67\left(\mathrm{t}, 2 \mathrm{H}, \mathrm{CH}_{2},{ }^{2} J_{\mathrm{HP}}=12.0 \mathrm{~Hz}\right), 2.72\left(\mathrm{~s}, 24 \mathrm{H}, \mathrm{NCH}_{3}\right), 7.12(\mathrm{~m}, 8 \mathrm{H}, \mathrm{Ar})$, 7.45 (m, 8H, Ar). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}, 1 \mathrm{~atm} \mathrm{CO}$ ): $\delta 43.0$ (s). IR ( KBr pellet): $v_{\mathrm{CO}}: 1798[\mathrm{~s}]$.

### 3.9.20 $\mathbf{P d}_{2} \mathbf{C l}_{2}$ (DEAD)(dmapm) $\cdot \mathbf{H}_{2} \mathrm{O}$

To a $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ solution containing $\mathrm{Pd}_{2} \mathrm{Cl}_{2}$ (dmapm) $(63 \mathrm{mg}, 0.075 \mathrm{mmol})$ was added DEAD ( $0.020 \mathrm{~mL}, 0.13 \mathrm{mmol}$ ). During 10 h , the solution changed from red to yellow, and some decomposition to Pd metal occurred. After filtration through Celite 545, the solution was reduced in vacuo to ca. 1 mL , and $\mathrm{Et}_{2} \mathrm{O}(20 \mathrm{~mL})$ was added to give the product as a fine yellow precipitate. This was isolated by filtration, washed with $\mathrm{Et}_{2} \mathrm{O}$ (3 $\times 3 \mathrm{~mL}$ ) and dried under vacuum. Yield: 44 mg ( $58 \%$ ). Anal. Calcd for $\mathrm{C}_{41} \mathrm{H}_{54} \mathrm{~N}_{4} \mathrm{Cl}_{2} \mathrm{O}_{5} \mathrm{P}_{2} \mathrm{Pd}_{2}$ : C, 47.9; H, 5.3; N, 5.4. Found: C, 47.8; H, 5.4; N, 5.4. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 325 \mathrm{~K}$ ): $\delta 31.6$ (s). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 325 \mathrm{~K}$ ): $\delta 1.47$ (t, $\left.6 \mathrm{H}, \mathrm{CH}_{2} \mathrm{CH}_{3},{ }^{3} J_{\mathrm{HH}}=6.9\right), 1.78\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{H}_{2} \mathrm{O}\right), 2.32\left(\mathrm{~s}, 12 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.84\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{NCH}_{3}\right)$, $2.89\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{NCH}_{3}\right), 3.19\left(\mathrm{dt}, 1 \mathrm{H}, \mathrm{PCH}_{2} \mathrm{P},{ }^{2} J_{\mathrm{HH}}={ }^{2} J_{\mathrm{HP}}=14.0\right), 3.70\left(\mathrm{~m}, 5 \mathrm{H}, \mathrm{PCH}_{2} \mathrm{P}\right.$ and $\mathrm{CH}_{2} \mathrm{CH}_{3}$ ), 6.90 (pt, 2H, Ar), 7.05 (m, 2H, Ar), 7.35 (m, 8H, Ar), 7.50 (pt, 2H, Ar), 8.55 (m, 2H, Ar).

### 3.9.21 Attempted isolation of a Heck catalytic intermediate

A mixture of $\mathrm{PtPdCl}_{4}(\mathrm{dmapm})(52 \mathrm{mg}, 0.052 \mathrm{mmol})$, DMF ( 1 mL ), a DMF solution containing $1.00 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{PhI}$ and $1.00 \mathrm{~mol} \mathrm{~L}^{-1}$ styrene $(1 \mathrm{~mL})$ and an $\mathrm{H}_{2} \mathrm{O}$ solution
containing $1.00 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~K}_{2} \mathrm{CO}_{3}(1 \mathrm{~mL})$ was heated to $100^{\circ} \mathrm{C}$ for 5 min under air. The volatiles were removed in vacuo and the residue taken up in $\mathrm{C}_{6} \mathrm{H}_{6}$. The resulting slurry was filtered through Celite 545 and the filtrate was reduced to $c a .0 .5 \mathrm{~mL}$. Addition of hexanes $(20 \mathrm{~mL})$ gave the product as an orange powder that was isolated by filtration and washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 3 \mathrm{~mL})$. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR data for the mixture of complexes thus isolated are given in Table 3.5.

### 3.9.22 Attempted preparation of $\mathbf{P t I}_{2}(\mathbf{P}, \mathbf{N}$-dmapmO)

$\mathrm{PdCl}_{2}$ (dmapm) was prepared in situ from trans $-\mathrm{PdCl}_{2}(\mathrm{PhCN})_{2}(89 \mathrm{mg}, 0.23 \mathrm{mmol})$ and dmapm ( $130 \mathrm{mg}, 0.23 \mathrm{mmol}$ ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$. To the yellow solution was added cumene hydroperoxide ( $0.080 \mathrm{~mL}, 0.43 \mathrm{mmol}$ ). After 2.5 h , the solvent was removed in vacuo and the Schlenk warmed gently with a hot air-gun so as to ensure the removal of all traces of the peroxide. CAUTION: cumene hydroperoxide may explode violently if heated above $82^{\circ} \mathrm{C}$. Solid $\mathrm{KCN}(98 \mathrm{mg}, 1.5 \mathrm{mmol})$, $\mathrm{EtOH}(5 \mathrm{~mL})$ and $\mathrm{H}_{2} \mathrm{O}(3 \mathrm{~mL})$ were added. The yellow colour disappeared within a few seconds. After 20 min the solvents were removed and the residue taken up in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$. The slurry was filtered through a mixture of Celite 545 and $\mathrm{MgSO}_{4}$ into a Schlenk tube containing $\mathrm{PtCl}_{2}$ (cod) ( $81 \mathrm{mg}, 0.22 \mathrm{mmol}$ ). An intense yellow colour developed and quickly faded. After 0.5 h , the solution was reduced in vacuo to $c a .1 \mathrm{~mL}$, and $\mathrm{Et}_{2} \mathrm{O}(20 \mathrm{~mL})$ was added to give the product as an off-white powder. This was isolated by filtration, washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times$ 3 mL ) and dried under vacuum. ${ }^{1} \mathrm{H}$ NMR spectroscopy indicated that this product contained a significant proportion of $\mathrm{PtCl}_{2}(\mathrm{cod})$. Nevertheless, the crude mixture was treated with NaI in a manner similar to that outlined in Section 3.9.12 in order to form the desired product. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR data for this compound and its chloro analogue appear in Section 3.6.2.4 (p. 133).

### 3.9.23 Heck reactions.

The catalyst precursor (ca. $1-2 \mu \mathrm{~mol}$ ) was dissolved in a stock DMF solution containing $1.00 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{PhI}$ and $1.00 \mathrm{~mol} \mathrm{~L}^{-1}$ styrene $(2 \mathrm{~mL})$. This was diluted by the addition of neat DMF ( 1 mL ) and preheated to $100^{\circ} \mathrm{C}$ in a 20 mL three-necked round-bottom flask fitted with a condenser. Over the course of about 30 s , a $1.00 \mathrm{~mol} \mathrm{~L}^{-1}$ stock solution of $\mathrm{K}_{2} \mathrm{CO}_{3}$
in $\mathrm{H}_{2} \mathrm{O}(2 \mathrm{~mL})$ was added. The beginning of this addition marked zero time. The temperature was maintained at $100^{\circ} \mathrm{C}$ throughout the course of the reaction on a thermostatted oil-bath. No precautions were taken to exclude $\mathrm{O}_{2}$. (If the reaction solution is allowed to cool following the catalysis $(2-3 \mathrm{~h})$, the stilbene product precipitates and can be isolated by simple filtration.)

Aliquots of the reaction mixture $(0.1 \mathrm{~mL})$ were withdrawn at 10 min intervals and diluted by addition to $\mathrm{CH}_{2} \mathrm{Cl}_{2}(1 \mathrm{~mL})$ at r.t. The $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution $(0.1 \mu \mathrm{~L})$ was then analysed by GC in order to determine the extent of reaction. This was accomplished by comparing the relative peak areas for PhI and cis- and trans-stilbene. Analysis of solutions containing known concentrations of PhI and trans-stilbene indicated that a weighting factor of 2.32 needed to be applied to the area of the peak due to PhI to compensate for its lower response factor at the FID. This ensured that the use of relative peak areas gave accurate representations of the relative concentrations of the two compounds in solution. The peak due to styrene was not used in the analysis due to its overlap with the tail of the peak due to DMF.

The GC parameters are summarised in Table 3.8, and the component elution times under these conditions are given in Table 3.9.

Table 3.8 GC parameters used in the determination of Heck reaction components.

| Parameter | Setting |
| :--- | :--- |
| Initial oven temperature | $80^{\circ} \mathrm{C}$ |
| Final oven temperature | $220^{\circ} \mathrm{C}$ |
| Rate | $20^{\circ} \mathrm{C} \mathrm{min}^{-1}$ |
| Initial time | 2 min |
| Final time | 1.5 min |
| Injector temperature | $220^{\circ} \mathrm{C}$ |
| Detector temperature | $220^{\circ} \mathrm{C}$ |
| Column head pressure | 105 kPa |

Table 3.9 Elution times for Heck reaction components under the GC conditions given in Table 3.8.

| Component | Retention time (min) |
| :--- | :--- |
| Styrene | 2.30 |
| Iodobenzene | 4.18 |
| Cis-stilbene | 8.26 |
| Trans-stilbene | 9.74 |

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## 4 Pyridyldiphosphine Ligands, Derivatives, and Pt and Pd Complexes

### 4.1 Introduction

In this chapter, the coordination chemistry of Pt and Pd with heteropolydentate ligands incorporating both "hard" (N) and "soft" (P) donors is extended to include the 2pyridyldiphosphines. The use of pyridylmonophosphines (i.e., those containing only one P-atom and 1-3 pyridyl groups) as ligands for transition metals has generated an extensive body of literature, and is the subject of a 1993 review. ${ }^{1}$ In addition to a large number of monometallic complexes, ${ }^{2-6}$ several bimetallic species ${ }^{7-11}$ as well as clusters ${ }^{12,13}$ and oligomers, ${ }^{14}$ the last three classes employing the ligand in a $P, N$ bridging mode, have been characterised. In addition, some homogeneous catalytic applications, including hydrogenation, ${ }^{1}$ hydroformylation, ${ }^{7,15,16}$ and carbonylation ${ }^{17}$ have been investigated.

A widely used pyridylmonophosphine is 2-pyridyldiphenylphosphine, $\mathrm{PPh}_{2}$ (py) (Type I, Chart 4.1; denoted $\mathrm{PN}_{1}$ throughout this thesis), which as a ligand can adopt three different coordination modes: $P$-monodentate, ${ }^{18-22} P, N$-chelate ${ }^{2,4}$ and $P, N$-bridge. ${ }^{7-14} \mathrm{Di}$ and tri-substituted 2-pyridylphosphines such as $\mathrm{PPh}(\mathrm{py})_{2}\left(\mathrm{PN}_{2}\right), \mathrm{P}(\mathrm{py})_{3}\left(\mathrm{PN}_{3}\right)$ and $\mathrm{XPPh}_{3}$ ${ }_{n}(\mathrm{py})_{n}\left(\mathrm{X}=\mathrm{O}, \mathrm{S}, \mathrm{AuCl}, \mathrm{Au}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right) ; n=2,3\right)$ can take on a variety of additional coordination modes using a combination of one or more of the Group 15/16 donor centres. ${ }^{23-27}$ Recent work within this laboratory has found an unprecedented $P, N, N^{\prime}$ 'coordination mode for $\mathrm{PPh}(\mathrm{py})_{2}$ and $\mathrm{P}(\mathrm{py})_{3} .{ }^{28}$ Detailed introductions to the 2pyridylmonophosphines, their complexes, and catalytic applications can be found in the PhD theses of Xie, ${ }^{29}$ Schutte ${ }^{30}$ and LePage. ${ }^{31}$

In contrast to the vast number of reports concerning the pyridylmonophosphines, pyridyldiphosphines have been less studied and, of those documented, two distinct structural classes are apparent. In the first class, two $-\mathrm{PR}_{2}$ moieties $(\mathrm{R}=\mathrm{Ph}$, typically) are directly bonded in the 2- and 6-positions of the pyridine ring, affording a $P N P$-ligand system (Type II). ${ }^{32-35}$ Ligands of this type readily bridge metal centres and have been
used to stabilize both homo- and heterobimetallic complexes. Introduction of a $-\mathrm{CH}(\mathrm{R})-$ $\left(\mathrm{R}=\mathrm{H}, \mathrm{Me}\right.$ ) spacer between the $-\mathrm{PPh}_{2}$ groups and the central pyridyl group (Type III) ${ }^{36,37}$ permits extra flexibility within the $P N P$-tridentate ligand and, in the case of $\mathrm{R}=$ Me, allows for the synthesis of $C_{2}$-symmetric chiral complexes, some of which have been used for the enantioselective hydrogenation of imines. ${ }^{38}$ This type of ligand favours bis five-membered chelate ring formation upon coordination to a mononuclear metal fragment. ${ }^{39-42}$ In the second class, two $-\mathrm{PR}(\mathrm{py})(\mathrm{R}=\mathrm{Ph}, \mathrm{py})$ fragments are linked by an aliphatic carbon spacer of variable length, linear, branched or cyclic (Type IV).43-45

## Chart 4.1




$$
\begin{gathered}
\text { Type II } \\
(\mathrm{R}=\mathrm{Ph}, \text { typically })
\end{gathered}
$$



Type III
( $\mathrm{R}=\mathrm{H}, \mathrm{Me}$ )


Type IV ( $\mathrm{R}=\mathrm{Ph}, \mathrm{py}$ )

### 4.2 Scope

This chapter reports the synthesis and characterisation (Section 4.7.1) of a new pyridyldiphosphine ligand containing a cyclopentane ring bridge between the two P atoms, dpypcp (Chart 4.2), which is isostructural with the previously described tetraphenyl chiral analogue, dppcp. ${ }^{46}$ The protonated (see Section 4.7.4 for synthesis, and Section 4.3.3 for discussion) and oxidised (Sections 4.7.2 and 4.3.2) forms of this ligand together with those of the known dpype ligand (see Sections 4.7.3 and 4.7.5 for syntheses) are also described.

## Chart 4.2


dpype

dрурср

The synthesis and characterisation of the range of $P, P^{\prime}$-bonded complexes $\mathrm{MX}_{2}(\mathrm{P}-\mathrm{P})(\mathrm{M}=\mathrm{Pd}, \mathrm{Pt} ; \mathrm{X}=\mathrm{Cl}, \mathrm{Br}, \mathrm{I} ; \mathrm{P}-\mathrm{P}=$ dpypcp, dpype) are presented (Sections 4.7.7-4.7.11 and 4.7.15-4.7.17) together with the molecular structures of $\mathrm{PtCl}_{2}$ (dpype) and $\mathrm{PtI}_{2}$ (dpypcp) (Section 4.4.2). In addition, a pair of coordination polymers which bear $P, P^{\prime}$-chelated, $P, N$-bridged $\left[\mathrm{Pt}_{2}(\mathrm{P}-\mathrm{P})_{2}\right]^{4+}$ "tethered paddlewheel" clusters connected by $\mathrm{AgNO}_{3}$ "bridges" are reported (Section 4.4.2.2).

The reactions of dpypcp and dpype with $\mathrm{M}(0)$ precursors to give tetrahedral complexes of the type $\mathrm{M}\left(\mathrm{PPh}_{3}\right)_{2}(\mathrm{P}-\mathrm{P})$ (see Sections 4.7.22 and 4.7.23 for syntheses) are discussed in Section 4.4.3. Reactions of the Pt complexes with electron-deficient olefins, which led to an investigation into cis to trans isomerisation of the coordinated olefin, and the molecular structure of the olefin-containing complex, $\mathrm{Pt}\left(\eta^{2}-\mathrm{dmf}\right)(\mathrm{dpypcp})$, are presented (Section 4.4.3.1).

### 4.3 The Pyridyldiphosphine Ligands and Derivatives

### 4.3.1 History and synthesis

The first report of a pyridylphosphine dates to $1944 .{ }^{47}$ Davies and Mann prepared, among other tertiary phosphines in which the P-atom was linked to 3 different alkyl or aryl groups, the compounds 2- and 3-pyridylphenyl-p-bromophenylphosphine, and also tri-2pyridylphosphine $\left(\mathrm{PN}_{3}\right)$ using standard Grignard methods. In 1948, 2pyridyldiphenylphosphine $\left(\mathrm{PN}_{1}\right)$ and di-2-pyridylphenylphosphine $\left(\mathrm{PN}_{2}\right)$ were prepared by Mann and Watson, also by Grignard methods. ${ }^{48}$ These syntheses typically gave low yields (e.g., $16 \%$ for $\mathrm{PN}_{2}$ ) and required high temperature $\left(160-180^{\circ} \mathrm{C}\right)$ fractional
vacuum distillation as a purification step. Although Davies and Mann had used Li in the preparation of phenyl-p-bromophenylethylphosphine, 47 it was not until the introduction of 2-lithiopyridine by Wibaut et al. in 1952,49 and the development of a revised procedure by Plazek and Tyka in 1957,50 that a higher-yielding, general route into the pyridylphosphines was uncovered. Reaction of 2-lithiopyridine and the appropriate chlorophosphine remains today as the standard synthetic strategy (see, for example, Scheme 4.1).

## Scheme 4.1



The syntheses of dpype and dpypcp represent modifications to the standard procedure for making $\mathrm{PN}_{3}{ }^{51}$ which has been adopted in this laboratory and described in detail by previous researchers Xie, ${ }^{29}$ Schutte ${ }^{30}$ and LePage. ${ }^{31}$ Although dpype was first reported in a 1986 Smithkline Beckman patent ${ }^{52}$ (its $\mathrm{Au}^{1}$ complexes effectively inhibiting the growth of animal tumor cells) and was mentioned in the open literature 1987,44 no synthetic or characterisation data appeared until the publication by Baird ${ }^{3}$ of this group in 1995. The ligand was prepared according to Baird's procedure during the course of this work, and its molecular structure was reported in 1999.53 Berners-Price and coworkers devised an alternate scheme for the synthesis of dpype which involved cleavage of $\mathrm{PN}_{3}$ by Li to generate lithium di-2-pyridylphosphide, followed by reaction with 1,2dibromoethane. ${ }^{54}$ These workers also reported the synthesis of the 3- and 4-pyridyl analogues according to a variation of the standard route.

The ligand dpypcp was first made by a Smith, a postdoctoral fellow in this laboratory during 1993-1994.55 It was characterised more fully by this author and reported together with the $\mathrm{Pt}^{\text {II }}$ complexes which constitute a significant portion of this chapter, and some $\mathrm{Ru}^{\text {II }}$ compounds, in $1999 .{ }^{53}$ The molecular structure was subsequently determined by X-ray crystallography and appears in the PhD thesis of LePage. ${ }^{31}$ The material is synthesised as a racemic mixture of $R, R$ and $S, S$ enantiomers, where the
absolute configuration designations refer to the two methine C -atoms in the cyclopentane "backbone" linking the two P-atoms (Chart 4.2 and Section 4.7.1). The compound is a white solid which is freely soluble in chlorinated solvents, partially soluble in acetone, $\mathrm{Et}_{2} \mathrm{O}$ and alcohols, and sparingly soluble in $\mathrm{H}_{2} \mathrm{O}$. It is freely soluble in dil. HCl (Section 4.3.3).

### 4.3.2 Pyridyldiphosphine dioxides

The syntheses of metal phosphine complexes (particularly air-sensitive materials) are often accompanied by the formation of phosphine oxides which arise because of the presence of adventitious $\mathrm{H}_{2} \mathrm{O}$ or $\mathrm{O}_{2}$, e.g., $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{4}$, which is made via reduction of $\left[\mathrm{PtCl}_{4}\right]^{2-}$ in the presence of excess $\mathrm{PPh}_{3}$, actually catalyses the oxidation of the phosphine. ${ }^{56}$ The pyridyldiphosphine dioxides were therefore made in order to establish their absence in the syntheses and reactions of, particularly, $\mathrm{Pt}^{0}$ complexes (Sections 4.7.22-4.7.27), and for completeness of characterisation (Sections 4.7.2 and 4.7.3). The standard method for the synthesis of pyridylphosphine oxides used in this laboratory is via reaction of aq. $\mathrm{H}_{2} \mathrm{O}_{2}$ and an organic solution containing the $\mathrm{P}^{\text {III }}$ compound in a twophase system. ${ }^{30}$ The synthesis presented here is a modification which involves only one phase. Thus, the ligand was dissolved in dil. HCl and peroxide was added. After the oxidation reaction was complete, KOH was added to deprotonate the oxidised ligand. At this point it was expected that the product would precipitate but, surprisingly, the pyridyldiphosphine dioxides show enhanced solubility in $\mathrm{H}_{2} \mathrm{O}$ compared to their $\mathrm{P}^{\text {III }}$ analogues, and a $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ wash was required to remove the dissolved oxide from the water phase.

The ligand dpypcp also reacts smoothly with $\mathrm{S}_{8}$ in refluxing $\mathrm{C}_{6} \mathrm{H}_{6}$ to give the pyridyldiphosphine disulphide (Section 4.7.6).

The most useful spectroscopic "handles" for the pyridyldiphosphines and their dioxides, together with those of $\mathrm{PN}_{2}$ and $\mathrm{OPN}_{2}$, are given in Table 4.1.

Table 4.1 Spectroscopic data for pyridylphosphine ligands and their oxides ( $\mathrm{tw}=$ this work).

| Compound | $\begin{aligned} & { }^{31} \mathbf{P}\left\{{ }^{\mathrm{I}} \mathbf{H}\right\} \text { NMR } \\ & \text { chemical shift }(\mathrm{ppm})^{\mathrm{a}} \end{aligned}$ | ${ }^{1} H$ NMR chemical shift of $\mathrm{H}_{6}$ protons ( ppm$)^{\text {a,b }}$ | $\mathbf{V}_{\mathbf{P}=0}\left(\mathrm{~cm}^{-1}\right)^{\text {c }}$ | Ref. |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{PN}_{2}$ | -2.6 | 8.72 | - | 30 |
| $\mathrm{OPN}_{2}$ | 17.3 | 8.79 | 1194 | 30 |
| dpype | -6.1 | 8.63 | - | 3 |
| dрурср | -2.2 | $8.38,8.49^{\text {d }}$ | - | tw |
| dpype( O$)_{2}$ | 29.1 | 8.70 | 1206 | tw |
| dрурср(О) 2 | 35.8 | 7.90, $8.45\left(\mathrm{D}_{2} \mathrm{O}\right)^{\text {d }}$ | 1194 | tw |
|  | $38.7\left(\mathrm{D}_{2} \mathrm{O}\right)$ |  |  |  |

${ }^{a}$ Measured in $\mathrm{CDCl}_{3}$ solution unless otherwise noted.
${ }^{b}$ These peaks appear as pseudo-doublets.
${ }^{c} \mathrm{KBr}$ pellet.
${ }^{d}$ dpypcp and dpypcp $(\mathrm{O})_{2}$ have two diastereotopic sets of $\mathrm{H}_{6}$ protons.

Apparent from Table 4.1 is that the pyridyldiphosphine ligands and their dioxides are spectroscopically very similar to each other and to their $\mathrm{PN}_{2}$ counterparts. This is to be expected, but is somewhat surprising in light of their different reactions with acids (Section 4.3.3). Oxidation of the P -atom shifts the ${ }^{31} \mathrm{P}$ resonances dramatically downfield as expected, but has little impact on the $\mathrm{H}_{6}$ resonances. The peaks due to the $\mathrm{H}_{6}$ protons (bonded to C immediately adjacent to the pyridyl- N ), easily identified by their characteristic downfield chemical shifts and multiplicity (pd), ${ }^{57,58}$ are useful in determining the number of equivalent pyridyl rings in a given metal complex (by integration) and therefore give insight into the bonding mode of the ligand. As judged by the effects of oxidation, the $\delta\left(\mathrm{H}_{6}\right)$ shifts of these peaks should not be greatly perturbed by $P, P^{\prime}$-bonding of a pyridyldiphosphine ligand but should be affected if N -bonding occurs.

### 4.3.3 Protonated pyridyldiphosphines

The protonated pyridyldiphosphine $\left[\operatorname{dpypcp}(\mathrm{H})_{2}\right]^{2+}$ has been prepared by LePage ${ }^{31}$ via reaction of triflic acid and the neutral ligand in EtOH . Such protonated ligands can also be made by adding $\mathrm{KPF}_{6}$ to a dil. HCl solution ( $\mathrm{pH} \sim 0$ ) containing the ligands; the insoluble $\left[\mathrm{P}-\mathrm{P}(\mathrm{H})_{2}\right]\left[\mathrm{PF}_{6}\right]_{2}$ precipitates $(\mathrm{P}-\mathrm{P}=$ dpype, dpypcp) (Sections 4.7.4 and 4.7.5). Because each proton requires a high molecular weight $\mathrm{PF}_{6}$ counter-ion, elemental analysis unequivocally establishes the presence of only 2 protons (e.g., Anal. Calcd for $\left[d \operatorname{pypcp}(\mathrm{H})_{2}\right]\left[\mathrm{PF}_{6}\right]_{2}: \mathrm{C}, 40.9 ; \mathrm{H}, 3.6 ; \mathrm{N}, 7.6$. Found: C, $\left.40.9 ; \mathrm{H}, 3.6 ; \mathrm{N}, 7.5.\right)$. This result is
perhaps surprising in that the reactions are conducted at a pH well below the $\mathrm{pK}_{\mathrm{a}}$ of pyridinium (5.25) and each of the ligands has 6 basic sites: 4 pyridyl N -atoms and 2 P atoms.

It should be noted that Mann and Watson isolated both $\mathrm{PN}_{2} \cdot 2 \mathrm{HCl}$ and $\mathrm{PN}_{3} \cdot 3 \mathrm{HCl}$ and thereby showing that there is no steric nor electrostatic reason why the number of protons taken up by the $\mathrm{PN}_{n}$ family should not equal $n .{ }^{48}$ In principle, each of the ligands here under study could "take up" a minimum of 4 protons.

By titration of a dil. HCl solution containing dpypep with $\mathrm{NaOH}, \mathrm{pK}_{\mathrm{a}}$ values of $3.66 \pm 0.02$ and $4.77 \pm 0.02$ were determined for $\left[\operatorname{dpypcp}(\mathrm{H})_{2}\right]^{2+}$ (Section 4.7.28). The dependence of pH on volume of NaOH added for an HCl solution containing dissolved dpypcp is shown in Figure 4.1. Also shown, is the number of protons bound by the ligand, $\bar{n}$, as a function of pH . This curve has a maximum of $\bar{n}=2$, in agreement with the elemental analysis data for the isolated $\left[\operatorname{dpypcp}(\mathrm{H})_{2}\right]\left[\mathrm{PF}_{6}\right]_{2}$.

One significant difference between the pyridyldiphosphine ligands and the $\mathrm{PN}_{n}$ family is that in the former, the P -atom is bonded to 2 aromatic rings and an alkyl fragment whereas in the latter, it is bonded solely to aromatic rings. Protonation at one of the pyridyl rings causes a decrease in electron density at the remaining pyridyl rings via an inductive mechanism mediated by the central P -atom; ${ }^{48}$ thus, electronic factors at this atom are crucially important in the controlling the number of protonations. For example, the tertiary amine $\mathrm{Npy}_{3}$ (py = 2-pyridyl) takes up only 2 protons when exposed to a saturated solution of HCl in $\mathrm{EtOH} ; 48$ the inductive deactivating effect of a protonation on a pyridyl rings appears to be transmitted more efficiently through an N -atom than through a P -atom. In addition, $\mathrm{OPN}_{3}$ takes up 1 equiv. of picric acid $\left(\mathrm{pK}_{\mathrm{a}} 0.38\right)$ while $\mathrm{PN}_{3}$ takes up 2 equiv..$^{48}$ Perhaps the substitution of one aromatic ring on the P -atom for an alkyl fragment is sufficient to enhance the ability of phosphorus to transmit the inductive effect and so reduce the propensity for multiple protonations.


Figure 4.1 TOP: pH dependence on vol. of $\mathrm{NaOH}\left(1.094 \times 10^{-1} \mathrm{~mol} \mathrm{~L}^{-1}\right)$ added for an HCl solution $\left(1.135 \times 10^{-2} \mathrm{~mol} \mathrm{~L}^{-1}\right)$ containing dissolved dpypcp ( $6.112 \times$ $10^{-4} \mathrm{~mol} \mathrm{~L}^{-1}$ ) (solid line), and the HCl solution alone (dashed line). BOTTOM: number of protons bound per dpypcp molecule $(\bar{n})$, as a function of pH .

As judged by their ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra, the protonated ligands bear chemically equivalent P -atoms. A plausible picture of, e.g., $\left[\text { dpype }(\mathrm{H})_{2}\right]^{2+}$, is shown in Chart 4.3,
where a proton is "chelated" by both pyridyl N -atoms. This is similar to the basic action of proton sponge. ${ }^{59,60}$

## Chart 4.3



### 4.4 Synthesis and Characterisation of Pyridyldiphosphine Complexes

### 4.4.1 A brief literature survey

The first report of a Type IV pyridyldiphosphine-transition metal complex was that in 1987 of an $\mathrm{Au}^{\mathrm{I}}$ complex of dpype, although no synthetic or characterisation data were presented. ${ }^{44}$ This was followed by the 1990 description by Budzedlaar et al. of bimetallic $\mathrm{Rh}^{\mathrm{I}}$ complexes supported by $(\mathrm{Ph})(\mathrm{py}) \mathrm{P}(\mathrm{X}) \mathrm{P}(\mathrm{py})(\mathrm{Ph})\left(\mathrm{X}=\mathrm{CH}_{2}, \mathrm{C}_{2} \mathrm{H}_{4}, \mathrm{C}_{3} \mathrm{H}_{6} ;\right.$ py $=2-$ pyridyl). ${ }^{45}$ James's group was first to report the synthesis and characterisation of dpype, ${ }^{3}$ this 1995 report also describing some $\mathrm{Ni}^{\mathrm{II}}$ complexes of the ligand. The Ni work was continued by LePage who extended it to include dpypcp. ${ }^{31}$ In 1998, Berners-Price et al. reported $\mathrm{Ag}^{1}$ complexes of dpype and uncovered their solution behaviour, ${ }^{43}$ and a year later published on the analogous $\mathrm{Au}^{\mathrm{I}}$ compounds ${ }^{61}$ and a review covering the syntheses, structures and solution behaviour of these complexes, as well as a summary of their in vitro activity against human tumour cell lines. ${ }^{62}$ In the same year, this author and other members of the James group reported the syntheses of a range of $\mathrm{Pt}^{\mathrm{II}}$ and $\mathrm{Ru}^{\mathrm{II}}$ complexes, and preliminary results for the catalytic hydrogenation of imines using the Ru compounds. ${ }^{53}$

The known coordination modes of the Type IV pyridyldiphosphine ligands with transition metal centres are illustrated in Chart 4.4, and the respective metal centres are given in Table 4.2.

## Chart 4.4



I


IV


II


V


III


VI

Table 4.2 The known coordination modes of the Type IV pyridyldiphosphine ligands and their respective metal centres (tw = this work).

| Coordination Mode | Metal $^{\text {ref }}$ |
| :---: | :---: |
| I | $\mathrm{Ni}(0)^{31} \mathrm{Ni}(\mathrm{II})^{3,31} \mathrm{Pd}(\mathrm{II})^{\text {tw }} \mathrm{Ag}(\mathrm{I})^{43} \mathrm{Pt}(0)^{\mathrm{tw}}$ |
|  | $\mathrm{Pt}(\mathrm{II})^{53, \mathrm{tw}} \mathrm{Au}(\mathrm{I}){ }^{61}$ |
| II | $\operatorname{Ru}(\mathrm{II})^{53}$ |
| III | $\mathrm{Ag}(\mathrm{I})^{43} \mathrm{Au}(\mathrm{I})^{61}$ |
| IV | $\operatorname{Rh}(\mathrm{I})^{45} \mathrm{Pt}(\mathrm{II})^{\mathrm{tw}}$ |
| V | $\operatorname{Rh}(\mathrm{I})^{45}$ |
| VI | $\mathrm{Pt}(\mathrm{II})\left[\mathrm{M}^{\prime}=\mathrm{Ag}(\mathrm{I})\right]^{63, \mathrm{tw}}$ |

### 4.4.2 Platinum(II) and palladium(II) pyridyldiphosphine complexes

The initial work on the synthesis and characterisation of $\mathrm{M}^{\mathrm{II}}(\mathrm{M}=\mathrm{Pd}, \mathrm{Pt})$ complexes of the pyridyldiphosphine ligands dpype and dpypcp was performed by Smith in this laboratory. ${ }^{55}$ Although some of the compounds which form the basis of this chapter had thus been made previously, sufficient characterisation (assigned ${ }^{1} \mathrm{H}$ NMR spectra, elemental analyses, etc) was lacking. In addition, no crystal structures had been obtained.

A more thorough investigation of these complexes was undertaken as the focus of my undergraduate research project, and was continued as the initial phase of this dissertation.

### 4.4.2.1 Monometallic platinum(II) complexes

The synthesis and chemistry of $\mathrm{Pt}^{\text {II }}$ (halo) pyridyldiphosphine complexes (type I, Chart 4.4) are unremarkable and closely mimic those of dppe. The precursor $\mathrm{PtCl}_{2}(\operatorname{cod})$ reacts cleanly and quantitatively with one or two equiv. of the pyridyldiphosphine ligands at r.t. in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution to form complexes of the type $\mathrm{PtCl}_{2}(\mathrm{P}-\mathrm{P})$ or $\left[\mathrm{Pt}(\mathrm{P}-\mathrm{P})_{2}\right] \mathrm{Cl}_{2}$, respectively ( $\mathrm{P}-\mathrm{P}=$ dpype, dpypcp) (Sections 4.7 .7 and 4.7.10). (In making $\mathrm{PtCl}_{2}(\mathrm{P}-\mathrm{P})$, care must be taken to administer a dilute solution of the ligand to a concentrated solution of the metal precursor to prevent the formation of $\left[\mathrm{Pt}(\mathrm{P}-\mathrm{P})_{2}\right] \mathrm{Cl}_{2}$.) The compounds are white, microcrystalline solids, and are freely soluble in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$, partially soluble in $\mathrm{CHCl}_{3}$, slightly soluble in low molecular weight alcohols and acetone, and insoluble in hexanes and $\mathrm{Et}_{2} \mathrm{O}$. In addition, the ionic complexes are partially soluble in water at r.t., while the neutral ones are completely insoluble. At $100^{\circ} \mathrm{C}$ in $0.1 \mathrm{~mol} \mathrm{~L}^{-1}$ maleic acid (catalytic hydration conditions, Chapter 5), all the compounds show a minimum solubility of $c a .1 \mathrm{mg} \mathrm{mL}^{-1}$.

The compounds $\mathrm{PtX}_{2}(\mathrm{P}-\mathrm{P})(\mathrm{X}=\mathrm{Br}, \mathrm{I})$ can be made either from the corresponding chloro compounds via halide metathesis with NaX in acetone/water ( Br ) or acetone (I) solution, or by reaction of the appropriate ligand with $\mathrm{PtX}_{2}(\operatorname{cod})$ (Sections 4.7.8, 4.7.9 and 4.7.11). Like the chloro complexes, $\mathrm{PtBr}_{2}$ (dpypcp) is white; the iodo complexes $\mathrm{PtI}_{2}(\mathrm{P}-\mathrm{P})$ are yellow. The chloride counter-ions in the ionic complexes $\left[\mathrm{Pt}(\mathrm{P}-\mathrm{P})_{2}\right] \mathrm{Cl}_{2}$ are easily substituted by $\mathrm{PF}_{6}{ }^{-}$by reaction with $\mathrm{NH}_{4} \mathrm{PF}_{6}$ in acetone (Sections 4.7.13 and 4.7.14).

In all of these compounds, the ligands are exclusively $P, P^{\prime}$-bonded as indicated by their ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra (Table 4.3) and representative crystal structures. The spectra show singlets for all compounds (two, in the case of $[\operatorname{Pt}(d p y p c p)]\left[\mathrm{PF}_{6}\right]_{2}$ due to diastereomers - vide infra) which indicate chemical equivalence of the 2 P -atoms due to molecular $C_{2}$-symmetry. In addition, large positive coordination shifts (e.g., $\Delta \delta=53.2$ for
$\mathrm{PtCl}_{2}$ (dpype), 20.1 for $\mathrm{PtCl}_{2}$ (dpypcp)) are observed, consistent with the formation of 5membered P-containing metallacycles. ${ }^{64}$

Table 4.3 ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR data $\left(\mathrm{CDCl}_{3}, 300 \mathrm{~K}\right)$ for Pt pyridyldiphosphine complexes.

| Complex | ${ }^{31} \mathbf{P}\left\{{ }^{1} \mathbf{H}\right\}$ chemical shift $(\mathrm{ppm})\left[{ }^{1} J_{\mathrm{PPt}}(\mathrm{Hz})\right]$ |
| :--- | :--- |
| $\mathrm{PtCl}_{2}($ (dpypcp) | $17.9[3490]$ |
| $\mathrm{PtBr}_{2}$ (dpypcp) | $17.6[3460]$ |
| $\mathrm{PtI}_{2}$ (dpypcp) | $12.6[3290]$ |
| $\mathrm{PtCl}_{2}$ (dpype) | $47.1[3480]$ |
| $\mathrm{PtI}_{2}$ (dpype) | $49.8[3280]$ |
| $\left[\mathrm{Pt}^{\left.(\text {dpypcp })_{2}\right]\left[\mathrm{PF}_{6}\right]_{2}}\right.$ | $18.4,18.5[2400]$ |
| $\left[{\left.\mathrm{Pt}(\text { dpype })_{2}\right]\left[\mathrm{PF}_{6}\right]_{2}}\right.$ | $54.4[2480]$ |

In all cases, the peaks due to the dpype complexes appear $30-40 \mathrm{ppm}$ downfield from those of their dpypcp counterparts. This phenomenon, as yet unexplained, has also been observed for a range of analogous Ni complexes. ${ }^{31}$ In addition, the signals reported in Table 4.3 are generally downfield of those of the corresponding P-bonded cis- and trans $-\mathrm{PtX}_{2}\left(\mathrm{PN}_{n}\right)_{2}$ complexes $(\mathrm{X}=\mathrm{Cl}, \mathrm{Br}, \mathrm{I})(\delta 6-20) .{ }^{6,29}$

Attempts have been made to rationalise ligand basicities by comparing the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR chemical shifts of ligands within a family. ${ }^{29,31}$ At the heart of these lie a simple shielding/deshielding argument: the more basic the phosphine, the greater the electron density at the P -atom and the more shielded (upfield) it is, and vice-versa for a less basic phosphine. The general scheme has also been extended to assess the strength of metal-ligand bonding by comparing the chemical shifts of the resulting complexes. ${ }^{29,31}$ While it is true, for example, that $\delta_{\mathrm{P}}$ shifts for the $\mathrm{PN}_{n}$ family increase with increasing $n$ ( $\delta-3.28,-1.70$ and -0.05 , for $n=1-3$, respectively), and that the scheme neatly accounts for this trend by assuming that successive substitution of Ph by py decreases the electron density at the P-atom, ${ }^{65}$ the diphosphines presented in this work do not fit comfortably into this paradigm. It is not obvious why dpypcp ( $\delta-2.2$ ) should be roughly as basic as $\mathrm{PN}_{2}$, and yet dpype ( $\delta-6.1$ ) should be significantly more basic than $\mathrm{PN}_{1}$, even though the P-atoms of both dpypcp and dpype are each bonded to 2 py rings and an alkyl fragment. In addition, the shielding/deshielding argument can only account for the sign of the coordination shifts (positive) experienced by these ligands, but not for their magnitudes
nor for their difference in magnitudes. Even the so-called ring contribution $\left(\Delta_{R}\right)$ to the coordination shift, ${ }^{66}$ aside from being arbitrary, seems of little use in that dpypcp and dpype have the same number of "backbone" C -atoms. Thus, such rationalisation warrants scepticism, and the approach throughout this thesis will be to describe chemical shifts phenomenologically.

The ${ }^{1} J_{\text {PPt }}$ values for the neutral complexes (Table 4.3) are in the range typically found for Pt complexes bearing cis-phosphine ligands, ${ }^{67}$ and are relatively independent of the nature of the pyridyldiphosphine ligand. These values increase with increasing field strength $(\mathrm{Cl}>\mathrm{Br}>\mathrm{I})$ of the trans halide ligand, a trend also observed for cis- and trans$\mathrm{PtX}_{2}\left(\mathrm{PN}_{n}\right)_{2}$ complexes. ${ }^{29}$ The smaller ${ }^{1} J_{\mathrm{PPt}}$ values for the ionic compounds are in the range typically found for Pt complexes bearing trans phosphine ligands; these are ca. $70 \%$ of the corresponding cis coupling constants. ${ }^{68}$

The complex $\left[\mathrm{Pt}(\mathrm{dpypcp})_{2}\right]\left[\mathrm{PF}_{6}\right]_{2}$ is distinct in bearing two chiral ligands. As the ligand is produced as a racemic mixture of $R, R$ and $S, S$ enantiomers, 4 equally probable ligand combinations on the metal are possible: $R, R, R, R, S, S, S, S, R, R, S, S$ and $S, S, R, R$, where the first enantiomeric pair are diastereomers of the second identical pair. Thus, distinct peaks due to the two diastereomeric groups can be seen in the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of this complex. The separation between the two ( $c a .0 .1 \mathrm{ppm}$ ) is smaller than those observed for trans $-\mathrm{RuCl}_{2}(\mathrm{dppcp})_{2}(0.5 \mathrm{ppm})^{53}$ and $H T-\mathrm{Pt}_{2} \mathrm{Cl}_{2}\left(\mu-\mathrm{PN}_{2}\right)_{2}(0.5 \mathrm{ppm}) .{ }^{11}$

The molecular structures of $\mathrm{PtCl}_{2}$ (dpype) $\cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$ and $\mathrm{PtI}_{2}$ (dpypcp) $\cdot 0.18 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ have been determined by X-ray crystallography and are shown in Figure 4.2 and 4.3, respectively. The latter compound exists as 2 crystallographically unique molecules in the unit cell; only one is shown. Relevant bond distances and angles appear in Table 4.4 and Table 4.5. As expected for both structures, the geometry about the metal centre is approximately square planar, and bond lengths and angles fall within the range of those typically observed for $\mathrm{Pt}^{\text {II }}$ complexes of chelating phosphine ligands. ${ }^{69}$ The structure of $\mathrm{PtCl}_{2}$ (dpype) is very similar to that of $\mathrm{PtCl}_{2}$ (dppe), ${ }^{70}$ a minor difference being the relative magnitudes of the $\mathrm{Pt}-\mathrm{P}$ bond lengths: these average $2.227(3) \AA$ for $\mathrm{PtCl}_{2}$ (dppe) and $2.210(2) \AA$ for $\mathrm{PtCl}_{2}$ (dpype). The shorter length in the latter may be due to the enhanced capacity for $\pi$-backbonding in this ligand which arises from the electron-withdrawing pyridyl substituents. Both dppe and dpype have a "bite" angle of ca. $87^{\circ}$.

The chirality at the methine carbon atoms in the dpypcp ligand backbone (Figure 4.3) is $S, S$, and the chelate ring is in the $\delta$-configuration; the same is true for the second crystallographically independent molecule. The $R, R$ enantiomers must also be present in the unit cell, as racemic dpypcp was used in the preparation of $\mathrm{PtI}_{2}$ (dpypcp) which crystallized in the achiral space group $P 2_{1} / \mathrm{c}$. The average $\mathrm{Pt} — \mathrm{P}$ bond length (2.246(2) $\AA$ ) is marginally longer than that observed in $\mathrm{PtCl}_{2}$ (dpype) $(2.210(2) \AA$ ), perhaps due to the stronger trans-influence of iodide versus chloride, although the comparison is drawn between two non-identical P-P ligands.


Figure 4.2 ORTEP representation of $\mathrm{PtCl}_{2}$ (dpype) $\cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$. Thermal ellipsoids for non-hydrogen atoms are drawn at $33 \%$ probability.

Table 4.4 Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for $\mathrm{PtCl}_{2}($ dpype $) \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$ with estimated standard deviations in parentheses.

| $\mathrm{Pt}(1)-\mathrm{Cl}(1)$ | $2.359(2)$ | $\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | $2.348(2)$ |
| :--- | :---: | :--- | :---: |
| $\mathrm{Pt}(1)-\mathrm{P}(1)$ | $2.209(2)$ | $\mathrm{Pt}(1)-\mathrm{P}(2)$ | $2.211(2)$ |
| $\mathrm{Cl}(1)-\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | $90.80(6)$ | $\mathrm{Cl}(1)-\mathrm{Pt}(1)-\mathrm{P}(1)$ | $177.19(6)$ |
| $\mathrm{Cl}(1)-\mathrm{Pt}(1)-\mathrm{P}(2)$ | $91.87(6)$ | $\mathrm{Cl}(2)-\mathrm{Pt}(1)-\mathrm{P}(1)$ | $91.18(6)$ |
| $\mathrm{Cl}(2)-\mathrm{Pt}(1)-\mathrm{P}(2)$ | $177.25(6)$ | $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{P}(2)$ | $86.17(6)$ |
| $\mathrm{Pt}(1)-\mathrm{P}(1)-\mathrm{C}(1)$ | $108.6(2)$ | $\mathrm{Pt}(1)-\mathrm{P}(1)-\mathrm{C}(3)$ | $113.7(2)$ |
| $\mathrm{Pt}(1)-\mathrm{P}(1)-\mathrm{C}(8)$ | $115.4(2)$ | $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{C}(3)$ | $106.9(3)$ |
| $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{C}(8)$ | $105.3(3)$ | $\mathrm{C}(3)-\mathrm{P}(1)-\mathrm{C}(8)$ | $106.4(3)$ |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{P}(1)$ | $108.5(4)$ | $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{P}(2)$ | $109.5(4)$ |
| $\mathrm{C}(2)-\mathrm{P}(2)-\mathrm{C}(13)$ | $105.1(3)$ | $\mathrm{C}(2)-\mathrm{P}(2)-\mathrm{C}(18)$ | $105.7(3)$ |
| $\mathrm{Pt}(1)-\mathrm{P}(2)-\mathrm{C}(2)$ | $109.5(2)$ | $\mathrm{Pt}(1)-\mathrm{P}(2)-\mathrm{C}(13)$ | $115.5(2)$ |
| $\mathrm{Pt}(1)-\mathrm{P}(2)-\mathrm{C}(18)$ | $115.6(2)$ | $\mathrm{C}(2)-\mathrm{P}(2)-\mathrm{C}(13)$ | $105.1(3)$ |
| $\mathrm{C}(2)-\mathrm{P}(2)-\mathrm{C}(18)$ | $105.7(3)$ | $\mathrm{C}(13)-\mathrm{P}(2)-\mathrm{C}(18)$ | $104.5(3)$ |
| $\mathrm{P}(1)-\mathrm{C}(8)-\mathrm{N}(2)$ | $114.1(5)$ | $\mathrm{P}(1)-\mathrm{C}(3)-\mathrm{N}(1)$ | $112.3(5)$ |
| $\mathrm{P}(2)-\mathrm{C}(18)-\mathrm{N}(4)$ | $114.0(5)$ | $\mathrm{P}(2)-\mathrm{C}(13)-\mathrm{N}(3)$ | $114.3(5)$ |



Figure 4.3 ORTEP representation of one of the 2 crystallographically independent molecules of $\mathrm{PtI}_{2}$ (dpypcp) in the unit cell of $\mathrm{PtI}_{2}$ (dpypcp) $\cdot 0.18 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ ( $50 \%$ probability ellipsoids). Except for the two bonded to the methine Catoms in the ligand "backbone", H-atoms have been omitted for clarity.

Table 4.5 Selected bond lengths ( $\AA$ ) and angles $\left({ }^{\circ}\right)$ for $\mathrm{PtI}_{2}$ (dpypcp) $\cdot 0.18 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ with estimated standard deviations in parentheses.

| $\mathrm{Pt}(1)-\mathrm{I}(1)$ | $2.639(1)$ | $\mathrm{Pt}(1)-\mathrm{I}(2)$ | $2.653(1)$ |
| :--- | :---: | :--- | :---: |
| $\mathrm{Pt}(1)-\mathrm{P}(1)$ | $2.244(2)$ | $\mathrm{Pt}(1)-\mathrm{P}(2)$ | $2.247(2)$ |
| $\mathrm{Pt}(2)-\mathrm{I}(3)$ | $2.651(1)$ | $\mathrm{Pt}(2)-\mathrm{I}(4)$ | $2.653(1)$ |
| $\mathrm{Pt}(2)-\mathrm{P}(3)$ | $2.243(2)$ | $\mathrm{Pt}(2)-\mathrm{P}(4)$ | $2.248(2)$ |
| $\mathrm{C}(1)-\mathrm{C}(2)$ | $1.480(1)$ | $\mathrm{C}(26)-\mathrm{C}(27)$ | $1.547(1)$ |
| $\mathrm{I}(1)-\mathrm{Pt}(1)-\mathrm{I}(2)$ | $91.43(2)$ | $\mathrm{I}(1)-\mathrm{Pt}(1)-\mathrm{P}(1)$ | $176.18(5)$ |
| $\mathrm{I}(1)-\mathrm{Pt}(1)-\mathrm{P}(2)$ | $92.08(5)$ | $\mathrm{I}(2)-\mathrm{Pt}(1)-\mathrm{P}(1)$ | $88.98(5)$ |
| $\mathrm{I}(2)-\mathrm{Pt}(1)-\mathrm{P}(2)$ | $175.07(5)$ | $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{P}(2)$ | $87.75(7)$ |
| $\mathrm{I}(3)-\mathrm{Pt}(2)-\mathrm{I}(4)$ | $92.38(2)$ | $\mathrm{I}(3)-\mathrm{Pt}(2)-\mathrm{P}(3)$ | $178.01(5)$ |
| $\mathrm{I}(3)-\mathrm{Pt}(2)-\mathrm{P}(4)$ | $91.17(5)$ | $\mathrm{I}(4)-\mathrm{Pt}(2)-\mathrm{P}(3)$ | $89.38(5)$ |
| $\mathrm{I}(4)-\mathrm{Pt}(2)-\mathrm{P}(4)$ | $176.15(5)$ | $\mathrm{P}(3)-\mathrm{Pt}(2)-\mathrm{P}(4)$ | $87.05(7)$ |

### 4.4.2.2 "Tethered paddlewheel" complexes

In an attempt to make halide-free $\mathrm{Pt}^{I I}$ complexes of the pyridyldiphosphine ligands, $\mathrm{PtI}_{2}$ (dpype) and $\mathrm{PtI}_{2}$ (dpypcp) were treated with excess $\mathrm{AgNO}_{3}$ in glacial acetic acid/EtOH. Halide abstraction occurred, but the anticipated monomeric $\operatorname{Pt}(\mathrm{P}-\mathrm{P})\left(\mathrm{NO}_{3}\right)_{2}$ complexes did not result. Instead, the crystalline, two-dimensional coordination polymers $\left[\mathrm{Pt}_{2}(\text { dpype })_{2} \mathrm{Ag}_{4}\left(\mathrm{NO}_{3}\right)_{8}\left(\mathrm{H}_{2} \mathrm{O}\right)\right]_{n}$ (1) and $\left[\mathrm{Pt}_{2}(\text { dpypcp })_{2} \mathrm{Ag}_{6}\left(\mathrm{NO}_{3}\right)_{10}\right]_{n}$ (2) deposited from the reaction mixtures (Sections 4.7 .19 and 4.7.20). Work on these systems has been published. ${ }^{63}$

1 and 2 contain $\mathrm{Pt}_{2}$ face-to-face dimers bridged by $\mathrm{AgNO}_{3}$ clusters. The face-toface dimers result from simultaneous $P, P^{\prime}$ chelation and $\operatorname{bis}(P, N)$ bridging of the pyridyldiphosphine ligand, and because of their shape I have dubbed them "tethered paddlewheels" (as a subclass of the "paddlewheel" or "lantern" complexes which are prevalent in the literature. See Chart 4.5.) The difference between the two types is that in the tethered paddlewheel case the supporting ligand must be at least tetradentate so as to both bridge and chelate; in the paddlewheel case, bridging only is sufficient. The only other known, tethered paddlewheel complexes are $\mathrm{Rh}_{2} \mathrm{Cl}_{2}\left(\mathrm{P}_{2} \mathrm{~N}_{2}\right)_{2} \quad\left(\mathrm{P}_{2} \mathrm{~N}_{2}=\right.$ $(\mathrm{Ph})($ py $) \mathrm{P}(\mathrm{X}) \mathrm{P}($ py $)(\mathrm{Ph}) ; \mathrm{X}=\left(\mathrm{CH}_{2}\right)_{2},\left(\mathrm{CH}_{2}\right)_{3} ;$ py $=2$-pyridyl). ${ }^{45}$

## Chart 4.5


"Paddlewheel" or "lantern"

"Tethered paddlewheel"

The short M-M contacts (2.7-3.1 $\AA$ ) displayed by the "paddlewheel" complexes $\mathrm{Pt}_{2}$ (bridge) ${ }_{4}{ }^{\mathrm{nt}}$, the fluorescence and phosphorescence properties of these compounds, ${ }^{71-73}$ and their capacity to stabilize unusual oxidation states (e.g. $\mathrm{Pt}^{\mathrm{III}}-\mathrm{Pt}^{\mathrm{III}} 74-76$ and $\mathrm{Pt}^{\mathrm{II}}-\mathrm{Pt}^{\mathrm{III}}$ ${ }^{77,78}$ ), have drawn attention in the past two decades. The intermetallic distances in these compounds are generally shorter than those of the vast array of doubly-bridged dimers which have been synthesised by the reaction of cisplatin and its analogues with DNA bases and their derivatives. ${ }^{79}$ Various types of usually bidentate bridging ligands have been successfully employed in the synthesis of such tetrabridged dimers. The bridges have been of the $N-N^{\prime}$ type as in $\left[\mathrm{Pt}_{2}(\mathrm{mtpo})_{4}\right] \cdot 4 \mathrm{H}_{2} \mathrm{O}$ (Hmtpo $=4,7-\mathrm{H}-5$-methyl-7oxo[1,2,4]triazolo[1,5a]pyrimidine), ${ }^{80}$ of the $O-O$ type as in $\mathrm{Ba}_{2}\left[\mathrm{Pt}_{2}\left(\mathrm{C}_{4} \mathrm{O}_{4}\right)_{4}\right] \cdot 6 \mathrm{H}_{2} \mathrm{O}\left(\mathrm{C}_{4} \mathrm{O}_{4}\right.$ $=$ squarate), ${ }^{81}$ of the $S-S$ type, as in $\mathrm{Pt}_{2}\left(\mathrm{~S}_{2} \mathrm{CCH}_{3}\right)_{4},{ }^{82}$ and of the $P-P$ type, as in $\mathrm{K}_{4}\left[\mathrm{Pt}_{2}\left(\mathrm{P}_{2} \mathrm{O}_{5} \mathrm{H}_{2}\right)_{4}\right] .{ }^{83}$

## Structure descriptions

The overall structure of 1 is a two-dimensional coordination polymer, a section of which is shown in Figure 4.4; selected bond lengths and angles are given in Table 4.6. Each $\mathrm{Pt}_{2}$ (dpype) $)_{2}^{4+}$ unit is connected to four others by way of a "net" two $\mathrm{Ag}_{2}\left(\mathrm{NO}_{3}\right)_{4}\left(\mathrm{H}_{2} \mathrm{O}\right)^{2-}$ bridges. The structure of such a bridge is shown in Figure 4.5 (p. 179). The two Ag -atoms are inequivalent: for the first, $\operatorname{Ag}(1)$, the coordination geometry could be described as a severely distorted trigonal bipyramid, with roughly apical pyridyl N -atoms ( $\mathrm{N}(2)$ and $\mathrm{N}(4)^{*}$, one arising from each of the dpype ligands in the $\mathrm{Pt}_{2}$ (dpype) $)^{4+}$ cluster), and three O-atoms belonging to two $\mathrm{NO}_{3}{ }^{-}$groups; the second, $\mathrm{Ag}(2)$, shows eight-fold coordination via the O -atoms of four chelated $\mathrm{NO}_{3}{ }^{-}$anions. Two short (2.35-2.45 $\AA$ ), three medium
length (2.54-2.64 $\AA$ ) and three long $(2.85-3.00 \AA) \mathrm{Ag}-\mathrm{O}$ bonds are evidenced in this coordination environment. In addition, an $\mathrm{H}_{2} \mathrm{O}$ molecule is H -bonded to $\mathrm{O}(1)$. In the $\mathrm{Ag}_{2}\left(\mathrm{NO}_{3}\right)_{4}\left(\mathrm{H}_{2} \mathrm{O}\right)^{2-}$ bridge portion of the polymer, three distinct $\mathrm{NO}_{3}{ }^{-}$coordination modes are displayed: $\eta^{2}$-chelating $(O(7), O(8)), \mu-\eta^{2}, \eta^{2}$-bis(chelating) and bridging $(O(4), O(5)$, $O(6))$, and $\mu-\eta^{1}, \eta^{2}$-chelating and bridging $(O(1), O(2), O(3))$.

The $\mathrm{Pt}_{2}$ (dpype) ${ }_{2}{ }^{4+}$ cluster shown in Figure 4.6 (p. 180) consists of face-to-face $\mathrm{Pt}^{I I}$ square planar moieties arranged in a head-to-tail conformation, regarding the location of the $P$ - and $N$-donors. Each pyridylphosphine acts as a $P, P^{\prime}$-chelating agent at one Pt centre as well as a $P, N$-bridging ligand across the two Pt-centres. Thus, the P -atoms of each dpype ligand coordinate to one Pt-centre in a cis fashion, while two of the four o-py N -atoms (on each dpype) coordinate to the second Pt -atom forming a five-membered chelate ring containing a $\mathrm{P}-\mathrm{C}-\mathrm{N}$ bridge; the remaining two pyridyl N -atoms bond to Ag as discussed above.

The structure of the repeating unit of $\mathbf{2}$ is shown in Figure 4.7; selected bond lengths and angles are given in Table 4.7. The $\mathrm{Pt}_{2}$ (dpypcp) ${ }_{2}{ }^{4+}$ cluster is structurally analogous to the corresponding unit in $\mathbf{1}$. The silver nitrate bridges in $\mathbf{2}$, however, differ from those in 1 by the inclusion of one further $\mathrm{Ag}\left(\mathrm{NO}_{3}\right)$ unit and by the absence of an H bonded $\mathrm{H}_{2} \mathrm{O}$ molecule.


Figure 4.4 ORTEP representation ( $33 \%$ probability) of a section of 1 showing the $\mathrm{Ag}\left(\mathrm{NO}_{3}\right)$ connections between $\mathrm{Pt}^{\mathrm{II}}{ }_{2}$ (dpype $)_{2}$ moieties. The longer $\mathrm{Ag}-\mathrm{O}$ bonds, H -atoms, and the pyridyl C -atoms not involved in bridges to metal centres have been omitted for clarity.


Figure 4.5 ORTEP representation (33 \% probability) of the " $\mathrm{Ag}\left(\mathrm{NO}_{3}\right)$ bridge" of 1. "Short" Ag-O bonds are indicated by heavy lines, "medium" length bonds by double lines and "long" bonds by single lines.


Figure 4.6 ORTEP representation ( $33 \%$ probability) of the "tethered paddlewheel" $\mathrm{Pt}^{\mathrm{II}}{ }_{2}$ (dpype) ${ }_{2}$ moiety of 1 . Also shown are two Ag-atoms, each bound to one pyridyl N -atom of each dpype ligand. H -atoms have been omitted for clarity.

Table 4.6 Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 1 with estimated standard deviations in parentheses.*

| $\mathrm{Pt}(1)-\mathrm{Pt}(1)^{\text {a }}$ | 2.7690 (7) | $\mathrm{Pt}(1)-\mathrm{P}(1)$ | 2.252(2) |
| :---: | :---: | :---: | :---: |
| $\mathrm{Pt}(1)-\mathrm{P}(2)$ | 2.234(2) | $\mathrm{Pt}(1)-\mathrm{N}(1)^{\mathrm{a}}$ | 2.148 (8) |
| $\mathrm{Pt}(1)-\mathrm{N}(3)^{\mathrm{a}}$ | $2.131(7)$ | $\mathrm{Ag}(1)-\mathrm{O}(1)$ | 2.638(11) |
| $\mathrm{Ag}(1)-\mathrm{O}(4)$ | 2.552(10) | $\mathrm{Ag}(1)-\mathrm{O}(5)$ | 2.892(9) |
| $\mathrm{Ag}(1)-\mathrm{N}(2)$ | 2.282(8) | $\mathrm{Ag}(1)-\mathrm{N}(4)^{\text {a }}$ | 2.257(9) |
| $\mathrm{Ag}(2)-\mathrm{O}(2)$ | $2.436(12)$ | $\mathrm{Ag}(2)-\mathrm{O}(3)$ | 2.995 (10) |
| $\mathrm{Ag}(2)-\mathrm{O}(4)^{\mathrm{b}}$ | 2.642(11) | $\mathrm{Ag}(2)-\mathrm{O}(6)^{\mathrm{b}}$ | 2.546 (9) |
| $\mathrm{Ag}(2)-\mathrm{O}(7)$ | 2.378(13) | $\mathrm{Ag}(2)-\mathrm{O}(8)$ | 2.778(15) |
| $\mathrm{Ag}(2)-\mathrm{O}(10)$ | 2.83(2) | $\mathrm{Ag}(2)-\mathrm{O}(11)$ | 2.639(15) |
| $\mathrm{Pt}(1){ }^{\text {a }}-\mathrm{Pt}(1)-\mathrm{P}(1)$ | 85.09(6) | $\mathrm{Pt}(1)^{\mathrm{a}}-\mathrm{Pt}(1)-\mathrm{P}(2)$ | 91.18(7) |
| $\mathrm{Pt}(1) \mathrm{a}-\mathrm{Pt}(1)-\mathrm{N}(1)$ | 93.3(2) | $\mathrm{Pt}(1)^{\mathrm{a}}-\mathrm{Pt}(1)-\mathrm{N}(3)$ | 90.1(2) |
| $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{P}(2)$ | 84.47(9) | $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{N}(1)^{\text {a }}$ | 173.3(2) |
| $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{N}(3)^{\text {a }}$ | 94.8(2) | $\mathrm{P}(2)-\mathrm{Pt}(1)-\mathrm{N}(1)^{\text {a }}$ | 89.0(2) |
| $\mathrm{P}(2)-\mathrm{Pt}(1)-\mathrm{N}(3)^{\text {a }}$ | 178.5(2) | $\mathrm{N}(1)-\mathrm{Pt}(1)-\mathrm{N}(3)^{\text {a }}$ | 91.8(3) |
| $\mathrm{O}(1)-\mathrm{Ag}(1)-\mathrm{O}(4)$ | 90.5(4) | $\mathrm{O}(1)-\mathrm{Ag}(1)-\mathrm{O}(5)$ | 95.8(3) |
| $\mathrm{O}(1)-\mathrm{Ag}(1)-\mathrm{N}(2)$ | 79.3(3) | $\mathrm{O}(1)-\mathrm{Ag}(1)-\mathrm{N}(4)^{\mathrm{a}}$ | 114.3(3) |
| $\mathrm{O}(4)-\mathrm{Ag}(1)-\mathrm{O}(5)$ | 45.3(3) | $\mathrm{O}(4)-\mathrm{Ag}(1)-\mathrm{N}(2)$ | 88.2(3) |
| $\mathrm{O}(4)-\mathrm{Ag}(1)-\mathrm{N}(4)^{\mathrm{a}}$ | 116.1(3) | $\mathrm{O}(5)-\mathrm{Ag}(1)-\mathrm{N}(2)$ | 133.5(3) |
| $\mathrm{O}(5)-\mathrm{Ag}(1)-\mathrm{N}(4)^{\text {a }}$ | 73.0 (3) | $\mathrm{N}(2)-\operatorname{Ag}(1)-\mathrm{N}(4)^{\text {a }}$ | 150.8(3) |
| $\mathrm{O}(2)-\mathrm{Ag}(2)-\mathrm{O}(3)$ | 44.7(3) | $\mathrm{O}(2)-\mathrm{Ag}(2)-\mathrm{O}(4)^{\mathrm{b}}$ | 110.2(4) |
| $\mathrm{O}(2)-\mathrm{Ag}(2)-\mathrm{O}(6)^{\mathrm{b}}$ | 87.5(3) | $\mathrm{O}(2)-\mathrm{Ag}(2)-\mathrm{O}(7)$ | 118.8(4) |
| $\mathrm{O}(2)-\mathrm{Ag}(2)-\mathrm{O}(8)$ | 77.9(4) | $\mathrm{O}(2)-\mathrm{Ag}(2)-\mathrm{O}(10)$ | 112.2(4) |
| $\mathrm{O}(2)-\mathrm{Ag}(2)-\mathrm{O}(11)$ | 95.9(4) | $\mathrm{O}(3)-\mathrm{Ag}(2)-\mathrm{O}(4)^{\text {b }}$ | 115.1(3) |
| $\mathrm{O}(3)-\mathrm{Ag}(2)-\mathrm{O}(6)^{\text {b }}$ | 68.7(3) | $\mathrm{O}(3)-\mathrm{Ag}(2)-\mathrm{O}(7)$ | 149.9(4) |
| $\mathrm{O}(3)-\mathrm{Ag}(2)-\mathrm{O}(8)$ | 122.0(3) | $\mathrm{O}(3)-\mathrm{Ag}(2)-\mathrm{O}(10)$ | 70.6(3) |
| $\mathrm{O}(3)-\mathrm{Ag}(2)-\mathrm{O}(11)$ | 78.1(3) | $\mathrm{O}(4)-\mathrm{Ag}(2)-\mathrm{O}(6)^{\mathrm{b}}$ | 48.7(3) |
| $\mathrm{O}(4)-\mathrm{bg}(2)-\mathrm{O}(7)$ | 93.6(4) | $\mathrm{O}(4){ }^{\mathrm{b}}-\mathrm{Ag}(2)-\mathrm{O}(8)$ | 87.7(4) |
| $\mathrm{O}(4){ }^{\mathrm{b}}-\mathrm{Ag}(2)-\mathrm{O}(10)$ | 114.3(3) | $\mathrm{O}(4){ }^{\mathrm{b}}-\mathrm{Ag}(2)-\mathrm{O}(11)$ | 152.8(3) |
| $\mathrm{O}(6)^{\mathrm{b}}-\mathrm{Ag}(2)-\mathrm{O}(7)$ | 141.3(4) | $\mathrm{O}(6)^{\mathrm{b}}-\mathrm{Ag}(2)-\mathrm{O}(8)$ | 125.3(4) |
| $\mathrm{O}(6)^{\mathrm{b}}-\mathrm{Ag}(2)-\mathrm{O}(10)$ | 86.0(3) | $\mathrm{O}(6)^{\mathrm{b}}-\mathrm{Ag}(2)-\mathrm{O}(11)$ | 128.3(3) |
| $\mathrm{O}(7)-\mathrm{Ag}(2)-\mathrm{O}(8)$ | 46.7(4) | $\mathrm{O}(7)-\mathrm{Ag}(2)-\mathrm{O}(10)$ | 106.7(4) |
| $\mathrm{O}(7)-\mathrm{Ag}(2)-\mathrm{O}(11)$ | 79.8(4) | $\mathrm{O}(8)-\mathrm{Ag}(2)-\mathrm{O}(11)$ | 105.7(4) |
| $\mathrm{O}(8)-\mathrm{Ag}(2)-\mathrm{O}(10)$ | 148.3(4) | $\mathrm{O}(10)-\mathrm{Ag}(2)-\mathrm{O}(11)$ | 45.1(3) |

[^3]

Figure 4.7 ORTEP representation ( $33 \%$ probability) of the repeating unit of 2. Hatoms have been omitted for clarity.

Table 4.7 Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 2 with estimated standard deviations in parentheses.

| $\mathrm{Pt}(1)-\mathrm{Pt}(1)^{\mathrm{a}}$ | $2.7644(6)$ | $\mathrm{Pt}(1)-\mathrm{P}(1)$ | $2.241(2)$ |
| :--- | :---: | :--- | :--- |
| $\mathrm{Pt}(1)-\mathrm{P}(2)$ | $2.255(2)$ | $\mathrm{Pt}(1)-\mathrm{N}(2)^{\mathrm{a}}$ | $2.144(7)$ |
| $\mathrm{Pt}(1)-\mathrm{N}(3)^{\mathrm{a}}$ | $2.125(7)$ | $\mathrm{Ag}(1)-\mathrm{N}(1)$ | $2.301(7)$ |
| $\mathrm{Ag}(1)-\mathrm{N}(4)^{\mathrm{a}}$ | $2.232(8)$ | $\mathrm{Ag}(1)-\mathrm{O}(97)$ | $2.518(10)$ |
| $\mathrm{Ag}(2)-\mathrm{O}(94)$ | $2.50(2)$ | $\mathrm{Ag}(2)-\mathrm{O}(90)$ | $2.537(10)$ |
| $\mathrm{Ag}(2)-\mathrm{O}(97)$ | $2.579(10)$ | $\mathrm{Ag}(3)-\mathrm{O}(90)$ | $2.513(11)$ |
| $\mathrm{Ag}(3)-\mathrm{O}(102)$ | $2.423(9)$ | $\mathrm{Ag}(3)-\mathrm{O}(99)$ | $2.362(11)$ |
| $\mathrm{Pt}(1)^{\mathrm{a}}-\mathrm{Pt}(1)-\mathrm{P}(1)$ | $89.54(6)$ | $\mathrm{Pt}(1)^{\mathrm{a}}-\mathrm{Pt}(1)-\mathrm{P}(2)$ | $86.78(6)$ |
| $\mathrm{Pt}(1)^{\mathrm{a}}-\mathrm{Pt}(1)-\mathrm{N}(2)^{\mathrm{a}}$ | $90.5(2)$ | $\mathrm{Pt}(1)^{\mathrm{a}}-\mathrm{Pt}(1)-\mathrm{N}(3)^{\mathrm{a}}$ | $93.0(2)$ |
| $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{P}(2)$ | $85.99(8)$ | $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{N}(2)^{\mathrm{a}}$ | $177.7(2)$ |
| $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{N}(3)^{\mathrm{a}}$ | $88.2(2)$ | $\mathrm{P}(2)-\mathrm{Pt}(1)-\mathrm{N}(2)^{\mathrm{a}}$ | $91.8(2)$ |
| $\mathrm{P}(2)-\mathrm{Pt}(1)-\mathrm{N}(3)^{\mathrm{a}}$ | $174.2(2)$ | $\mathrm{N}(2)^{\mathrm{a}}-\mathrm{Pt}(1)-\mathrm{N}(3)^{\mathrm{a}}$ | $94.1(3)$ |
| $\mathrm{N}(4)^{\mathrm{a}}-\mathrm{Ag}(1)-\mathrm{N}(1)$ | $153.6(3)$ | $\mathrm{N}(4)^{\mathrm{a}}-\mathrm{Ag}(1)-\mathrm{O}(97)$ | $123.6(3)$ |
| $\mathrm{N}(1)-\mathrm{Ag}(1)-\mathrm{O}(97)$ | $79.6(3)$ | $\mathrm{O}(94)-\mathrm{Ag}(2)-\mathrm{O}(90)$ | $130.9(4)$ |
| $\mathrm{O}(94)-\mathrm{Ag}(2)-\mathrm{O}(97)$ | $126.6(5)$ | $\mathrm{O}(90)-\mathrm{Ag}(2)-\mathrm{O}(97)$ | $80.9(4)$ |
| $\mathrm{O}(99)-\mathrm{Ag}(3)-\mathrm{O}(102)$ | $144.3(4)$ | $\mathrm{O}(99)-\mathrm{Ag}(3)-\mathrm{O}(90)$ | $122.7(4)$ |
| $\mathrm{O}(102)-\mathrm{Ag}(3)-\mathrm{O}(90)$ | $91.0(3)$ | $\mathrm{Ag}(1)-\mathrm{O}(97)-\mathrm{Ag}(2)$ | $137.7(4)$ |
| $\mathrm{Ag}(2)-\mathrm{O}(90)-\mathrm{Ag}(3)$ | $154.4(4)$ |  |  |

${ }^{a}$ Refers to the symmetry operations: 2-x, $-y, 1-z$.

All four of the P -atoms in 1 and 2, as well as all four of the methine C -atoms $(C(1), C(1 A), C(5), C(5 A))$ in the ligand backbones of 2 are chiral. The fact that $\mathbf{1}$ and 2 crystallize in a centrosymmetric space group, with the centre of inversion lying midway between the Pt-atoms, ensures that each enantiomeric centre is represented by equal populations of $R$ and $S$ absolute configurations.

## Pt-Pt bonding

As the Pt-Pt separations in the $\mathrm{Pt}_{2} \mathrm{~L}_{2}{ }^{4+}$ cores of polymers 1 and 2 are comparable to the intermetallic distances found for some dimers which contain formal Pt-Pt single bonds, the metal centres of these clusters are definitely within range to interact. The Pt-Pt distances in $1(2.769 \AA)$ and $2(2.764 \AA)$ are essentially the same as those found in the relatively rare $\mathrm{d}^{7}-\mathrm{d}^{7} \mathrm{Pt}^{I I I}{ }_{2}$ dimers which are unsupported by bridging ligands, e.g. cis- and trans- $\left[\mathrm{PtCl}_{3}(\mathrm{HN}=\mathrm{C}(\mathrm{Me})(\mathrm{OMe}))_{2}\right]_{2}\left(2.765\right.$ and $2.758 \AA$, respectively), ${ }^{84}$ and in the $\mathrm{d}^{8}-\mathrm{d}^{8}$ $\mathrm{Pt}^{\mathrm{II}}{ }_{2} \mathrm{~T}$-over-square $\left(\mathrm{ML}_{4}-\mathrm{ML}_{3}\right)$ dimers, e.g. $\left[(\mathrm{Me})_{2} \mathrm{Pt}(\mu-\mathrm{dppm})_{2} \mathrm{Pt}(\mathrm{Me})\right]^{+}(2.769 \AA) .85$

Face-to-face $\mathrm{d}^{8}-\mathrm{d}^{8}$ dimers of the type $\mathrm{M}_{2} \mathrm{~L}_{8}{ }^{\mathrm{n+}}$ of formal $\sigma^{2} \pi^{4} \delta^{2} \delta^{* 2} \pi^{* 4} \sigma^{* 2}$ configuration display a net $\mathrm{M}-\mathrm{M}$ bond order of 0 ; in addition, Cotton et al. have determined by $\mathrm{X} \alpha \mathrm{MO}$ calculations ${ }^{86}$ that, at least in the case of the model compounds $\mathrm{M}^{\mathrm{II}}{ }_{2}(\mathrm{HNCHNH})_{4}(\mathrm{M}=\mathrm{Ni}, \mathrm{Pd})$, no pair of $n \mathrm{~s}$ or $n \mathrm{p}$ orbitals on different metal centres overlaps in such a way as to provide an additional bonding orbital that can be filled at the expense of an antibonding d-based orbital. Therefore, it is often difficult to determine whether there is indeed an M-M interaction or whether the metal centres are merely held in proximity by the bridging ligands. ${ }^{87}$ Cotton's calculations and those of Mealli et al. ${ }^{88}$ do show, however, that a weak M-M bond arises through hybridization of the metal $n \mathrm{~d}_{z}{ }^{2}$ with the $(n+1) \mathrm{s}$ and $(n+1) \mathrm{p}_{z}$ orbitals. In addition, calculations by Navarro et al. ${ }^{80}$ for the model compound $\mathrm{Pt}_{2}\left(\mathrm{HNCHN}\left(\mathrm{C}\left(=\mathrm{CH}_{2}\right) \mathrm{Me}\right)\right)_{4}$ locate stabilizing charge density (of cylindrical symmetry) between the Pt-atoms equal to roughly half of that located between the Pt - and N -atoms. These things being so, a weak Pt-Pt bond probably does exist in the $\mathrm{Pt}_{2} \mathrm{~L}_{2}{ }^{4+}$ cores of polymers $\mathbf{1}$ and 2.

Pauling's resonating valence bond theory of metals (RVBM), ${ }^{89,90}$ which has been successful in correlating empirical data, relates the distance between two closely juxtaposed and interacting metal centres to the bond order between them by

$$
\begin{equation*}
\mathrm{D}_{\mathrm{n}}=\mathrm{D}_{0}-a \log n \tag{4.1}
\end{equation*}
$$

where $\mathrm{D}_{\mathrm{n}}$ is the intermetallic distance, $\mathrm{D}_{0}$ is twice the covalent radius of the metal (2.590 $\AA$ for Pt ), $a$ is an empirically-derived constant and $n$ is the bond order. Investigations by Reis and Peterson into partially-oxidized Pt blues ${ }^{91}$ fix the value of $a=0.68$ for Pt. For comparison with $\mathbf{1}$ and 2, the Pt-Pt distances and respective bond orders calculated by eq. 4.1 for some paddlewheel complexes are collected in Table 4.8; the data imply significant Pt-Pt interaction in $\mathbf{1}$ and $\mathbf{2}$, with bond orders of magnitude similar to those found for other tetrabridged structures.

Table 4.8 Pt-Pt separations and calculated bond orders for some known paddlewheel complexes (tw = this work).

| Type of Bridge | Compound | Pt-Pt $(\AA)$ | Bond <br> Order, $n$ | Ref. |
| :---: | :--- | :---: | :---: | :---: |
| P-P | $\mathrm{K}_{4}\left[\mathrm{Pt}_{2}\left(\mathrm{P}_{2} \mathrm{O}_{5} \mathrm{H}_{2}\right)_{4}\right] \cdot 2 \mathrm{H}_{2} \mathrm{O}$ | 2.925 | 0.29 | 83 |
| $\mathrm{~N}-\mathrm{N}$ | $\mathrm{Pt}_{2}(\mathrm{mtpo})_{4} \cdot 4 \mathrm{H} 2 \mathrm{O}$ | 2.744 | 0.57 | 80 |
| $\mathrm{O}-\mathrm{O}$ | $\mathrm{Ba}_{2}\left[\mathrm{Pt}_{2}\left(\mathrm{C}_{4} \mathrm{O}_{4}\right)_{4}\right] \cdot 6 \mathrm{H}_{2} \mathrm{O}$ | 3.061 | 0.18 | 81 |
| $\mathrm{~S}-\mathrm{S}$ | $\mathrm{Pt}_{2}\left(\mathrm{~S}_{2} \mathrm{CCH}_{3}\right)_{4}$ | 2.767 | 0.52 | 82 |
| $\mathrm{P}-\mathrm{N}$ | $\left[\mathrm{Pt}_{2}(\text { dpype })_{2} \mathrm{Ag}_{4}\left(\mathrm{NO}_{3}\right)_{8}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]_{n}, \mathbf{1}$ | 2.769 | 0.52 | tw |
| $\mathrm{P}-\mathrm{N}$ | $\left[\mathrm{Pt}_{2}(\text { dpypcp })_{2} \mathrm{Ag}_{6}\left(\mathrm{NO}_{3}\right)_{10}\right]_{n}, \mathbf{2}$ | 2.764 | 0.53 | tw |

## Aqueous solution chemistry

Although aqueous solutions of 1 slowly precipitate Ag metal (over ca. 48 h ) even when stored in the dark, the UV-vis spectra of the solutions (from $350-800 \mathrm{~nm}$ ) are invariant over time. In addition, the ${ }^{1} \mathrm{H}$ NMR spectrum of 1 in $\mathrm{D}_{2} \mathrm{O}$ shows no splitting in the pyridyl region (specifically in the doublet at $\delta 8.58$ which is attributed to $\mathrm{H}_{6}{ }^{57,58}$ ) and thus the absence of 3-bond ${ }^{1} \mathrm{H}-{ }^{107 / 109} \mathrm{Ag}$ coupling. These facts, taken in conjunction with the known low formation constants of Ag-pyridine species, ${ }^{92}$ show that upon dissolution of 1 in $\mathrm{H}_{2} \mathrm{O}$ the $\mathrm{Ag}^{1}$ ions dissociate from the $\mathrm{Pt}_{2} \mathrm{~L}_{2}^{4+}$ core and that it is this core which is responsible for the observed solution spectra. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of 1 in $\mathrm{D}_{2} \mathrm{O}$ shows a basic singlet for equivalent P -atoms with Pt-satellites via one- and three-bond coupling (cf. Figure 4.6).

The $\mathrm{Pt}_{2}$ (dpype) ${ }_{2}{ }^{4+}$ core can be synthesised independently, i.e., in the absence of $\mathrm{Ag}^{+}$. This is accomplished by reacting $\mathrm{PtI}_{2}(\operatorname{cod})$ with $\mathrm{AgNO}_{3}$ in $\mathrm{EtOH} / \mathrm{H}_{2} \mathrm{O}$ (which results presumably either in $\left[\mathrm{Pt}(\mathrm{S})_{2}(\operatorname{cod})\right]\left[\mathrm{NO}_{3}\right]_{2}\left(\mathrm{~S}=\mathrm{H}_{2} \mathrm{O}\right.$ or EtOH$)$ or $\left.\mathrm{Pt}\left(\mathrm{NO}_{3}\right)_{2}(\operatorname{cod})\right)$ and
removing the solid AgI prior to addition of 1 equiv. of the dpype ligand (Section 4.7.21). In this manner, the complex $\left[\mathrm{Pt}_{2}(\mathrm{dpype})_{2}\right]\left[\mathrm{NO}_{3}\right]$ can be isolated as a dihydrate. This complex has solution UV and NMR spectroscopic properties identical to those of the analogous coordination polymer.

### 4.4.2.3 Palladium(II) pyridyldiphosphine complexes

Whereas the $\mathrm{Pt}^{\mathrm{II}}$ dpypcp complexes are straightforward to make, the $\mathrm{Pd}^{\mathrm{II}}$ analogues pose a slight synthetic challenge, because Pd is generally more reactive than Pt. Thus, if no precautions are taken to control the relative concentrations of the reactants, addition of solvent to a $1: 1$ mixture of trans $-\mathrm{PdCl}_{2}(\mathrm{PhCN})_{2}$ and dpypcp generates three products. The first is a beige precipitate, easily isolated from the other two components by filtration prior to the work-up; this powder is completely insoluble in all common deuterated solvents and could not be analysed by solution NMR spectroscopy. Elemental analysis showed, however, that it has the empirical formula $\mathrm{Pd}_{2} \mathrm{Cl}_{4}(\mathrm{dpypcp})$. The formation of this precipitate could never be completely eliminated. The remaining two components are $\mathrm{PdCl}_{2}$ (dpypcp) and $\left[\mathrm{Pd}(\text { dpypcp })_{2}\right] \mathrm{Cl}_{2}$. Although the analogous synthesis of $\mathrm{PtCl}_{2}$ (dpypcp) is sometimes complicated by the production of $\left[\mathrm{Pt}(\mathrm{dpypcp})_{2}\right] \mathrm{Cl}_{2}$, its abundance is not as great as in the case of Pd . This is attributed to two factors: $\mathrm{PdCl}_{2}$ (dpypcp) is more reactive toward a second dpypcp molecule than is $\mathrm{PtCl}_{2}$ (dpypcp), and Pd has a higher affinity for the pyridyl N -atoms than does Pt , which presumably causes formation of the 2:1 adduct $\mathrm{Pd}_{2} \mathrm{Cl}_{4}$ (dpypcp). Formation of this species lowers the concentration of trans$\mathrm{PdCl}_{2}(\mathrm{PhCN})_{2}$ in solution and raises the ligand:metal ratio, so promoting the formation of $\left[\operatorname{Pd}(\text { dpypcp })_{2}\right] \mathrm{Cl}_{2}$. The formation of the $2: 1$ adduct was retarded by appropriate choice of Pd precursor. Thus, use of $\mathrm{PdCl}_{2}$ (cod) gives better results as cod is less easily displaced than PhCN (Sections 4.7.15, 4.7.16 and 4.7.17).

Once again, the presence of downfield singlets in the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra of all the $\mathrm{Pd}^{\text {II }}$ pyridyldiphosphine compounds indicates molecular $C_{2}$ symmetry and exclusive $P, P$ ' bonding of the ligand in 5 -membered metallacycles (see Section 4.4.2.1). Contrary to the case of $\mathrm{Pd}^{11}$ complexes of the $\mathrm{PN}_{n}$ ligand family, ${ }^{29}$ there is no cis/trans ambiguity here: the complexes are exclusively cis as enforced by the cyclopentane ring linking the two P -atoms of the ligand.

### 4.4.3 $\quad \mathbf{P t}^{\mathbf{0}}$ and $\mathbf{P d}^{\mathbf{0}}$ pyridyldiphosphine complexes

The initial work on the synthesis and characterisation of $\mathrm{M}^{0}(\mathrm{M}=\mathrm{Pd}, \mathrm{Pt})$ complexes of the pyridyldiphosphine ligands dpype and dpypcp was performed by Smith. ${ }^{55}$ Although several complexes were reported as being prepared in situ, they were not isolated, and characterisations were limited to ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR data.

Smith ascertained that these compounds could be accessed by two basic routes: by reduction of the appropriate $\left[\mathrm{M}(\mathrm{P}-\mathrm{P})_{2}\right] \mathrm{Cl}_{2}$ compound with either $\mathrm{N}_{2} \mathrm{H}_{4}$ in DMSO or $\mathrm{NaBH}_{4}$ in MeOH , or by reaction of a suitable $\mathrm{M}^{0}$ precursor (e.g., $\left.\mathrm{M}\left(\mathrm{PPh}_{3}\right)_{4}\right)$ with either 1 or 2 equiv. of the ligand. The latter ligand substitution route was chosen in this work because the reduction route was not as high yielding.

The pyridyldiphosphine ligands react with $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{4}$ in $\mathrm{C}_{6} \mathrm{H}_{6}$ solution at r.t. to form the presumably tetrahedral $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}(\mathrm{P}-\mathrm{P})$ and $\mathrm{Pt}(\mathrm{P}-\mathrm{P})_{2}$ depending on the metal:ligand ratio (Sections 4.7.22-4.7.25). Unlike the $\mathrm{Pt}^{I I}$ case, 1 equiv. of ligand reacts to form $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)(\mathrm{P}-\mathrm{P})$ exclusively; no sign of the $1: 2$ adduct is observed, even if no precautions are taken to control the relative concentrations of the reactants. This result contrasts with that of the analogous reaction of $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{4}$ with 1 equiv. of dppe which produces predominantly the $1: 2$ adduct $\operatorname{Pt}(\mathrm{dppe})_{2} .{ }^{55}$ There is no obvious reason for this difference although it may involve the lower basicity of the pyridyldiphosphines with respect to their phenyl analogues (see Section 4.4.2.1).

Xie made both $\operatorname{Pt}\left(\mathrm{PN}_{3}\right)_{4}$ and $\operatorname{Pt}\left(\mathrm{PN}_{1}\right)_{3}$ by methods analogous to those used in the preparation of $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{4}$ and has shown that in contrast to the $\mathrm{PPh}_{3}$ compound, which undergoes significant dissociation in $\mathrm{C}_{6} \mathrm{H}_{6}$ at r.t. to give $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{3},{ }^{93}$ the $\mathrm{PN}_{n}$ complexes show no tendency to lose phosphine. ${ }^{18}$ The same observation holds for $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}(\mathrm{P}-\mathrm{P})$; these compounds give rise to sharp NMR spectra that contain no peaks due to free $\mathrm{PPh}_{3}$ or P-P.

The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of $\operatorname{Pt}\left(\mathrm{PPh}_{3}\right)_{2}($ dpypcp) (Figure 4.8) is the expected result for a non-fluxional, 4-coordinate complex in which two sets of two chemically equivalent P -atoms couple with each other and with ${ }^{195} \mathrm{Pt}$ to give 18 lines. By virtue of its similar chemical shift in the corresponding spectrum of $\operatorname{Pt}\left(\mathrm{PPh}_{3}\right)_{2}($ dpype $)(\delta 21.3)$, the triplet at $\delta 23.1$ is assigned to the P -atoms associated with the $\mathrm{PPh}_{3}$ ligands. This assignment results in $\delta 14.6$ and 32.0 for the P -atoms associated with the
pyridyldiphosphine ligands of $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}$ (dpypcp) and $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}$ (dpype), respectively, and is consistent with the fact that in all previously made pyridyldiphosphine complexes of $\mathrm{Ni}^{\mathrm{II}},{ }^{31} \mathrm{Pd}^{\text {II }}$ (Section 4.4.2.3) and $\mathrm{Pt}^{\mathrm{II}}$ (Section 4.4.2.1), the peaks due to dpype fall significantly downfield of those due to dpypcp. Accordingly, the ${ }^{1} J_{\mathrm{PPt}}$ values for the $\mathrm{PPh}_{3}$ ligands are significantly larger than those of the pyridyldiphosphine ligands (by 660 and 850 Hz for $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}$ (dpypcp) and $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}$ (dpype), respectively). This result is consistent with studies by Chatt et al. ${ }^{94}$ and Al-Ohaly and Nixon ${ }^{95}$ on the series of compounds $\mathrm{Pt}(\mathrm{P})(\mathrm{P}-\mathrm{P}-\mathrm{P})$ ( $\mathrm{P}=$ a monodentate tertiary phosphine; $\mathrm{P}-\mathrm{P}-\mathrm{P}=$ triphos ). These researchers found that although the magnitude of ${ }^{1} J_{\text {PPt }}$ increases with increasing electronegativity of the groups directly bonded to the ligand P (e.g., ${ }^{1} J_{\mathrm{PPt}}=5400$ and 10200 Hz for $\mathrm{P}=\mathrm{PPh}_{3}$ and $\mathrm{PF}_{3}$, respectively), small $\mathrm{P}-\mathrm{Pt}-\mathrm{P}$ angles imposed by chelating ligands result in smaller than predicted ${ }^{1} J_{\text {PPt }}$ values. Thus, the anticipated result that the pyridyldiphosphine ligand should show larger ${ }^{1} J_{\mathrm{PPt}}$ values than the $\mathrm{PPh}_{3}$ ligand because of the greater electronegativity of py vs. Ph is not observed in $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)(\mathrm{P}-\mathrm{P})$. In addition, the ${ }^{2} J_{\mathrm{PP}}$ values recorded for this series of complexes range from $51-95 \mathrm{~Hz}$, which makes $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)($ dpypcp $)\left({ }^{2} J_{\mathrm{PP}}=52 \mathrm{~Hz}\right)$ and $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}($ dpype $)\left({ }^{2} J_{\mathrm{PP}}=53 \mathrm{~Hz}\right)$ typical.


Figure 4.8 The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \quad \mathrm{NMR} \quad\left(162 \mathrm{MHz}, ~ \mathrm{C}_{6} \mathrm{D}_{6}, \quad 300 \mathrm{~K}\right)$ spectrum of $\operatorname{Pt}\left(\mathrm{PPh}_{3}\right)_{2}$ (dpypcp).

Suspension of $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{4}$ in boiling EtOH gives the isolable, yellow, trigonal planar $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{3} .{ }^{93}$ Reaction of this with 1 equiv. of dpypcp gave $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}$ (dpypcp) exclusively and not the intended 3-coordinate complex $\operatorname{Pt}\left(\mathrm{PPh}_{3}\right)$ (dpypcp). A possible explanation is that the bite angle of dpypcp constrains the P -atoms so as to prohibit the $\mathrm{P} — \mathrm{Pt}-\mathrm{P}$ angle of $120^{\circ}$ required to stabilise trigonal planar $\mathrm{M}^{0}$ complexes. In another attempt to make a 3-coordinate complex, $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}(\mathrm{dpypcp})$ was subjected to an excess of the bulky and basic $\mathrm{PCy}_{3}$. It was reasoned that the steric demand of this ligand would compensate for the small bite angle of the chelating pyridyldiphosphine and stabilise the 3-coordinate substitution product. However, there was no reaction.

The $\operatorname{Pt}\left(\mathrm{PPh}_{3}\right)_{2}(\mathrm{P}-\mathrm{P})$ compounds are orange, air-stable, microcrystalline solids which in solution are $\mathrm{O}_{2}$-sensitive; exposure to air of $\mathrm{C}_{6} \mathrm{H}_{6}$ solutions containing the complexes results in the slow formation of $\mathrm{P}-\mathrm{P}(\mathrm{O})_{2}$ and $\mathrm{OPPh}_{3}$, presumably due the mechanism outlined by Halpern and Sen. ${ }^{56}$ The 1:2 adducts $\operatorname{Pt}(\mathrm{P}-\mathrm{P})_{2}$ are air-sensitive, red solids.

The analogous $\mathrm{Pd}^{0}$ complexes, $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{2}(\mathrm{P}-\mathrm{P})$, were not isolated because of the lability and reactivity of the $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}$ precursor, but $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{2}$ (dpype) was prepared in situ. Reaction of 1 equiv. of $\mathrm{P}-\mathrm{P}$ with $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}$ in $\mathrm{C}_{6} \mathrm{H}_{6}$ at r.t. resulted in partial formation of $\mathrm{Pd}(\mathrm{P}-\mathrm{P})_{2}$. To work around this problem, the same reaction was conducted on an ice-bath in the presence of a 5 -fold excess of $\mathrm{PPh}_{3}$; these conditions limited the dissociation of $\mathrm{PPh}_{3}$ from Pd , and reaction with dpype gave $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{2}$ (dpype) as the major product: $\delta_{\mathrm{P}} 26.7\left(\mathrm{t},{ }^{2} J_{\mathrm{PP}}=24.7 \mathrm{~Hz}\right), 29.1\left(\mathrm{t},{ }^{2} J_{\mathrm{PP}}=24.7 \mathrm{~Hz}\right)$. The only reported $\mathrm{Pd}^{0}{ }^{0}$ pyridylphosphines are $\operatorname{Pd}\left(\mathrm{PN}_{1}\right)_{3}, \operatorname{Pd}\left(\mathrm{PN}_{1}\right)_{2}(\mathrm{dba})$ and $\operatorname{Pd}\left(\mathrm{PN}_{1}\right)_{2}\left(\eta^{2}\right.$-DMAD).${ }^{96}$

### 4.4.3.1 Reaction of $\operatorname{Pt}\left(\mathrm{PPh}_{3}\right)_{2}(\mathbf{P}-\mathbf{P})$ with maleic and fumaric acid diesters

Reactions between prochiral olefins and $C_{2}$-symmetric chiral metal-diphosphine complexes continue to attract attention because of their relevance to asymmetric catalysis. ${ }^{97}$ The two routes to $\mathrm{Pt}^{0}$-olefin complexes are reduction of $\mathrm{Pt}^{\text {II }}$ precursors in the presence of the olefin, and displacement of a labile ligand from $\mathrm{Pt}^{0}$ by the olefin. Thus, for example, stilbene complexes can be made by reduction of $\mathrm{PtCl}_{2}\left(\mathrm{PPh}_{3}\right)_{2}$ with $\mathrm{N}_{2} \mathrm{H}_{4}$ followed by addition of the olefin; 98 and treatment of $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{4}$ with chloro-, ${ }^{99}$ fluoro-100
and cyanoolefins ${ }^{101}$ in refluxing $\mathrm{C}_{6} \mathrm{H}_{6}$ gives the corresponding $\operatorname{Pt}\left(\mathrm{PPh}_{3}\right)_{2}\left(\eta^{2}\right.$-olefin $)$ complexes. The latter route was chosen as the synthetic method for $\mathrm{Pt}^{0}$-olefin complexes of the pyridyldiphosphines.

The $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}(\mathrm{P}-\mathrm{P})$ complexes react with dimethyl- and diethylmaleate (dmm and dem, respectively) to form $\operatorname{Pt}\left(\eta^{2}\right.$-olefin $)(\mathrm{P}-\mathrm{P})$ complexes. The fumarate compounds $\operatorname{Pt}\left(\eta^{2}-\mathrm{dmf}\right)($ dpypcp $)$ and $\operatorname{Pt}\left(\eta^{2}-\mathrm{def}\right)(d p y p c p)$ were isolated from the corresponding reactions with dmm and dem (see Sections 4.7.26 and 4.7.27, respectively, for syntheses, and below for discussion); these compounds were characterised by ${ }^{1} \mathrm{H}$ and ${ }^{31} \mathrm{P}$ NMR spectroscopy and elemental analysis, and, in the case of the former complex, by X-ray crystallography. The maleate analogues were characterised in situ in $\mathrm{C}_{6} \mathrm{D}_{6}$ solution by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy. A summary of the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR data is given in Table 4.9.

Table $4.9 \quad{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR data for $\mathrm{Pt}(\mathrm{P}-\mathrm{P})\left(\eta^{2}\right.$-olefin $)$ complexes.

| $\mathbf{P}-\mathbf{P}$ | Olefin | ${ }^{31} \mathbf{P}\{\mathbf{H} \mathbf{H}\}$ NMR chemical shift $(\mathrm{ppm})\left[{ }^{1} J_{\mathrm{Ppt}}(\mathrm{Hz})\right]$ |
| :---: | :---: | :---: |
| dpypcp | $\operatorname{dmf}^{a, b}$ | Major: $33.1[3360]$ |
|  | $\operatorname{def}^{a, b}$ | Minor: $31.8[3400]$ |
|  |  | Major: $33.6[3360]$ |
|  | dem $^{c, d}$ | Minor: $32.1[3410]$ |
| dpype | $\operatorname{def}^{c}$ | $35.4[3260], 33.3[3290]$ |
|  | $\operatorname{dem}^{c}$ | $60.3[3290]$ |
|  |  | $59.8[3300]$ |

[^4]The isolated product from the reaction of excess dmm with $\operatorname{Pt}\left(\mathrm{PPh}_{3}\right)_{2}(\mathrm{dpypcp})$ was not the expected $\operatorname{Pt}\left(\eta^{2}-\mathrm{dmm}\right)(d p y p c p)$ but rather $\operatorname{Pt}\left(\eta^{2}-\mathrm{dmf}\right)($ dpypcp) (Section 4.7.26); and indeed, this reaction produced crystals whose molecular structure is depicted in Figure 4.12 (p. 196). Selected bond distances and angles are given in Table 4.10. Although this result indicated that the metal mediated a cis to trans olefin isomerisation, doubt arose about this when analysis by GC of the dmm used showed that it contained $c a$. $2 \% \mathrm{dmf}$, a more than sufficient amount to react with all of the Pt , and the isolated yield was only $47 \%$. The same observations were made for the dem reaction, although the
abundance of def was approximately $10 \%$ as determined by NMR spectroscopy. Monitoring the $1: 1$ reaction between $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}$ (dpypcp) and dem in $\mathrm{C}_{6} \mathrm{D}_{6}$ by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR over 2 d indicated that both $\operatorname{Pt}\left(\eta^{2}-\mathrm{dem}\right)\left(\right.$ dpypcp ) and $\operatorname{Pt}\left(\eta^{2}-\mathrm{def}\right)($ dpypcp $)$ were formed initially (in the expected 9:1 ratio) and that their relative concentrations did not change over time. In addition, reaction between excess dem and $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}$ (dpypcp) did not result in the catalytic conversion of dem to def.

This result contrasts with that observed by Xie and James who determined that the initial product, $\operatorname{Pt}\left(\mathrm{PN}_{1}\right)_{2}\left(\eta^{2}\right.$-dem $)$, of the reaction between dem and $\operatorname{Pt}\left(\mathrm{PN}_{1}\right)_{3}$ converted over hours into $\operatorname{Pt}\left(\mathrm{PN}_{1}\right)_{2}\left(\eta^{2}\right.$-def $)$ in $\mathrm{CDCl}_{3}$ solution at $293 \mathrm{~K} .{ }^{18}$ If the cis to trans isomerisation proceeds through an ylide transition state as shown in Scheme 4.2, ${ }^{102}$ then the process should occur more readily in polar solvents that would tend to stabilise the charge separation. This has been proposed earlier in the substitution reaction between $\operatorname{Pt}\left(\mathrm{PPh}_{3}\right)_{2}\left(\eta^{2}\right.$-stilbene) and an excess of a $1: 1$ mixture of cis/trans-1,2-dichloro-1,2difluoroethylene which gave $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}\left(\eta^{2}-\mathrm{ClFC}=\mathrm{CFCl}\right)$ in a trans:cis ratio of 2.3:1 when the reaction was conducted in $\mathrm{Et}_{2} \mathrm{O}$ and in a 2.9:1 ratio in $\mathrm{CH}_{3} \mathrm{CN} .{ }^{102}$ In order to determine whether the difference in the olefin isomerisation behaviour of $\operatorname{Pt}\left(\mathrm{PN}_{1}\right)_{3}$ in $\mathrm{CDCl}_{3}$ and $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}$ (dpypcp) in $\mathrm{C}_{6} \mathrm{D}_{6}$ was due to a solvent effect, excess dem was reacted with $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}$ (dpypcp) in $\mathrm{CDCl}_{3}$ solution and the reaction monitored at 300 K by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy.

## Scheme 4.2



A portion of the $300 \mathrm{~K}^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}$ (dpypcp) dissolved in $\mathrm{CDCl}_{3}$ (in the absence of dem) is shown in Figure 4.9. This spectrum is dramatically different from that observed for the same complex in $\mathrm{C}_{6} \mathrm{D}_{6}$ (Figure 4.8). It consists of (1) a $2^{\text {nd }}$-order pattern centred at $\delta 23.6$ and a pseudo-triplet at $\delta 17.2$ that together constitute
an ABX pattern; (2) a broad peak at $\delta-5$ due to $\mathrm{PPh}_{3}$ which is involved in a fluxional process; and (3) singlets at $\delta 18.5$ and 29.6 due to $\mathrm{PtCl}_{2}$ (dpypcp) and $\mathrm{OPPh}_{3}$, respectively.


Figure 4.9 The $\delta 15-29$ range of the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ) spectrum of $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}$ (dpypcp). The peak due to $\mathrm{PtCl}_{2}$ (dpypcp) is marked by an asterisk (*), and those of $\left[\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)(\mathrm{dpypcp})\right]^{+}$by the number symbol (\#). Pt satellites for all peaks fall outside of this window.

The ABX pattern is consistent with a Pt complex in which 3 P -atoms are coordinated at the corners of a " $T$ ", indicating a change in geometry from tetrahedral to square planar on dissolution of $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}$ (dpypcp) in $\mathrm{CDCl}_{3}$. One P -atom holds a cis disposition to the other two while the remaining pair are each cis to one P -atom and trans to each other; this is reflected in the ${ }^{2} J_{\mathrm{PP}}$ values: two are small ( $c a .18 \mathrm{~Hz}$ ), consistent with cis P -atoms giving rise to the pseudo-triplet due to their very similar magnitudes, while the other is much larger $(384 \mathrm{~Hz})$ and consistent with trans P -atoms. In accordance with this, two ${ }^{1} J_{\mathrm{PPt}}$ values are consistent with mutually trans P-atoms ( 2370 and 2440 Hz ), while the other lies in the range observed for cis P-atoms ( 3640 Hz ). ${ }^{67,68}$

The ${ }^{1} J_{\mathrm{PPt}}$ and ${ }^{2} J_{\mathrm{PP}}$ values for the complex giving rise to the ABX pattern are very similar to those observed by Anderson and Lumetta for the broad family of cations $[\mathrm{Pt}(\mathrm{P}-$ $\mathrm{P})(\mathrm{P}) \mathrm{Cl}]^{+}\left(\mathrm{P}-\mathrm{P}=\right.$ dppe, dmpe, dppm; $\left.\mathrm{P}=\mathrm{PEt}_{3}, \mathrm{PMePh}_{2}, \mathrm{PBu}_{3}, \mathrm{PPh}_{3}\right): 2995-3551 \mathrm{~Hz}$ for ${ }^{1} J_{\mathrm{PPt}}(\mathrm{cis}) ; 1867-2414 \mathrm{~Hz}$ for ${ }^{1} J_{\mathrm{PPt}}$ (trans); $4-17 \mathrm{~Hz}$ for ${ }^{2} J_{\mathrm{PP}}$ (cis) (P-P = dppe, dmpe), 8$66 \mathrm{~Hz}(\mathrm{P}-\mathrm{P}=\mathrm{dppm})$; and $368-414 \mathrm{~Hz}$ for ${ }^{2} J_{\mathrm{PP}}$ (trans). ${ }^{103}$ The findings strongly suggest
that dissolution of $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}($ dpypcp $)$ in $\mathrm{CDCl}_{3}$ gives rise to the square planar $\mathrm{Pt}^{\mathrm{II}}$ species $\left[\mathrm{PtCl}\left(\mathrm{PPh}_{3}\right)(\text { dpypcp })\right]^{+}$resulting from initial oxidative addition of the solvent (Scheme 4.3). The identity of the species giving the ABX pattern was confirmed by the in situ reaction between $\mathrm{PtCl}_{2}$ (dpypcp) and excess $\mathrm{PPh}_{3}$ which reproduced the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR pattern exactly; the complex responsible is undoubtedly $\left[\mathrm{PtCl}\left(\mathrm{PPh}_{3}\right)(\mathrm{dpypcp})\right] \mathrm{Cl}$.

## Scheme 4.3

$$
\begin{align*}
& \left.\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}(\mathrm{dpypcp})+\mathrm{CDCl}_{3} \longrightarrow \mathrm{PtCl}_{\left(\mathrm{CDCl}_{2}\right)(\mathrm{dpypcp})+2 \mathrm{PPh}_{3}}^{2 \mathrm{PtCl}\left(\mathrm{CDCl}_{2}\right)(\text { dpypcp }) \longrightarrow \mathrm{PtCl}_{2}(\text { dpypcp })+\mathrm{PtCl}(\mathrm{CDClCDCl}} 2\right)(\mathrm{dpypcp})  \tag{4.2}\\
& \mathrm{PtCl}\left(\mathrm{CDClCDCl}_{2}\right)(\text { dpypcp }) \longrightarrow \mathrm{PtCl}_{2}(\text { dpypcp })+\mathrm{CDCl}=\mathrm{CDCl}  \tag{4.3}\\
& \mathrm{PtCl}_{2}(\text { dpypcp })+\mathrm{PPh}_{3} \longrightarrow\left[\mathrm{PtCl}\left(\mathrm{PPh}_{3}\right)(\text { dpypcp })\right] \mathrm{Cl} \tag{4.4}
\end{align*}
$$

The oxidative addition step (eq. 4.2) may be preceded by dissociation of one $\mathrm{PPh}_{3}$ ligand to generate the (presumably reactive) 3-coordinate species $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)($ dpypcp $)$. Steps such as 4.3 (the oxidative addition of $\mathrm{C}-\mathrm{Cl}$ of one Pt chloromethyl complex to another, followed by reductive elimination) and 4.4 ( $\beta$-chloride elimination) have been proposed by McCrindle et al. for decomposition of a range of cischloro(chloromethyl)palladium complexes but no direct evidence was provided. ${ }^{104}$ This group has studied the solution stabilities of several chloromethyl $\mathrm{Pt}^{105}$ and $\mathrm{Pd}^{104}$ complexes, and determined that complexes of the type cis- $\mathrm{PtCl}\left(\mathrm{CH}_{2} \mathrm{Cl}\right)(\mathrm{P}-\mathrm{P})(\mathrm{P}=\mathrm{dppe}$, dppp), when pure, are indefinitely stable with respect to decomposition to cis $-\mathrm{PtCl}_{2}(\mathrm{P}-\mathrm{P})$ in $\mathrm{CDCl}_{3}$ solution under vacuum and, in the case of $\mathrm{PtCl}\left(\mathrm{CH}_{2} \mathrm{Cl}\right)($ dppe $)$, even in the presence of water. In this thesis work, dissolution of $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}$ (dpypcp) in $\mathrm{CDCl}_{3}$ rapidly gives $\mathrm{PtCl}_{2}$ (dpypcp), but as noted by McCrindle et al. "small amounts of impurities may have a marked effect on the apparent stability of a transition metal compound." ${ }^{105}$ They found that the chloromethyl complexes underwent rapid decomposition in the reaction mixture used to create them, but showed enhanced stability in the same solvent after purification. In the case under study here, the system involves a dichloromethyl species, and also contains $\mathrm{PPh}_{3}$. In addition, the involvement of radical processes cannot be excluded.

In an attempt to observe $\mathrm{PtCl}\left(\mathrm{CHCl}_{2}\right)(\mathrm{dpypcp}), \mathrm{CHCl}_{3}$ was added to a $\mathrm{C}_{6} \mathrm{D}_{6}$ solution of $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)($ dpypcp $)$, and the system monitored by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy. After 2 h , the only species observed were the unreacted $\mathrm{Pt}^{0}$ complex, and trace, equal quantities of $\mathrm{PtCl}_{2}$ (dpypcp) and free $\mathrm{PPh}_{3}$. Once again, this result points to the instability of any chloro(dichloromethyl) intermediate and also suggests perhaps that $\mathrm{PPh}_{3}$ dissociation is necessary prior to oxidative addition of $\mathrm{CHCl}_{3}$. This seems reasonable in light of the fact that even in the presence of a substantial excess of $\mathrm{CHCl}_{3}$, $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}$ (dpypcp) reacts very slowly in $\mathrm{C}_{6} \mathrm{D}_{6}$ whereas the corresponding reaction in neat $\mathrm{CDCl}_{3}$ is complete within the mixing time.

The decomposition of $\mathrm{Pt}^{0}$ phosphine complexes to the corresponding $\mathrm{Pt}^{\mathrm{II}}$ dichlorides is frequently observed; e.g., dissolution of $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{4}$ in $\mathrm{CCl}_{4}$ produces cis$\mathrm{PtCl}_{2}\left(\mathrm{PPh}_{3}\right)_{2} .{ }^{106}$

The $\mathrm{CDCl}_{3}{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of isolated $\mathrm{Pt}\left(\eta^{2}-\mathrm{dmf}\right)$ (dpypcp) consists of two singlets (with corresponding Pt "satellites") at $\delta 33.1$ and 31.8 in a ratio of ca. 5:1 (Figure 4.10). On the basis of a comparative study of the in situ reactions of def and dem with $\operatorname{Pt}\left(\mathrm{PPh}_{3}\right)_{2}($ dpypcp $)$, these singlets have been assigned to the two configurational diastereomers ${ }^{107}$ which can result from the combination of the prochiral olefin dmf with $R, R$ and $S, S$ " $P t(d p y p c p) "$. In this study, the reactions of slight excesses of def and dmf with $\operatorname{Pt}\left(\mathrm{PPh}_{3}\right)_{2}$ (dpypcp) in $\mathrm{C}_{6} \mathrm{D}_{6}$ were followed by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy. Within the time taken to make the first measurement ( 4 min ), reaction with dem gave three products, giving rise to two singlets at $\delta 33.2$ and $34.4\left({ }^{1} J_{\mathrm{PPt}}=3360\right.$ and 3330 Hz ) and an AB pattern ( $\delta 33.3$ and $35.4,{ }^{1} J_{\mathrm{PPt}}=3290$ and $3260,{ }^{2} J_{\mathrm{PP}}=13 \mathrm{~Hz}$ ). This spectrum can be rationalised in the following manner: the AB pattern is due to $\mathrm{Pt}\left(\eta^{2}\right.$-dem)(dpypcp) while the singlets are due to the configurational diastereomers of $\operatorname{Pt}\left(\eta^{2}\right.$-def) (dpypcp) which arise due to the def contaminant. No diastereomers can result from the former compound because dem is not prochiral (i.e., its faces are homotopic). That the P -atoms in $\operatorname{Pt}\left(\eta^{2}-\right.$ dem)(dpypcp) should be chemically inequivalent, while those in $\operatorname{Pt}\left(\eta^{2}-\mathrm{def}\right)(\mathrm{dpypcp})$ should not, can be accounted for if it is assumed that there is restricted rotation about the axis bisecting the Pt atom and the mid-point of the olefinic bond; Chart 4.6 shows the maleate and fumarate complexes as viewed down this axis ( Pt -atoms, $\mathrm{P}-\mathrm{Pt}$ bonds, P substituents and 3 of the 5 cyclopentyl C-atoms of each dpypcp ligand have been omitted
for clarity; $\mathrm{R}=\mathrm{CO}_{2} \mathrm{Et}$ ). Reaction with def gives only the singlets at $\delta 33.2$ and 34.4 which confirms these assignments.


Figure 4.10 $\quad{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \quad \mathrm{NMR} \quad$ spectrum $\quad\left(\mathrm{CDCl}_{3}, \quad 202 \mathrm{MHz}, \quad 300 \mathrm{~K}\right)$ of $\operatorname{Pt}\left(\eta^{2}-\right.$ $\mathrm{dmf})($ dpypcp).

## Chart 4.6


maleate

fumarate

Over the course of 45 min , the peak at $\delta 33.2$ gradually disappeared while the one at $\delta 34.4$ intensified. This represents the conversion of the kinetic to thermodynamic distribution of configurational diastereomers of $\operatorname{Pt}\left(\eta^{2}-\operatorname{def}\right)($ dpypcp $)$. A positive assignment of the two peaks could not be made in the def case, but if it is assumed that the diastereomeric form observed in the crystal of $\operatorname{Pt}\left(\eta^{2}-\mathrm{dmf}\right)(\mathrm{dpypcp})$ represents the thermodynamically more stable isomer, then assignment of the peaks in the $\mathrm{CDCl}_{3}$ ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of $\operatorname{Pt}\left(\eta^{2}-\mathrm{dmf}\right)($ dpypcp $)$ is possible because of the structure
determination. The larger ( $\delta 33.1$ ) is due to the $S, S, R, R / R, R ; S, S$ pair (only the former of these is illustrated in Figure 4.12, but the latter must be present in equal abundance as demanded by the centrosymmetric $\mathrm{P}_{1} /$ a space group); the smaller ( $\delta 31.8$ ) is due to the $R, R, R, R / S, S, S, S$ pair. The quadrant diagram shown in Figure 4.11 clearly illustrates that the former diastereomer is more stable than the latter based on steric interactions between the bound olefin and the metal-diphosphine fragment. The AB pattern due to $\operatorname{Pt}\left(\eta^{2}-\right.$ dem)(dpypcp) maintained its intensity throughout the course of the study.


Figure 4.11 Quadrant diagram showing steric interactions between a chiral $C_{2}$ symmetric metal-diphosphine fragment and a bound olefin, looking down the $\mathrm{M}-\mathrm{mp}$ axis ( $\mathrm{mp}=\mathrm{C}=\mathrm{C}$ mid-point). The grey rectangles represent steric bulk presented by the diphosphine ligand, and the black circles represent the substituents on the olefin. The left-hand diagram illustrates the sterically more favourable diastereomer.

The reaction between excess dem (containing ca. $10 \mathrm{~mol} \%$ def) and $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}$ (dpype) in $\mathrm{C}_{6} \mathrm{D}_{6}$ was also followed by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy. In this case, diastereomers could not result as dpype is achiral. The reaction was complete within 0.5 h and gave two products which were manifested by singlets at $\delta_{\mathrm{P}} 60.3$ and 59.8 in a $1: 2$ ratio. In an independent reaction between def and $\operatorname{Pt}\left(\mathrm{PPh}_{3}\right)_{2}$ (dpype), the peak at $\delta 60.3$ was identified as being due to $\operatorname{Pt}\left(\mathrm{PPh}_{3}\right)_{2}\left(\eta^{2}\right.$-def $)$. Because the relative abundances did not correspond to the relative abundances of dem and $\operatorname{def}(9: 1)$ in the reacting olefin mixture, def must react faster than dem with $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}$ (dpype). In addition, as the relative concentrations of the products did not change over time, there is no metal-mediated cis to trans isomerisation of the olefin.


Figure 4.12 ORTEP representation of $\operatorname{Pt}\left(\eta^{2}-\mathrm{dmf}\right)(\mathrm{dpypcp}) \cdot 2 \mathrm{CDCl}_{3}$. Except for the 2 olefinic ones, H -atoms have been omitted for clarity ( $50 \%$ ellipsoids).

Table 4.10 Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for $\operatorname{Pt}\left(\eta^{2}-\mathrm{dmf}\right)(\mathrm{dpypcp}) \cdot 2 \mathrm{CDCl}_{3}$ with estimated standard deviations in parentheses.

| $\mathrm{Pt}(1)-\mathrm{P}(1)$ | $2.2602(9)$ | $\mathrm{Pt}(1)-\mathrm{P}(2)$ | $2.2543(9)$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{Pt}(1)-\mathrm{C}(27)$ | $2.116(3)$ | $\mathrm{Pt}(1)-\mathrm{C}(28)$ | $2.132(3)$ |
| $\mathrm{C}(27)-\mathrm{C}(28)$ | $1.471(5)$ | $\mathrm{D}(1)-\mathrm{N}(1)$ | 2.49 |
| $\mathrm{D}(1)-\mathrm{O}(4)$ | 2.07 | $\mathrm{H}(1)-\mathrm{O}(3)$ | 2.42 |
| $\mathrm{H}(2)-\mathrm{O}(1)$ | 2.49 | $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{P}(2)$ | $86.91(3)$ |
| $\mathrm{C}(27)-\mathrm{Pt}(1)-\mathrm{C}(28)$ | $40.52(12)$ |  |  |

The molecular structure of $\operatorname{Pt}\left(\eta^{2}-\mathrm{dmf}\right)(\mathrm{dpypcp})$ (Figure 4.12, Table 4.10) embodies all the features typical of known $\mathrm{Pt}^{0}$-olefin complexes. ${ }^{108}$ These are a lengthening of the $\mathrm{C}-\mathrm{C}$ double bond upon coordination, a bending back of the olefinic substituents out of the plane of the double bond and away from the Pt-centre, and a
twisting by a few degrees of the olefin out of the plane containing the Pt -atom, the ligating atoms of the 2 ancillary ligands and the mid point of the double bond (Chart 4.6). In addition, and in contrast to $\mathrm{Pt}^{\prime \prime}$-olefin complexes, the barrier to rotation of the olefin about the Pt—mp is high in this class of compounds.

For a $\mathrm{d}^{10}$ metal centre there is no difference between the ligand field stabilisation energies of tetrahedral and square planar arrangements, and so the ligands separate as much as possible to minimise steric interactions, i.e., a tetrahedron results. ${ }^{109}$ However, if a strongly $\pi$-accepting ligand such as an olefin bearing electron-withdrawing groups is coordinated and the $\sigma$-donating ability of this ligand is comparatively small, then the metal centre will be left with slightly less than 10 electrons and will distort according to the Jahn-Teller theorem to give a flattened tetrahedron which approximates a square plane. The most accommodating qualitative theoretical treatment of $\mathrm{Pt}^{0}$-olefin bonding, both for its merits in rationalising the gross coordination geometry at the metal centre, and for its accounts of the other experimentally observed phenomena outlined above, is the Dewar-Chatt-Duncanson model. ${ }^{110,111}$ In the specific case of olefinic bonding to $" \mathrm{Pt}^{0}$ (phosphine) $)_{2}$ ", this model embodies $\sigma$-donation from the olefin $\pi$-bond into a $\mathrm{dp}^{2}$ hybrid on the metal (formed from $\mathrm{d}_{\mathrm{xy}}, \mathrm{p}_{\mathrm{x}}, \mathrm{p}_{\mathrm{y}}$ ) and $\pi$-back donation from the metal $\mathrm{d}_{\mathrm{x} 2-\mathrm{y} 2}$ to the $\pi^{*}$ orbital on the olefin, if the complex is oriented along the axes shown in Chart 4.7.

## Chart 4.7




Several $\operatorname{Pt}\left(\eta^{2}\right.$-olefin $)\left(\mathrm{PPh}_{3}\right)_{2}$ complexes have been structurally characterised, and by far the majority bear one or more electron-withdrawing substituents such as $\mathrm{F}, 112$ $\mathrm{Cl},{ }^{112,113} \mathrm{CN},{ }^{113-116} p-\mathrm{NO}_{2} \mathrm{C}_{6} \mathrm{H}_{4}{ }^{117}$ on the olefin; however, only one report of a structurally characterised $\mathrm{Pt}^{0}$ phosphine complex bearing a $\mathrm{CO}_{2} \mathrm{R}$-substituted olefin has appeared. ${ }^{118}$ The known $\mathrm{C}-\mathrm{Pt}-\mathrm{C}$ angles in these compounds range from $38.8^{\circ}$ (olefin $=$ trans $-\mathrm{CH}\left(p-\mathrm{NO}_{2} \mathrm{C}_{6} \mathrm{H}_{4}\right)=\mathrm{CH}\left(p-\mathrm{NO}_{2} \mathrm{C}_{6} \mathrm{H}_{4}\right)^{118}$ ) to $47.1^{\circ}$ (olefin $=\mathrm{CCl}_{2}=\mathrm{CCl}_{2}{ }^{112}$ ). The corresponding angle in $\operatorname{Pt}\left(\eta^{2}-\mathrm{dmf}\right)(\mathrm{dpypcp})\left(40.5^{\circ}\right)$ is thus typical for this class of
compounds and is similar to that found for $\operatorname{Pt}\left(\eta^{2}-\mathrm{CH}\left(\mathrm{CO}_{2} \mathrm{Me}\right)=\mathrm{C}\left(\mathrm{CO}_{2} \mathrm{Me}_{2}\right)\left(\mathrm{PPh}_{3}\right)_{2}\right.$ $\left(39.5^{\circ}\right) .{ }^{118}$ The dihedral angles between the $\mathrm{C}-\mathrm{Pt}-\mathrm{C}$ and $\mathrm{P}-\mathrm{Pt}-\mathrm{P}$ planes of complexes in this family lie in the range $1.0-22.1^{\circ}$, and in this respect, $\operatorname{Pt}\left(\eta^{2}\right.$ dmf)(dpypcp), with its corresponding angle of $9.6^{\circ}$, is also unremarkable.

Not surprisingly, the $\mathrm{P}-\mathrm{Pt}-\mathrm{P}$ angles of the $\mathrm{PPh}_{3}$ complexes are all significantly larger $\left(>100^{\circ}\right)$ than the corresponding angle in $\operatorname{Pt}\left(\eta^{2}-\mathrm{dmf}\right)(\mathrm{dpypcp})\left(86.9^{\circ}\right)$. A fairer comparison can be made to $\operatorname{Pt}\left(\eta^{2}\right.$-trans-stilbene)(chiraphos) in which this angle is restricted to 87.1 and $86.6^{\circ}$ (found for two crystallographically independent forms). ${ }^{97}$

The crystal structure of dmf does not appear in the Cambridge Structure Database, but the average $\mathrm{C}=\mathrm{C}$ bond distance for two independent measurements of fumaric acid is $1.324 \AA .{ }^{119,120}$ The corresponding distance for the coordinated $d m f$ in $\operatorname{Pt}\left(\eta^{2}-\right.$ dmf)(dpypcp) is significantly longer ( $1.471 \AA$ ), consistent with the Dewar-ChattDuncanson model.

## Hydrogen bonding in $\mathrm{Pt}\left(\eta^{2}-d m f\right)(d p y p c p) \cdot 2 \mathrm{CDCl}_{3}$

The most reliable indicator of a hydrogen bond $\mathrm{X}-\mathrm{H} \cdots \mathrm{Y}$ is that the $\mathrm{H} \cdots \mathrm{Y}$ distance is less than the sum of the van der Waals radii of H and $\mathrm{Y} .{ }^{121}$ When the proton cannot be located and the $\mathrm{X}-\mathrm{H} \cdots \mathrm{Y}$ linkage is linear or near-linear, an X -to- Y distance less than the sum of the van der Waals radii of $X$ and $Y$ is a sufficient indicator of hydrogen bonding; indeed, when this difference is $\geq 0.3 \AA$, the hydrogen bonding is termed strong and the interaction is better depicted as $\mathrm{X}-\mathrm{H}-\mathrm{Y} .{ }^{122}$

The structure of $\operatorname{Pt}\left(\eta^{2}-\mathrm{dmf}\right)($ dpypcp $) \cdot 2 \mathrm{CDCl}_{3}$ shows 2 intramolecular $\mathrm{C}-\mathrm{H} \cdots \mathrm{O}$ contacts, as well as intermolecular $\mathrm{C}-\mathrm{D} \cdots \mathrm{N}$ and $\mathrm{C}-\mathrm{D} \cdots \mathrm{O}$ hydrogen bonds, the latter possibly being the strongest interaction of its type ever to be observed (vide infra). The intramolecular contacts exist between each olefinic proton and the $O \mathrm{Me} \mathrm{O}$-atom of the ester group on the opposite C -atom of the olefin. The $\mathrm{C}-\mathrm{D} \cdots \mathrm{N}$ bond lies between one of the pyridyl N -atoms and the D -atom of one of the $\mathrm{CDCl}_{3}$ solvates, while the other $\mathrm{CDCl}_{3}$ solvate is bonded to the carbonyl O-atom of one of the ester groups. The H-bonding interactions shown in Figure 4.12 are summarised in Table 4.11.

Table 4.11 Relevant parameters for the intra- and intermolecular H-bonding interactions in $\operatorname{Pt}\left(\eta^{2}-\mathrm{dmf}\right)($ dpypcp $) \cdot 2 \mathrm{CDCl}_{3}$.

| $\mathrm{X}-\mathrm{H} / \mathrm{D} \cdots \mathrm{Y}^{\mathrm{a}}$ | $\mathrm{A} \ldots \mathrm{Y}$ <br> $(\AA)^{\mathrm{b}}$ | $\mathrm{H} / \mathrm{D} \cdots \mathrm{Y}$ <br> $(\AA)$ | $\mathrm{X}-\mathrm{H} / \mathrm{D} \cdots \mathrm{Y}$ <br> $\left({ }^{\circ}\right)$ | $\mathrm{d}(\AA)^{\mathrm{c}, \mathrm{d}}$ |
| :--- | :---: | :---: | :---: | :---: | :---: | $\mathrm{d}^{\prime}(\AA)^{\mathrm{d,e}} \mathrm{e}$.

${ }^{\mathrm{b}}$ This is the straight-line X-to-Y distance.
${ }^{c} \mathrm{~d}=\mathrm{r}(\mathrm{X})+\mathrm{r}(\mathrm{Y})-\mathrm{A} . . \mathrm{Y}$, where $\mathrm{r}(\mathrm{X})$ and $\mathrm{r}(\mathrm{Y})$ are the van der Waals radii of X and Y , respectively.
${ }^{d}$ The van der Waals radii are $1.75,1.55,1.50$ and $1.20 \AA$ for $\mathrm{C}, \mathrm{O}, \mathrm{N}$ and H , respectively. ${ }^{121}$
${ }^{e} d^{\prime}=r(H)+r(Y)-H / D \cdots Y$.

To this author's knowledge, the only $\mathrm{C}-\mathrm{H} \cdots \mathrm{O} \mathrm{H}$-bond shorter than the $2.07 \AA$ observed here is that of $2.045 \AA$ determined by neutron diffraction for the intermolecular interaction between 1-methylthymine molecules in the crystalline material. ${ }^{123}$ However, as the relevant D-atom was not located in the structure of $\operatorname{Pt}\left(\eta^{2}-\mathrm{dmf}\right)(\mathrm{dpypcp}) \cdot 2 \mathrm{CDCl}_{3}$, the $\mathrm{D} \cdots \mathrm{O}$ distance is not known accurately and therefore, a better comparison of the two H-bonds may be their d-values; these are $0.18 \AA$ for 1 -methylthimine and $0.27 \AA$ for the Pt complex. Thus, the $\mathrm{C}-\mathrm{H} / \mathrm{D} \cdots \mathrm{O}$ interaction observed here may be stronger than that observed before.

### 4.5 Conclusions

A new "cyclopentyl-bridged" ligand, dpypcp, was successfully synthesised and characterised. In addition, the diprotonated, $\left[\operatorname{dpypcp}(\mathrm{H})_{2}\right]^{2+}$, and oxidised, $\operatorname{dpypcp}(\mathrm{O})_{2}$, forms were isolated, as were those of the known "ethyl-bridged" ligand, dpype. The $\mathrm{pK}_{\mathrm{a}} \mathrm{s}$ of $\left[\text { dpypcp }(\mathrm{H})_{2}\right]^{2+}$ are 3.66 and 4.77.

Dpypcp and dpype form exclusively $P, P^{\prime}$-bonded complexes with $\mathrm{M}^{\mathrm{II}}$-halo precursors: $\mathrm{MX}_{2}(\mathrm{P}-\mathrm{P})$ (for $\mathrm{M}=\mathrm{Pt}, \mathrm{X}=\mathrm{Cl}, \mathrm{Br}$, I when $\mathrm{P}-\mathrm{P}=\mathrm{dpypcp}$, and $\mathrm{X}=\mathrm{Cl}$, I when $\mathrm{P}-\mathrm{P}=$ dpype; for $\mathrm{M}=\mathrm{Pd}, \mathrm{X}=\mathrm{Cl}, \mathrm{Br}, \mathrm{I}, \mathrm{P}-\mathrm{P}=$ dpypcp $)$ and $\left[\mathrm{M}(\mathrm{P}-\mathrm{P})_{2}\right]\left[\mathrm{PF}_{6}\right]_{2}(\mathrm{P}-\mathrm{P}=$ dpypcp, dpype) have been isolated and characterised by ${ }^{1} \mathrm{H}$ and ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy and elemental analysis (some of the complexes are isolated as
monohydrates), and in the cases of $\mathrm{PtI}_{2}$ (dpypcp) and $\mathrm{PtCl}_{2}$ (dpype) by X-ray crystallography.

Both pyridyldiphosphines serve as supports for "tethered paddlewheel" complexes that contain $[\mathrm{Pt}(\mathrm{P}-\mathrm{P})]_{2}^{4+}$ moieties in which the ligand adopts $P, P^{\prime}$-chelating and $\operatorname{bis}(P, N$-bridging) coordination modes. These complexes can be made either by treatment of $\mathrm{PtI}_{2}(\mathrm{P}-\mathrm{P})$ with $\mathrm{AgNO}_{3}$ (in which case $\mathrm{Ag}^{+}$ions become incorporated via coordination by the "unused" pyridyl N -atoms), or by reaction of the ligand with the halide-free precursor $\operatorname{Pt}\left(\mathrm{NO}_{3}\right)_{2}$ (cod). In these compounds, the metal centres are separated by a distances of $c a .2 .76 \AA$, corresponding to a $\mathrm{Pt}-\mathrm{Pt}$ bond-order of $c a .0 .52$ according to Pauling's RVBM.

Dpypcp and dpype react with $\mathrm{M}\left(\mathrm{PPh}_{3}\right)_{4}(\mathrm{M}=\mathrm{Pd}, \mathrm{Pt})$ to form $P, P^{\prime}$-chelated $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}(\mathrm{P}-\mathrm{P})$ and $\mathrm{Pd}(\mathrm{P}-\mathrm{P})_{2}$ complexes $\left(\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{2}(\right.$ dpypcp $)$ was observed in situ in the presence of a 5 -fold excess of $\left.\mathrm{PPh}_{3}\right) . \mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}($ dpypcp $)$ reacts with $\mathrm{CDCl}_{3}$ to form $\left[\mathrm{PtCl}\left(\mathrm{PPh}_{3}\right)(\text { dpypcp })\right]^{+}$.

The $\mathrm{Pt}^{0}$ complexes react with the electron-deficient olefins dimethyl- and diethylmaleate and fumarate to form $\operatorname{Pt}\left(\eta^{2}\right.$-olefin $)(\mathrm{P}-\mathrm{P})$ complexes. Although complexes bearing the trans, i.e., fumaric, olefin were isolated from reactions of $\operatorname{Pt}\left(\mathrm{PPh}_{3}\right)_{2}(\mathrm{dpypcp})$ with the cis, i.e., maleic, isomer, the metal does not mediate a cis to trans isomerisation. However, reactions of def and dmf with $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}(\mathrm{dpypcp})$ give rise to configurational diastereomers whose relative abundances vary with time; the $S, S, R, R / R, R, S, S$ pair is thermodynamically favoured due to steric interactions between the coordinated olefin and the anilinyldiphosphine ligand.

### 4.6 Recommendations for Future Work

### 4.6.1 Synthesis of dpypm, $\mathbf{P d}_{\mathbf{2}}{ }^{\mathbf{1}}$ complexes, and the WGS reaction

A modification to the synthesis of dpypcp (Section 4.7.1) should give access to the ligand 1,1-bis(di-o-pyridylphosphino)methane, or dpypm (Chart 4.8, (a)). Using this ligand, it should be possible to make bimetallic complexes like (b).

## Chart 4.8

(a)

(b)

(c)


(d)


The pyridylmonophosphine-bridged $\mathrm{Pd}_{2}{ }^{1}$ complex $\mathrm{Pd}_{2} \mathrm{Cl}_{2}\left(\mu-\mathrm{PN}_{1}\right)_{2}$ (c) does not react for example with CO to give an "A-frame" insertion product in the same way that $\mathrm{Pd}_{2} \mathrm{Cl}_{2}(\mathrm{P}-$ $\mathrm{P})_{2}\left(\mathrm{P}-\mathrm{P}=\mathrm{dmpm}\right.$, dppm, etc.) compounds do ${ }^{124}$ because of the inflexibility of the bridging ligand. ${ }^{125}$ The $\mathrm{PN}_{3}$ analogue dissolves in $\mathrm{H}_{2} \mathrm{O}$ to give $\left[\mathrm{Pd}_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\left(\mu-\mathrm{PN}_{3}\right)_{2}\right] \mathrm{Cl}_{2}$, (d). ${ }^{6}$ It is thought that $\mathrm{Pd}_{2} \mathrm{Cl}_{2}(\mu \text {-dpypm) })_{2}$ should both be water-soluble (with dissociation of chloride) and be able to react with small molecules in water to form "A-frame" insertion products. The only known, water-soluble $\mathrm{Pd}_{2}{ }^{\mathrm{I}}$ compounds that react with small molecules $\left(\mathrm{CO}\right.$ and $\left.\mathrm{H}_{2} \mathrm{~S}\right)$ in water are $\mathrm{Pd}_{2} \mathrm{Cl}_{2}(\mathrm{dmpm})_{2}$ and $\mathrm{Pd}_{2} \mathrm{Cl}_{2}(\mathrm{depm})_{2}$; the former has been studied by Kubiak's group as an aqueous-phase WGS catalyst, ${ }^{126}$ and it would be of interest to determine whether the pyridyldiphosphine analogue has the same capacity.

### 4.7 Experimental

### 4.7.1 Racemic-dpypep

To $\mathrm{Et}_{2} \mathrm{O}(100 \mathrm{~mL})$, cooled to $-77^{\circ} \mathrm{C}$ in a dry ice / acetone bath, was added ${ }^{n} \mathrm{BuLi}$ $(100 \mathrm{~mL}, 160 \mathrm{mmol})$ by cannula, and the mixture allowed to cool for 5 min . To this solution was added 2-bromopyridine ( $16 \mathrm{~mL}, 160 \mathrm{mmol}$ ) which caused an immediate
colour change from pale yellow to brown-red. Over 4 h the solution became deep red. Trans-1,2-( $\left.\mathrm{Cl}_{2} \mathrm{P}\right)_{2} \mathrm{C}_{5} \mathrm{H}_{8}(7 \mathrm{~mL}, 40 \mathrm{mmol})$ in $\mathrm{Et}_{2} \mathrm{O}(30 \mathrm{~mL})$ was then added dropwise over 15 min , and stirring was continued for 2 h at $-77^{\circ} \mathrm{C}$. This resulted in the formation of a brown suspension. The mixture was then allowed to warm to r.t., whereupon the slurry was extracted with $\mathrm{H}_{2} \mathrm{SO}_{4}\left(2 \times 100 \mathrm{~mL}, 2 \mathrm{~mol} \mathrm{~L}{ }^{-1}\right)$ and the red aqueous layer was removed by cannula from the yellow organic layer. The extract was neutralized by the dropwise addition of saturated $\mathrm{NaOH}(c a .35 \mathrm{~mL}$ ) which resulted in the formation of an "oily mass". This mixture was filtered to yield a dark orange "grease" which was resuspended in acetone ( 60 mL ) to give a fine, white powder and red-brown filtrate. The solid was collected, washed with acetone $(3 \times 2 \mathrm{~mL})$ and then thoroughly with $\mathrm{H}_{2} \mathrm{O}$ (ca. 150 mL ). Reprecipitation from acetone/hexanes yielded a cream-coloured solid which was collected, and dried under vacuum at $100^{\circ} \mathrm{C}$ for 72 h . Yield: $6.28 \mathrm{~g}(35 \%)$. Anal. Calcd for $\mathrm{C}_{25} \mathrm{H}_{24} \mathrm{~N}_{4} \mathrm{P}_{2}$ : C, 67.9; $\mathrm{H}, 5.5 ; \mathrm{N}, 12.7$. Found: $\mathrm{C}, 67.9 ; \mathrm{H}, 5.5 ; \mathrm{N} 12.6$. The atomnumbering scheme for dpypcp is given in Chart 4.9. Assignments have been made on the basis of APT, ${ }^{1} \mathrm{H}-{ }^{1} \mathrm{H}$ COSY and ${ }^{13} \mathrm{C}-{ }^{1} \mathrm{H}$ HETCOR NMR experiments. Peaks in the ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of this compound generally appear as multiplets due to coupling to ${ }^{31} \mathrm{P}$, and, although the coupling constants have not been determined, the number of lines observed in each case is given in parentheses following the peak frequency. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}, 300 \mathrm{~K}$ ): $\delta 1.74\left(\mathrm{qn}, 2 \mathrm{H}^{9},{ }^{3} J_{\mathrm{HH}}=5.3\right.$ ), $1.97\left(\mathrm{~m}, 2 \mathrm{H}^{8}\right), 2.38(\mathrm{~m}$, $\left.2 \mathrm{H}^{8}\right), 3.90\left(\mathrm{ddd}, 2 \mathrm{H}^{7},{ }^{2} J_{\mathrm{HP}}=11.47,{ }^{3} J_{\mathrm{HH}(\text { anti) }}=7.78,{ }^{3} J_{\mathrm{HH} \text { (gauche) }}=3.21\right), 6.47\left(\mathrm{dd}, 2 \mathrm{H}^{5},{ }^{3} J_{\mathrm{HH}}\right.$ $\left.=4.8,{ }^{3} J_{\mathrm{HH}}=7.6\right), 6.51\left(\mathrm{dd}, 2 \mathrm{H}^{5},{ }^{3} J_{\mathrm{HH}}=4.8,{ }^{3} J_{\mathrm{HH}}=7.6\right), 6.87\left(\mathrm{~m}, 4 \mathrm{H}^{4}\right), 7.32\left(\mathrm{~m}, 2 \mathrm{H}^{3}\right)$, $7.46\left(\mathrm{~m}, 2 \mathrm{H}^{3}\right.$. This pattern could be simulated with unassigned coupling constants of 7.7, 1.9 and 1.8 Hz$), 8.38\left(\mathrm{pd}, 2 \mathrm{H}^{6},{ }^{3} J_{\mathrm{HH}}=10.1\right), 8.49\left(\mathrm{pd}, 2 \mathrm{H}^{6},{ }^{3} J_{\mathrm{HH}}=10.1\right) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(50 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta 25.1\left(3, \mathrm{C}^{9}\right), 30.2\left(3, \mathrm{C}^{8}\right), 39.1\left(4, \mathrm{C}^{7}\right), 122.5(2), 129.3$ (8), $135.2\left(4, \mathrm{C}^{4}\right), 149.8\left(6, \mathrm{C}^{6}\right) 162.9\left(1, \mathrm{C}^{2}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \operatorname{NMR}\left(121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta-$ 2.2 (s). The diphosphine was made as a mixture of $R, R$ - and $S, S$-enantiomers, the chirality designators referring to the $\mathrm{C}^{7}$-atoms of the cyclopentane backbone.

## Chart 4.9



### 4.7.2 Racemic-dpypcp $(O)_{2}$

To a $0.2 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{HCl}$ solution ( 15 mL ) containing dpypcp ( $160 \mathrm{mg}, 0.36 \mathrm{mmol}$ ) in a flask open to the atmosphere was added dropwise aq. $30 \% \mathrm{H}_{2} \mathrm{O}_{2}$ solution ( 2 mL ). The colourless solution was stirred for 1 h , cooled on ice, and then made basic using a saturated KOH solution. The aqueous phase was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 25 \mathrm{~mL})$ and the combined organic fractions dried over $\mathrm{MgSO}_{4}$. This mixture was filtered and the filtrate reduced to $c a .2 \mathrm{~mL}$ under reduced pressure. $\mathrm{Et}_{2} \mathrm{O}(30 \mathrm{~mL})$ was then added to afford the product as a white precipitate, which was collected, washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times$ 3 mL ) and dried in vacuo. Yield: 91 mg ( $53 \%$ ). Anal. Calcd for $\mathrm{C}_{25} \mathrm{H}_{24} \mathrm{~N}_{4} \mathrm{O}_{2} \mathrm{P}_{2}$ : C, 63.3; H, 5.1; N, 11.8. Found: C, 63.1; H, 5.1; N 11.8. The atom-numbering scheme is the same as that used for dpypcp (Chart 4.9). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{D}_{2} \mathrm{O}, 300 \mathrm{~K}$ ): $\delta 1.55(\mathrm{~m}, 2 \mathrm{H}$, $\mathrm{CH}_{2}$ ), 1.70 (br m, 2H, CH2), 1.92 (br m, $2 \mathrm{H}, \mathrm{CH}_{2}$ ), 3.64 (br m, $2 \mathrm{H}, \mathrm{CH}$ ), 7.15 (m, 2 H , py), 7.32 (m, 2H, py), 7.62 (br m, 4H, py), 7.71 (br m, 4H, py), 7.90 (pd, 2H, py), 8.45 (pd, 2H, py). ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 26.2\left(1, \mathrm{C}^{9}\right), 28.8\left(1, \mathrm{C}^{8}\right), 35.0$ $\left(2, \mathrm{C}^{7}\right), 124.7(2), 128.2(5), 135.5\left(2, \mathrm{C}^{4}\right), 150.0\left(5, \mathrm{C}^{6}\right), 168.2\left(1, \mathrm{C}^{2}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $(121 \mathrm{MHz}, 300 \mathrm{~K}): \delta 35.8$ (s) $\left[\mathrm{CDCl}_{3}\right] ; 38.7$ (s) $\left[\mathrm{D}_{2} \mathrm{O}\right] . v_{\mathrm{PO}}: 1194$ (s).

### 4.7.3 dруре $(\mathrm{O})_{2}$

This compound was made in the same manner as dpypcp $(\mathrm{O})_{2}$ except that hexanes was used rather than $\mathrm{Et}_{2} \mathrm{O}$ to precipitate the product. Thus, reaction between dpype ( 87 mg , 0.22 mmol ) and a $30 \% \mathrm{H}_{2} \mathrm{O}_{2}$ solution ( 3 mL ) in aq. HCl gave $38 \mathrm{mg}(41 \%$ ) of a white powder. The elemental analysis of this compound is poor, possibly because of a small KCl impurity. Anal. Calcd for $\mathrm{C}_{22} \mathrm{H}_{20} \mathrm{~N}_{4} \mathrm{O}_{2} \mathrm{P}_{2}$ : C, 60.8; $\mathrm{H}, 4.6 ; \mathrm{N}, 12.9$. Found: C, 59.8; H , 4.5; N, 12.4. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 2.88\left(\mathrm{pd}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 7.34(\mathrm{~m}, 4 \mathrm{H}, \mathrm{py})$,
7.76 (m, 4H, py), 8.06 (m, 4H, py), 8.70 (pd, 4H, py). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CDCl}_{3}$, $300 \mathrm{~K}): \delta 29.1(\mathrm{~s}) . \mathrm{v}_{\mathrm{PO}}: 1206(\mathrm{~s})$.

### 4.7.4 $\left[\mathbf{d p y p c p}(H)_{2}\right]\left[\mathrm{PF}_{6}\right]_{2}$

Some dpypcp ( $82 \mathrm{mg}, 0.19 \mathrm{mmol}$ ) was dissolved in aq. $\mathrm{HCl}\left(20 \mathrm{~mL}, 1.2 \mathrm{~mol}^{-1}\right)$ to give a colourless solution. To this was added solid $\mathrm{KPF}_{6}(95 \mathrm{mg}, 0.52 \mathrm{mmol}$ ) which immediately gave a white precipitate. The slurry was stirred for 0.5 h and then filtered to give a white powder which was washed with $\mathrm{H}_{2} \mathrm{O}(2 \times 5 \mathrm{~mL})$, $\mathrm{EtOH}(3 \mathrm{~mL})$ and $\mathrm{Et}_{2} \mathrm{O}$ ( $2 \times 5 \mathrm{~mL}$ ) and dried in vacuo. Yield: $97 \mathrm{mg}(71 \%)$. Anal. Calcd for $\mathrm{C}_{25} \mathrm{H}_{26} \mathrm{~N}_{4} \mathrm{~F}_{12} \mathrm{P}_{4}: \mathrm{C}$, 40.9; H, 3.6; N, 7.6. Found: C, 40.9; H, 3.6; N, 7.5. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR (121 MHz, acetone- $\mathrm{d}_{6}$, $300 \mathrm{~K}): \delta-25.5(\mathrm{~s}),-143\left(\mathrm{spt}, \mathrm{PF}_{6}{ }^{-1}{ }^{1} J_{\mathrm{PF}}=710\right)$.

### 4.7.5 [dpype( $\left.\mathbf{H})_{2}\right]\left[\mathrm{PF}_{6}\right]_{2}$

The compound was prepared in the same manner as for $\left[\operatorname{dpypcp}(\mathrm{H})_{2}\right]\left[\mathrm{PF}_{6}\right]_{2}$. Thus, reaction of dpype ( $57 \mathrm{mg}, 0.14 \mathrm{mmol}$ ) and $\mathrm{KPF}_{6}(91 \mathrm{mg}, 0.49 \mathrm{mmol})$ in aq. HCl gave 33 mg ( $34 \%$ ) of a white powder. The elemental analysis of this compound is poor, possibly because of a small $\mathrm{KPF}_{6}$ and/or KCl impurity. Anal. Calcd for $\mathrm{C}_{22} \mathrm{H}_{22} \mathrm{~N}_{4} \mathrm{~F}_{12} \mathrm{P}_{4}$ : C, 38.1; H, 3.2; N, 8.1. Found: C, 37.3; H, 3.2; N, 7.7. ${ }^{1} \mathrm{H}$ NMR ( 300 MHz , acetone- $\mathrm{d}_{6}$, $300 \mathrm{~K}): \delta 2.54\left(\mathrm{t}, 4 \mathrm{H}, \mathrm{CH}_{2},{ }^{2} J_{\mathrm{HP}}=5.32\right), 7.91(\mathrm{~m}, 4 \mathrm{H}, \mathrm{py}), 8.03(\mathrm{~m}, 4 \mathrm{H}, \mathrm{py}), 8.34(\mathrm{pt}, 4 \mathrm{H}$, py), 9.01 (pd, 4H, py), ca. $11.8\left(\mathrm{br}, \mathrm{H}^{+}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 121 MHz , acetone- $\mathrm{d}_{6}, 300 \mathrm{~K}$ ): $\delta$ $-21.4(\mathrm{~s}),-143\left(\mathrm{spt}, \mathrm{PF}_{6}^{-},{ }^{1} J_{\mathrm{PF}}=710\right)$.

### 4.7.6 Racemic-dpypcp(S $)_{2}$

A $\mathrm{C}_{6} \mathrm{H}_{6}$ solution ( 15 mL ) containing dpypcp ( $250 \mathrm{mg}, 0.57 \mathrm{mmol}$ ) and $\mathrm{S}_{8}(38 \mathrm{mg}$, 0.15 mmol ) was brought to reflux for 3 h . The solution was allowed to cool and then reduced to approximately $1 / 2$ its original volume in vacuo. An off-white solid began to deposit, and $\mathrm{Et}_{2} \mathrm{O}(20 \mathrm{~mL})$ was added to complete the precipitation. The product was isolated by filtration, washed with $\mathrm{C}_{6} \mathrm{H}_{6}(1 \times 3 \mathrm{~mL})$ and $\mathrm{Et}_{2} \mathrm{O}(2 \times 3 \mathrm{~mL})$ and air-dried. Yield: $240 \mathrm{mg}(84 \%) .{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 1.79\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.05$ (m, 2H, CH2 $), 2.18\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 4.69(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}), 6.99(\mathrm{~m}, 2 \mathrm{H}, \mathrm{py}), 7.25(\mathrm{~m}, 2 \mathrm{H}, \mathrm{py})$, 7.53 (m, 2H, py), 7.68 (m, 2H, py), 8.09 (pd, 2H, py), 8.23 (m, 2H, py), $8.31(\mathrm{~m}, 2 \mathrm{H}, \mathrm{py})$, $8.70(\mathrm{pd}, 2 \mathrm{H}, \mathrm{py}) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta 54.6(\mathrm{~s})$.

### 4.7.7 $\quad \mathbf{P t C l}_{2}$ (dpypcp)

$\mathrm{A} \mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$ solution containing dpypcp ( $100 \mathrm{mg}, 0.24 \mathrm{mmol}$ ) was added dropwise via cannula over 5 min to a $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ solution of $\mathrm{PtCl}_{2}$ (cod) ( $93 \mathrm{mg}, 0.25 \mathrm{mmol}$ ). The resulting colourless solution was stirred for 1 h , and the volume was then reduced to $c a .2 \mathrm{~mL}$. The product was afforded as a fine white precipitate by the addition of $\mathrm{Et}_{2} \mathrm{O}$ $(30 \mathrm{~mL})$, isolated by filtration, and washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 5 \mathrm{~mL})$. Reprecipitation from $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and drying in vacuo at $100^{\circ} \mathrm{C}$ yielded pure product. Yield: $144 \mathrm{mg}(86 \%)$. Anal. Calcd for $\mathrm{C}_{25} \mathrm{H}_{24} \mathrm{~N}_{4} \mathrm{Cl}_{2} \mathrm{P}_{2} \mathrm{Pt}: \mathrm{C}, 42.4 ; \mathrm{H}, 3.5 ; \mathrm{N}, 7.9$. Found: C, 42.6; H, 3.4; $\mathrm{N}, 7.6 .{ }^{1} \mathrm{H}$ NMR ( $200 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 1.6\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.1\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 3.6(\mathrm{pt}, 2 \mathrm{H}$, $\mathrm{CH}), 7.3-8.8\left(\mathrm{~m}, 16 \mathrm{H}\right.$, py). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(81 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta 17.9\left(\mathrm{~s},{ }^{1} \mathrm{~J}_{\mathrm{PPt}}=\right.$ 3490).

### 4.7.8 $\quad \mathbf{P t B r}_{2}$ (dpypcp)

This complex was made in the same manner as for $\mathrm{PtCl}_{2}$ (dpypcp). Thus, reaction of $\operatorname{PtBr}_{2}(\mathrm{cod})(61 \mathrm{mg}, 0.13 \mathrm{mmol})$ and dpypcp ( $60 \mathrm{mg}, 0.14 \mathrm{mmol}$ ) gave $62 \mathrm{mg}(59 \%)$ of an off-white powder. Anal. Calcd for $\mathrm{C}_{25} \mathrm{H}_{24} \mathrm{~N}_{4} \mathrm{Br}_{2} \mathrm{P}_{2} \mathrm{Pt}$ : $\mathrm{C}, 37.7 ; \mathrm{H}, 3.0 ; \mathrm{N}, 7.0$. Found: C , 38.0; $\mathrm{H}, 3.2 ; \mathrm{N}, 6.9 .{ }^{\mathrm{I}} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 300 \mathrm{~K}\right.$ ): $\delta 1.56\left(\mathrm{br} \mathrm{m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 1.80$ (br m, 2H, CH2), $2.12\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 3.59(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}), 7.42(\mathrm{~m}, 2 \mathrm{H}, \mathrm{py}), 7.48(\mathrm{~m}, 2 \mathrm{H}$, py), 7.78 (m, 2H, py), 7.92 (m, 2H, py), 7.97 (m, 2H, py), 8.55 (pt, 2H, py), 8.75 (pt, 4H, py). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 300 \mathrm{~K}$ ): $\delta 17.6\left(\mathrm{~s},{ }^{1} J_{\mathrm{PPt}}=3460\right)$.

### 4.7.9 $\quad \mathbf{P t I}_{\mathbf{2}}$ (dрypcp)

Preparation of this complex in the same manner as that outlined for $\mathrm{PtCl}_{2}$ (dpypcp) yielded, in addition, a small quantity of $\left[\mathrm{Pt}(\text { dpypcp })_{2}\right]_{2}$, as determined by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy (see Section 4.7.13). This contaminant was removed by washing the product with dil. $\mathrm{HCl}(c a .50 \mathrm{~mL})$. Thus, reaction of $\mathrm{PtI}_{2}(\mathrm{cod})(100 \mathrm{mg}, 0.18 \mathrm{mmol})$ and dpypcp ( $79 \mathrm{mg}, 0.18 \mathrm{mmol}$ ) yielded $129 \mathrm{mg}(80 \%)$ of a yellow powder. Anal. Calcd for $\mathrm{C}_{25} \mathrm{H}_{24} \mathrm{~N}_{4} \mathrm{I}_{2} \mathrm{P}_{2} \mathrm{Pt}$ : C, 33.7; H, 2.7; N, 6.3. Found: C, 34.1; H, 2.7; N, 6.0. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 1.55\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 1.75\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.10\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right)$, $3.65(2 \mathrm{H}, \mathrm{m}, \mathrm{CH}), 7.3-8.8(\mathrm{~m}, 16 \mathrm{H}, \mathrm{py}) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta$
$12.6\left(\mathrm{~s},{ }^{1} J_{\mathrm{PPt}}=3290\right)$. Crystals of $\mathrm{PtI}_{2}($ dpypcp $) \cdot 0.18 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ were isolated after 72 h from a $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution onto which $\mathrm{Et}_{2} \mathrm{O}$ had been layered.

### 4.7.10 $\mathbf{P t C l}_{\mathbf{2}}$ (dpype)

This compound was prepared in the same manner as for $\mathrm{PtCl}_{2}$ (dpypcp), except that the product was washed with MeOH instead of $\mathrm{Et}_{2} \mathrm{O}$. Reaction of $\mathrm{PtCl}_{2}$ (cod) ( 230 mg , $0.60 \mathrm{mmol})$ and dpype ( $240 \mathrm{mg}, 0.60 \mathrm{mmol}$ ) yielded $300 \mathrm{mg}(70 \%)$ of a white powder. Anal. Calcd for $\mathrm{C}_{22} \mathrm{H}_{20} \mathrm{~N}_{4} \mathrm{Cl}_{2} \mathrm{P}_{2} \mathrm{Pt}$ : C, 39.5; H, 3.0; $\mathrm{N}, 8.4$. Found: C, 39.7; H, 3.0; N, 8.1. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 2.9\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 7.4-8.7$ ( $\mathrm{m}, 16 \mathrm{H}$, pyridyl). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta 47.1\left(\mathrm{~s},{ }^{1} J_{\mathrm{PPt}}=3480\right)$. Colourless crystals of $\mathrm{PtCl}_{2}$ (dpype) $\cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$, suitable for study by X-ray diffraction, were isolated after 24 h from a $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution which had been layered with $\mathrm{Et}_{2} \mathrm{O}$.

### 4.7.11 PtI $_{2}$ (dpype)

This compound was prepared in the same manner as for $\mathrm{PtCl}_{2}$ (dpypcp). Thus, reaction of $\mathrm{PtI}_{2}(\mathrm{cod})(71 \mathrm{mg}, 0.13 \mathrm{mmol})$ and dpype ( $51 \mathrm{mg}, 0.13 \mathrm{mmol}$ ) yielded $50 \mathrm{mg}(46 \%)$ of a yellow powder. Anal. Calcd for $\mathrm{C}_{22} \mathrm{H}_{20} \mathrm{~N}_{4} \mathrm{I}_{2} \mathrm{P}_{2} \mathrm{Pt}$ : C, 31.0; H, 2.4; N, 6.6. Found: C, 31.2; $\mathrm{H}, 2.4 ; \mathrm{N}, 6.4 .{ }^{1} \mathrm{H} \mathrm{NMR}\left(300 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 300 \mathrm{~K}\right) \delta 2.73\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 7.25-8.85(\mathrm{~m}$, 16 H, py). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right) \delta 49.8\left(\mathrm{~s},{ }^{1} J_{\mathrm{PPt}}=3400\right)$.

### 4.7.12 $\left[\mathrm{Pt}(\mathbf{P}-\mathrm{P})_{2}\right] \mathrm{X}_{\mathbf{2}}(\mathrm{X}=\mathrm{Cl}, \mathrm{I})$

Preparations of the compounds $\left[\mathrm{Pt}(\mathrm{P}-\mathrm{P})_{2}\right] \mathrm{X}_{2}(\mathrm{P}-\mathrm{P}=$ dpype, dpypcp; $\mathrm{X}=\mathrm{Cl}, \mathrm{I})$ either by reaction of two equiv. of the ligand with $\mathrm{PtX}_{2}(\operatorname{cod})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ or, in the case of the iodide salts, by metathesis of $\left[\mathrm{Pt}(\mathrm{P}-\mathrm{P})_{2}\right] \mathrm{Cl}_{2}$ with NaI in acetone, were successful as determined by ${ }^{1} \mathrm{H}$ and ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopies. However, satisfactory elemental analyses were not obtained for these complexes.

### 4.7.13 $\left[\operatorname{Pt}(\text { dpypep })_{2}\right]\left[\mathrm{PF}_{6}\right]_{2} \cdot \mathrm{H}_{2} \mathrm{O}$

To a Schlenk tube charged with $\mathrm{PtCl}_{2}$ (cod) $(14 \mathrm{mg}, 0.04 \mathrm{mmol}$ ), dpypcp ( 34 mg , $0.08 \mathrm{mmol})$ and $\mathrm{NH}_{4} \mathrm{PF}_{6}(13 \mathrm{mg}, 0.08 \mathrm{mmol})$ were added $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \mathrm{~mL})$ and acetone $(4 \mathrm{~mL})$. The resulting cloudy mixture was stirred at r.t. for 75 min and then filtered through Celite 545. The volume of the colourless filtrate was reduced to $c a .2 \mathrm{~mL}$ under
vacuum and the product, afforded as a white precipitate by the addition of $\mathrm{Et}_{2} \mathrm{O}(20 \mathrm{~mL})$, was isolated by filtration and dried overnight in vacuo. Yield: 39 mg ( $73 \%$ ). Anal. Calcd for $\mathrm{C}_{50} \mathrm{H}_{50} \mathrm{~N}_{8} \mathrm{~F}_{12} \mathrm{OP}_{6} \mathrm{Pt}: \mathrm{C}, 43.3 ; \mathrm{H}, 3.8 ; \mathrm{N}, 8.1$. Found: C, 43.1; H, 3.6; N, 8.0. ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta 1.27$ (br m$, 4 \mathrm{H}, \mathrm{CH}_{2}$ ), $1.56\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{H}_{2} \mathrm{O}\right), 1.72(\mathrm{~m}, 4 \mathrm{H}$, $\mathrm{CH}_{2}$ ), 2.13 (m, 4H, CH2), $3.45(\mathrm{~m}, 4 \mathrm{H}, \mathrm{C} H), 7.15-8.75\left(\mathrm{~m}, 32 \mathrm{H}\right.$, py).${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(81 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta 18.40,18.44\left(\mathrm{~s},{ }^{1} J_{\mathrm{PPt}}=2400\right),-144\left(\mathrm{spt}, \mathrm{PF}_{6}{ }^{-},{ }^{1} J_{\mathrm{PF}}=710\right)$.

### 4.7.14 $\left[\operatorname{Pt}(\text { dpype })_{2}\right]\left[\mathrm{PF}_{6}\right]_{2}$

An impure sample of $\left[\mathrm{Pt}(\mathrm{dpype})_{2}\right] \mathrm{Cl}_{2}(50 \mathrm{mg}, c a .0 .05 \mathrm{mmol})$ and $\mathrm{NH}_{4} \mathrm{PF}_{6}(16 \mathrm{mg}$, 0.01 mmol ) were dissolved in acetone ( 20 mL ) and the resulting cloudy solution was stirred for 30 min ; the mixture was filtered through Celite 545 which was subsequently washed with acetone ( $3 \times 5 \mathrm{~mL}$ ) and the combined filtrate reduced to $c a .2 \mathrm{~mL}$. The product was afforded as a white precipitate by the addition of $\mathrm{Et}_{2} \mathrm{O}(30 \mathrm{~mL})$, isolated by filtration, washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 5 \mathrm{~mL})$ and dried in vacuo. Yield: $42 \mathrm{mg}(77 \%)$. Anal. Calcd for $\mathrm{C}_{44} \mathrm{H}_{40} \mathrm{~N}_{8} \mathrm{~F}_{12} \mathrm{P}_{6} \mathrm{Pt}: \mathrm{C}, 41.0 ; \mathrm{H}, 3.1 ; \mathrm{N}, 8.7$. Found: C, 40.8; H, 3.0; N, 8.5. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}, 300 \mathrm{~K}$ ): $\delta 1.30\left(\mathrm{~m}, 8 \mathrm{H}, \mathrm{CH}_{2}\right), 5.7-7.1(\mathrm{~m}, 32 \mathrm{H}, \mathrm{py}) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $81 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}, 300 \mathrm{~K}$ ): $\delta 54.4$ (s, ${ }^{1} \mathrm{JPPt}=2480$ ), -144 ( $\mathrm{spt}, \mathrm{PF}_{6}{ }^{-1},{ }^{1} J_{\mathrm{PF}}=710$ ).

### 4.7.15 $\mathbf{P d C l}_{2}$ (dpypcp)

To a $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution ( 10 mL ) containing $\mathrm{PdCl}_{2}(\operatorname{cod})(57 \mathrm{mg}, 0.20 \mathrm{mmol})$ was added a $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$ solution containing dpypcp $(87 \mathrm{mg}, 0.20 \mathrm{mmol})$ over the course of $c a$. 2 min . Although the solution was stirred for 2 h , the colour change from orange to yellow was complete within 0.5 h . A fine precipitate which formed during this time was removed by filtration through Celite 545 . The yellow filtrate was concentrated to ca. 2 mL and $\mathrm{Et}_{2} \mathrm{O}(20 \mathrm{~mL})$ was added to give the product as a yellow powder. This was isolated by filtration, washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 3 \mathrm{~mL})$ and dried in vacuo. Yield: $100 \mathrm{mg}(94 \%)$. Anal. Calcd for $\mathrm{C}_{25} \mathrm{H}_{24} \mathrm{~N}_{4} \mathrm{Cl}_{2} \mathrm{P}_{2} \mathrm{Pd}$ : C, 48.4; H, 3.9; N, 9.0. Found: C, 48.0; H, 3.8; N, 8.8. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 1.66\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 1.82\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.10(\mathrm{~m}, 2 \mathrm{H}$, $\mathrm{CH}_{2}$ ), 3.81 (m, 2H, CH), $7.40(\mathrm{~m}, 4 \mathrm{H}, \mathrm{py}), 7.73(\mathrm{~m}, 2 \mathrm{H}, \mathrm{py}), 7.84(\mathrm{~m}, 2 \mathrm{H}, \mathrm{py}), 8.14(\mathrm{~m}$, 2 H, py), 8.49 (m, 2H, py), 8.69 (m, 4H, py). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(162 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta$ 39.3 (s).

### 4.7.16 $\mathrm{PdBr}_{2}$ (dрурср) $\cdot \mathrm{H}_{2} \mathrm{O}$

This complex was made in the same manner as for $\mathrm{PdCl}_{2}$ (dpypcp). Thus, reaction of $\mathrm{PdBr}_{2}$ (cod) ( $47 \mathrm{mg}, 0.12 \mathrm{mmol}$ ) and dpypcp ( $55 \mathrm{mg}, 0.12 \mathrm{mmol}$ ) gave $81 \mathrm{mg}(92 \%)$ of a yellow powder. Anal. Calcd for $\mathrm{C}_{25} \mathrm{H}_{26} \mathrm{~N}_{4} \mathrm{Br}_{2} \mathrm{OP}_{2} \mathrm{Pd}$ : C, $41.3 ; \mathrm{H}, 3.6 ; \mathrm{N}, 7.7$. Found: C , 41.4; $\mathrm{H}, 3.5 ; \mathrm{N}, 7.5 .{ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right.$ ): $\delta 1.56$ (s, $2 \mathrm{H}, \mathrm{H}_{2} \mathrm{O}$ ), 1.65 (br m, $2 \mathrm{H}, \mathrm{CH}_{2}$ ), 1.83 (br m, $2 \mathrm{H}, \mathrm{CH}_{2}$ ), $2.10\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right.$ ), 3.85 (br m, $2 \mathrm{H}, \mathrm{CH}$ ), $7.38(\mathrm{~m}, 2 \mathrm{H}$, py), $7.45(\mathrm{~m}, 2 \mathrm{H}$, py), $7.74(\mathrm{~m}, 2 \mathrm{H}$, py), $7.88(\mathrm{~m}, 2 \mathrm{H}, \mathrm{py}), 8.08(\mathrm{~m}, 2 \mathrm{H}, \mathrm{py}), 8.58(\mathrm{~m}, 2 \mathrm{H}$, py), 8.67 (pd, 2 H, py), 8.73 (pd, 2 H , py). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta$ 36.9 (s).

### 4.7.17 PdI $_{2}$ (dpypcp)

This complex was made in the same manner as for $\mathrm{PdCl}_{2}$ (dpypcp). Thus, reaction of $\mathrm{PdI}_{2}(\mathrm{cod})(58 \mathrm{mg}, 0.13 \mathrm{mmol})$ and dpypcp ( $55 \mathrm{mg}, 0.12 \mathrm{mmol}$ ) gave $73 \mathrm{mg}(73 \%)$ of an orange powder. Anal. Calcd for $\mathrm{C}_{25} \mathrm{H}_{24} \mathrm{~N}_{4} \mathrm{I}_{2} \mathrm{P}_{2} \mathrm{Pd}$ : C, 37.4; H, 3.0; N, 7.0. Found: C, 37.6; $\mathrm{H}, 3.0 ; \mathrm{N}, 6.8 .{ }^{1} \mathrm{H} \mathrm{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right.$ ): $\delta 1.57$ (br m, 2H, $\mathrm{CH}_{2}$ ), 1.74 (br m, $2 \mathrm{H}, \mathrm{CH}$ ), $2.07\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 3.81$ (br m, $2 \mathrm{H}, \mathrm{CH}$ ), 7.34 (m, $2 \mathrm{H}, \mathrm{py}$ ), 7.45 (m, $2 \mathrm{H}, \mathrm{py}$ ), $7.73(\mathrm{~m}, 2 \mathrm{H}, \mathrm{py}), 7.88(\mathrm{~m}, 2 \mathrm{H}, \mathrm{py}), 8.05(\mathrm{pd}, 2 \mathrm{H}, \mathrm{py}), 8.62(\mathrm{~m}, 2 \mathrm{H}, \mathrm{py}), 8.66(\mathrm{pd}, 2 \mathrm{H}$, py), 8.75 (pd, 2H, py). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 30.0$ (s).

### 4.7.18 $\left[\mathbf{P d}(\text { dpypcp })_{2}\right]\left[\mathrm{PF}_{6}\right]_{2} \cdot \mathbf{H}_{2} \mathrm{O}$

This complex was made in the same manner as for $\left[\operatorname{Pt}(\text { dpypcp })_{2}\right]\left[\mathrm{PF}_{6}\right]_{2} \cdot \mathrm{H}_{2} \mathrm{O}$. Thus, reaction of trans $-\mathrm{PdCl}_{2}(\mathrm{PhCN})_{2}$ ( $23 \mathrm{mg}, 0.06 \mathrm{mmol}$ ), dpypcp ( $54 \mathrm{mg}, 0.12 \mathrm{mmol}$ ) and $\mathrm{NH}_{4} \mathrm{PF}_{6}(37 \mathrm{mg}, 0.22 \mathrm{mmol})$ gave $61 \mathrm{mg}(80 \%)$ of a pale yellow powder. Anal. Calcd for $\mathrm{C}_{50} \mathrm{H}_{50} \mathrm{~N}_{8} \mathrm{~F}_{12} \mathrm{OP}_{6} \mathrm{Pd}$ : C, 46.2; H, 3.9; N, 8.6. Found: C, 46.1; H, 3.8; N, 8.4. This compound exists as a $1: 1$ mixture of diastereomers. Where the peaks for each are resolved they are given as comma-separated pairs. ${ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 300 \mathrm{~K}\right)$ : $\delta 1.56\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{H}_{2} \mathrm{O}\right), 1.97$ (br m, 4H, CH2), 1.61, 1.71 (br m, 4H, CH2), 1.98, 2.07 (br m, $4 \mathrm{H}, \mathrm{CH}_{2}$ ), 3.49, $3.62(\mathrm{br} \mathrm{m}, 4 \mathrm{H}, \mathrm{CH}), 7.26(\mathrm{~m}, 4 \mathrm{H}, \mathrm{py}), 7.37(\mathrm{~m}, 2 \mathrm{H}, \mathrm{py}), 7.66(\mathrm{~m}, 16 \mathrm{H}$, py), $7.54\left(\mathrm{~m}, 2 \mathrm{H}\right.$, py), $8.16,8.54$ (pd, 4 H, py), $8.38,8.76$ (pd, 4 H, py). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 300 \mathrm{~K}$ ): $\delta 29.6,30.2(\mathrm{~s}),-144\left(\mathrm{spt},{ }^{1} J_{\mathrm{PF}}=710\right)$.

### 4.7.19 Preparation of $\left[\mathrm{Pt}_{\mathbf{2}}(\text { dpype })_{2} \mathbf{A g}_{4}\left(\mathrm{NO}_{3}\right)_{\mathbf{8}}\left(\mathbf{H}_{\mathbf{2}} \mathrm{O}\right)_{\mathbf{2}}\right]_{\mathbf{n}}, \mathbf{1}$

To a mixture of glacial acetic acid ( 4 mL ) and EtOH ( 15 mL ) in a Schlenk tube open to the atmosphere were added $\operatorname{Ptt}_{2}($ dpype $)(110 \mathrm{mg}, 0.13 \mathrm{mmol})$ and $\mathrm{AgNO}_{3}(250 \mathrm{mg}, 1.5$ $\mathrm{mmol})$, and the resulting yellow slurry was stirred for 4.5 h . Distilled $\mathrm{H}_{2} \mathrm{O}(\sim 1 \mathrm{~mL})$ was then added and the mixture was stirred for a further 48 h when it became cream in colour. The suspension was then filtered through Celite 545 to afford a pale yellow solution. Yellow crystals of $\mathbf{1}$ deposited by slow evaporation of this solution in the dark over a period of 3 months. Yield (of isolated crystals, based on Pt ): 12\%. Anal. Calcd for $\mathrm{C}_{44} \mathrm{H}_{44} \mathrm{~N}_{16} \mathrm{O}_{26} \mathrm{P}_{4} \mathrm{Pt}_{2}$ : C, 24.5; H, 2.1; N, 10.4. Found: C, 24.1; H, 2.0; N, 10.5. ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{D}_{2} \mathrm{O}, 300 \mathrm{~K}\right): \delta 3.05\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 4.10\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 7.53(\mathrm{pt}, 4 \mathrm{H}, \mathrm{py}), 7.53$ (pt, $4 \mathrm{H}, \mathrm{py}), 8.00(\mathrm{~m}, 16 \mathrm{H}, \mathrm{py}), 8.58\left(\mathrm{~d}, 4 \mathrm{H}_{6},{ }^{1} J_{\mathrm{HH}}=4.53\right), 8.78\left(\mathrm{~d}, 4 \mathrm{H}_{6}{ }^{\prime},{ }^{1} J_{\mathrm{HH}}=5.05\right)$. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(81 \mathrm{MHz}, \mathrm{D}_{2} \mathrm{O}, 300 \mathrm{~K}\right): \delta 41.5\left(\mathrm{~s},{ }^{1} J_{\mathrm{PPt}}=3200 ;{ }^{3} J_{\mathrm{PPt}}=69\right)$. UV-vis $\left(\mathrm{H}_{2} \mathrm{O}\right)$ : 346 [6030].

### 4.7.20 Preparation of $\left[\mathrm{Pt}_{2}(\text { dpypcp })_{2} \mathrm{Ag}_{6}\left(\mathrm{NO}_{3}\right)_{10}\right]_{\mathrm{n}}, \mathbf{2}$

In a procedure similar to that used for the synthesis of $\mathbf{1}$, addition of $\mathrm{PtI}_{2}(\mathrm{dpypcp})$ (ca. 5 $\mathrm{mg}, 0.006 \mathrm{mmol}$ ) and a large excess of $\mathrm{AgNO}_{3}$ to a mixture of glacial acetic acid ( 1 mL ) and $\mathrm{EtOH}(3 \mathrm{~mL})$ resulted in the formation of a yellow solution which, by slow evaporation in the dark over 3 weeks, yielded a small number of orange crystals. The yield was not determined. ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{D}_{2} \mathrm{O}, 300 \mathrm{~K}\right): \delta 1.30\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 1.46$ (dq, 2H, CH2 $), 1.74\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.15\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.33\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 2.80(\mathrm{~m}, 4 \mathrm{H}$, $\mathrm{CH}), 7.43(\mathrm{pt}, 1 \mathrm{H}, \mathrm{py}), 7.61(\mathrm{~m}, 6 \mathrm{H}, \mathrm{py}), 7.84(\mathrm{~m}, 6 \mathrm{H}, \mathrm{py}), 8.11(\mathrm{~m}, 11 \mathrm{H}, \mathrm{py}), 8.32(\mathrm{~d}$, 1 H, py), 8.61 (d, 1H, py), 8.75 (pd, 2H, py), 8.90 (pd, 2H, py), 8.97 (d, 1H, py), 9.05 (pd, 1 H, py). UV-vis $\left(\mathrm{H}_{2} \mathrm{O}\right): 348$ [5500]. The limited amount of 2 obtained precluded elemental analysis determination and measurement of ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR data.

### 4.7.21 $\left[\mathrm{Pt}_{2}\right.$ (dpype) $\left.{ }_{2}\right]\left[\mathrm{NO}_{3}\right]_{4} \cdot \mathbf{2} \mathrm{H}_{2} \mathrm{O}$

To a combination of $\mathrm{PtI}_{2}(\mathrm{cod})(180 \mathrm{mg}, 0.32 \mathrm{mmol})$ and $\mathrm{AgNO}_{3}(110 \mathrm{mg}, 0.64 \mathrm{mmol})$ was added $\mathrm{EtOH}(5 \mathrm{~mL})$ and $\mathrm{H}_{2} \mathrm{O}(2 \mathrm{~mL})$, and the mixture was stirred in the dark for 1 h . The solvent was removed at the pump, the residue was taken up in MeOH and the mixture filtered through Celite 545 . Some dpype ( $130 \mathrm{mg}, 0.32 \mathrm{mmol}$ ) was added to the filtrate as a solid. The pale yellow solution was stirred overnight and a yellow precipitate
formed. This was isolated by filtration and washed with $\mathrm{MeOH}(3 \times 3 \mathrm{~mL})$ in which it was slightly soluble. Yield of first crop: $31 \mathrm{mg}(13 \%)$. The filtrate was stirred for a further 2.5 h during which more product deposited. The slurry was reduced in vacuo about $1 / 5^{\text {th }}$ of its original volume. Acetone $(10 \mathrm{~mL})$ and $\mathrm{Et}_{2} \mathrm{O}(15 \mathrm{~mL})$ were added to complete the precipitation of the second crop which was isolated by filtration and dried in vacuo at r.t. Yield: 83 mg ( $36 \%$ ). Anal. Calcd for $\mathrm{C}_{44} \mathrm{H}_{44} \mathrm{~N}_{12} \mathrm{O}_{14} \mathrm{P}_{4} \mathrm{Pt}_{2}$ : C, 35.7; H, 3.0; N, 11.4. Found: C, 35.7; H, 3.0; N, 11.3. An attempt to remove the hydrates by heating the complex to $100^{\circ} \mathrm{C}$ under vacuum resulted in decomposition. The NMR and UV-vis spectroscopic data were the same as those found for 1.

### 4.7.22 $\mathbf{P t}\left(\mathbf{P P h}_{3}\right)_{2}$ (dpypcp)

To a combination of dpypcp ( $58 \mathrm{mg}, 0.13 \mathrm{mmol}$ ) and $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{4}(160 \mathrm{mg}, 0.13 \mathrm{mmol})$ was added $\mathrm{C}_{6} \mathrm{H}_{6}(10 \mathrm{~mL})$ and the resulting orange solution was stirred for 2 h . The solvent was removed in vacuo, and $\mathrm{Et}_{2} \mathrm{O}(3 \times 10 \mathrm{~mL})$ was added to the residue which was triturated to give a finely-divided solid in an orange solution. The product was isolated by filtration, washed thoroughly with $\mathrm{Et}_{2} \mathrm{O}(3 \times 10 \mathrm{~mL})$ to remove $\mathrm{PPh}_{3}$ and dried under vacuum. Yield: 130 mg ( $84 \%$ ). Anal. Calcd for $\mathrm{C}_{61} \mathrm{H}_{54} \mathrm{~N}_{4} \mathrm{P}_{4} \mathrm{Pt}: \mathrm{H}, 63.1 ; \mathrm{H}, 4.7 ; \mathrm{N}, 4.8$. Found: C, 63.1; H, 4.7; N, 4.9. ${ }^{\mathrm{l}} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}, 300 \mathrm{~K}$ ): $\delta 2.24$ (br m, 2H, $\mathrm{CH}_{2}$ ), 2.72 (br m, $\mathrm{CH}_{2}$ ), 3.10 (br m, $2 \mathrm{H}, \mathrm{CH}_{2}$ ), 4.84 (br m, $2 \mathrm{H}, \mathrm{CH}$ ), 6.47 (pt, 2 H , py), 6.77 (pt, 2H, py), 6.88 (pt, 2H, py), 7.00 (pd, 2H, py), 7.15 ( $\mathrm{m}, 8 \mathrm{H}$, py and $p$ - Ph ), 7.67 (m, 24H, $o$ - and $m-\mathrm{Ph}$ ), 8.28 (pd, $2 \mathrm{H}, \mathrm{py}$ ), 8.50 (pd, $2 \mathrm{H}, \mathrm{py}$ ), 8.94 (pd, $2 \mathrm{H}, \mathrm{py}) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}, 300 \mathrm{~K}$ ): $\delta 14.6\left(\mathrm{t},{ }^{2} J_{\mathrm{PP}}=52,{ }^{1} J_{\mathrm{PPt}}=3550\right), 23.1\left(\mathrm{t},{ }^{2} J_{\mathrm{PP}}=52,{ }^{1} J_{\mathrm{PPt}}\right.$ $=4210$ ) .

### 4.7.23 $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}$ (dpype)

The complex was made in the same manner as for $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}(\mathrm{dpypcp})$. Thus, reaction of $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{4}(240 \mathrm{mg}, 0.19 \mathrm{mmol})$ and dpype ( $77 \mathrm{mg}, 0.19 \mathrm{mmol}$ ) gave $150 \mathrm{mg}(69 \%)$ of an orange powder. Anal. Calcd for $\mathrm{C}_{58} \mathrm{H}_{50} \mathrm{~N}_{4} \mathrm{P}_{4} \mathrm{Pt}$ : C, $62.1 ; \mathrm{H}, 4.5 ; \mathrm{N}, 5.0$. Found: 61.6; H, 4.7; N, 4.9. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}, 300 \mathrm{~K}$ ): $\delta 3.63$ (m, $4 \mathrm{H}, \mathrm{CH}_{2}$ ), 6.32 (pt, $4 \mathrm{H}, \mathrm{py}$ ), 6.64 (pt, 4H, py), 6.88 (m, py and Ph), 7.33 (m, Ph), 8.34 (pd, 2H, py). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(121 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}, 300 \mathrm{~K}\right): \delta 21.3\left(\mathrm{t},{ }^{2} J_{\mathrm{PP}}=53,{ }^{1} J_{\mathrm{PPt}}=4180\right), 32.0\left(\mathrm{t},{ }^{2} J_{\mathrm{PP}}=53,{ }^{1} J_{\mathrm{PPt}}=\right.$ 3330).

### 4.7.24 $\mathrm{Pt}(\text { dpypcp })_{2}$

This compound was made in the same manner as for $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}$ (dpypcp) except that a ligand:metal ratio of $2: 1$ was used. Thus, reaction of dpypep ( $50 \mathrm{mg}, 0.11 \mathrm{mmol}$ ) and $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{4}(70 \mathrm{mg}, 0.056 \mathrm{mmol})$ gave $36 \mathrm{mg}(59 \%)$ of a red powder. Because of the airsensitivity of this compound, satisfactory elemental analysis could not be obtained. The best is given by: Anal. Calcd for $\mathrm{C}_{50} \mathrm{H}_{48} \mathrm{~N}_{8} \mathrm{P}_{4} \mathrm{Pt}$ : C, 55.6 ; $\mathrm{H}, 4.5$; $\mathrm{N}, 10.4$. Found: C, 54.3; $\mathrm{H}, 4.5$. N, 9.6. 'H NMR ( $300 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}, 300 \mathrm{~K}$ ): Major diastereomer: $\delta 1.47$ (br m, 4H, $\mathrm{CH}_{2}$ ), 1.95 (br m, 4H, $\mathrm{CH}_{2}$ ), 2.07 (br m, $4 \mathrm{H}, \mathrm{CH}_{2}$ ), $3.80(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}), 6.47,6.90,7.67$, 8.09, 8.37, 8.45. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}, 300 \mathrm{~K}$ ): Major diastereomer: $\delta 20.1$ (s, ${ }^{1} J_{\mathrm{PPt}}=3570$ ). Minor diastereomer: $\delta 23.5\left(\mathrm{~s},{ }^{1} J_{\mathrm{PPt}}=3580\right)$.

### 4.7.25 $\mathbf{P t}(\text { dpype })_{2}$

This compound was made in the same manner as for $\mathrm{Pt}(\mathrm{dpypcp})_{2}$. Thus, an overnight reaction between $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{4}(62 \mathrm{mg}, 0.050 \mathrm{mmol})$ and dpype ( $41 \mathrm{mg}, 0.010 \mathrm{mmol}$ ) gave $27 \mathrm{mg}(56 \%)$ of an orange powder. Once again, the air-sensitivity of this compound precluded satisfactory elemental analysis. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}, 300 \mathrm{~K}$ ): $\delta 3.35$ (m, $8 \mathrm{H}, \mathrm{CH}_{2}$ ) , 6.39 (pt, $8 \mathrm{H}, \mathrm{py}$ ), 6.72 (pt, $8 \mathrm{H}, \mathrm{py}$ ), 7.50 (pd, $8 \mathrm{H}, \mathrm{py}$ ), 8.34 (pd, $8 \mathrm{H}, \mathrm{py}$ ). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $121 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}, 300 \mathrm{~K}$ ): $\delta 41.2\left(\mathrm{~s},{ }^{1} J_{\mathrm{PPt}}=3600\right)$.

### 4.7.26 $\operatorname{Pt}\left(\boldsymbol{\eta}^{2}\right.$-dmf)(dpypcp)

To an orange $\mathrm{C}_{6} \mathrm{H}_{6}$ solution ( 5 mL ) containing $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{2}$ (dpypcp) $(33 \mathrm{mg}, 0.029 \mathrm{mmol})$ was added dmm ( 0.2 mL ). The solution was stirred for 2 h when it became colourless. The volume was reduced in vacuo to $<1 \mathrm{~mL}$ and $\mathrm{Et}_{2} \mathrm{O}(10 \mathrm{~mL})$ and hexanes $(20 \mathrm{~mL})$ were added. The solution was then cooled over liquid- $\mathrm{N}_{2}$, and a white precipitate formed. This was isolated by filtration and dried in vacuo. Yield: $11 \mathrm{mg}(47 \%)$. Anal. Calcd for $\mathrm{C}_{31} \mathrm{H}_{32} \mathrm{~N}_{4} \mathrm{O}_{4} \mathrm{P}_{2} \mathrm{Pt}$ : C, 47.6; H, 4.1; $\mathrm{N}, 7.2$. Found: C, 47.1; H, 4.1; $\mathrm{N}, 6.4 .{ }^{1} \mathrm{H}\left\{{ }^{31} \mathrm{P}\right\}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): Major diastereomer: $\delta 1.60$ (br m, $2 \mathrm{H}, \mathrm{CH}_{2}$ ), 2.18 (br m, 2 H , $\left.\left.\mathrm{CH}_{2}\right), 2.27\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{C} H_{2}\right), 3.13(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}), 3.30(\mathrm{~s}, 6 \mathrm{H}, \mathrm{CH})_{3}\right), 3.58\left(\mathrm{~s}, 2 \mathrm{H},=\mathrm{CH},{ }^{2} J_{\mathrm{HPt}}=\right.$ 60.7 ; turning off the ${ }^{31} \mathrm{P}$ decoupler gives ${ }^{3} J_{\mathrm{HP}}=8.05$ ), 7.18 (pdd, $2 \mathrm{H}, \mathrm{Ar},{ }^{3} J_{\mathrm{HH}}=4.83$, $\left.{ }^{3} J_{\mathrm{HH}}=7.56\right), 7.29\left(\mathrm{pdd}, 2 \mathrm{H}, \mathrm{Ar},{ }^{3} J_{\mathrm{HH}}=4.91,{ }^{3} J_{\mathrm{HH}}=6.80\right), 7.60\left(\mathrm{pdt}, 2 \mathrm{H}, \mathrm{Ar},{ }^{3} J_{\mathrm{HH}}=7.65\right.$, $\left.{ }^{4} J_{\mathrm{HH}}=1.69\right), 7.72\left(\mathrm{pd}, 2 \mathrm{H}, \mathrm{Ar},{ }^{3} J_{\mathrm{HH}}=6.86\right), 7.76\left(\mathrm{pdt}, 2 \mathrm{H}, \mathrm{Ar},{ }^{3} J_{\mathrm{HH}}=7.69,{ }^{4} J_{\mathrm{HH}}=1.68\right)$, $8.09\left(\mathrm{pd}, 2 \mathrm{H}, \mathrm{Ar},{ }^{3} J_{\mathrm{HH}}=7.77\right), 8.60\left(\mathrm{pd}, 2 \mathrm{H}, \mathrm{Ar},{ }^{3} J_{\mathrm{HH}}=4.72\right), 8.69\left(\mathrm{pd}, 2 \mathrm{H}, \mathrm{Ar},{ }^{3} J_{\mathrm{HH}}=\right.$
4.84). Minor diastereomer: $\delta 2.05$ (br m, $2 \mathrm{H}, \mathrm{CH}_{2}$ ), 2.12 (br m, $2 \mathrm{H}, \mathrm{CH}_{2}$ ), 3.24 ( $\mathrm{s}, 6 \mathrm{H}$, $\left.\mathrm{CH}_{3}\right), 7.56\left(\mathrm{pd}, 2 \mathrm{H}, \mathrm{Ar},{ }^{3} J_{\mathrm{HH}}=7.78\right), 7.65\left(\mathrm{pdt}, 2 \mathrm{H}, \mathrm{Ar},{ }^{3} J_{\mathrm{HH}}=7.71,{ }^{4} J_{\mathrm{HH}}=1.59\right), 8.12$ (pd, $2 \mathrm{H}, \mathrm{Ar},{ }^{3} J_{\mathrm{HH}}=7.52$ ), $8.64\left(\mathrm{pd}, 2 \mathrm{H}, \mathrm{Ar},{ }^{3} J_{\mathrm{HH}}=4.71\right.$ ). All other peaks are obscured by those of the major diastereomer. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $202 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): Major diastereomer: $\delta 33.1$ ( $\mathrm{s},{ }^{1} J_{\mathrm{PPt}}=3360$ ). Minor diastereomer: $\delta 31.8\left(\mathrm{~s},{ }^{1} J_{\mathrm{PPt}}=3400\right)$.

### 4.7.27 $\operatorname{Pt}\left(\boldsymbol{\eta}^{2}\right.$-def)(dpypcp)

To solid $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{4}(99 \mathrm{mg}, 0.071 \mathrm{mmol})$ and dpypcp ( $32 \mathrm{mg}, 0.072 \mathrm{mmol}$ ) was added $\mathrm{C}_{6} \mathrm{H}_{6}(1 \mathrm{~mL})$ and the resulting orange solution was stirred for 45 min . $\mathrm{An} \mathrm{Et}_{2} \mathrm{O}(1 \mathrm{~mL})$ solution containing dem $(0.1 \mathrm{~mL})$ was then added via cannula. This caused the immediate formation of a white precipitate which was isolated by filtration, washed with $\mathrm{Et}_{2} \mathrm{O}(5 \times$ 3 mL ) and dried in vacuo. Yield: $32 \mathrm{mg}(56 \%)$. Dissolution of the product in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$, filtration through Celite 545 and reprecipitation with $\mathrm{Et}_{2} \mathrm{O}$ gave the analytically pure product. Anal. Calcd for $\mathrm{C}_{33} \mathrm{H}_{36} \mathrm{~N}_{4} \mathrm{O}_{4} \mathrm{P}_{2} \mathrm{Pt}$ : C 49.0; H 4.5; N 6.7. Found: C 48.7; H 4.5; N 6.7. ${ }^{1} \mathrm{H}\left\{{ }^{31} \mathrm{P}\right\}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): Major diastereomer: $\delta 0.87(\mathrm{t}, 6 \mathrm{H}$, $\mathrm{CH}_{2} \mathrm{CH}_{3},{ }^{3} J_{\mathrm{HH}}=7.12$ ), $1.53\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.17\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.27\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 3.11$ ( $\mathrm{m}, 2 \mathrm{H}, \mathrm{CH},{ }^{3} J_{\mathrm{HPt}}=38.2$ ), $3.58\left(\mathrm{~d}, 2 \mathrm{H},=\mathrm{CH},{ }^{2} J_{\mathrm{HPt}}=61.2\right.$; turning off the ${ }^{31} \mathrm{P}$ decoupler gives ${ }^{3} J_{\mathrm{HP}}=8.19$ ), 3.72 ( $\mathrm{m}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{CH}_{3},{ }^{2} J_{\mathrm{HH}} \sim 9-10$ (by simulation ${ }^{127}$ ), ${ }^{3} J_{\mathrm{HH}}=7.21$ ), $3.82\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH} \mathrm{CH}_{3},{ }^{2} J_{\mathrm{HH}} \sim 9-10\right.$ (by simulation), ${ }^{3} J_{\mathrm{HH}}=7.21$ ), 7.17 (ddd, $2 \mathrm{H}, \mathrm{Ar},{ }^{3} J_{\mathrm{HH}}$ $\left.=7.65,{ }^{3} J_{\mathrm{HH}}=4.80,{ }^{4} J_{\mathrm{HH}}=1.16\right), 7.29\left(\mathrm{ddd}, 2 \mathrm{H}, \mathrm{Ar},{ }^{3} J_{\mathrm{HH}}=7.65,{ }^{3} J_{\mathrm{HH}}=4.80,{ }^{4} J_{\mathrm{HH}}=\right.$ 1.16), 7.59 (pdt, $2 \mathrm{H}, \mathrm{Ar},{ }^{3} J_{\mathrm{HH}}=7.69,{ }^{4} J_{\mathrm{HH}}=1.80$ ), $7.73\left(\mathrm{pd}, 2 \mathrm{H}, \mathrm{Ar},{ }^{3} J_{\mathrm{HH}}=6.48\right), 7.75$ (pdt, $2 \mathrm{H}, \mathrm{Ar},{ }^{3} J_{\mathrm{HH}}=7.71,{ }^{4} J_{\mathrm{HH}}=1.77$ ), 8.19 (pd, $2 \mathrm{H}, \mathrm{Ar},{ }^{3} J_{\mathrm{HH}}=7.76$ ), 8.58 (pdd, $2 \mathrm{H}, \mathrm{Ar}$, $\left.{ }^{3} J_{\mathrm{HH}}=4.74,{ }^{4} J_{\mathrm{HH}}=0.81\right), 8.70\left(\mathrm{pdd}, 2 \mathrm{H}, \mathrm{Ar},{ }^{3} J_{\mathrm{HH}}=4.87,{ }^{4} J_{\mathrm{HH}}=0.76\right)$. Minor diastereomer: $\delta 0.98\left(\mathrm{t}, 6 \mathrm{H}, \mathrm{CH}_{3},{ }^{3} J_{\mathrm{HH}}=7.12\right), 3.54\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CH},{ }^{1} J_{\mathrm{HPt}}=59.3\right)$. All other peaks are obscured by those of the major diastereomer. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(202 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.$, 300 K ): Major diastereomer: $\delta 33.6$ ( $\mathrm{s},{ }^{1} J_{\mathrm{PPt}}=3360$ ). Minor diastereomer: $\delta 32.1\left(\mathrm{~s},{ }^{1} J_{\mathrm{PPt}}\right.$ $=3410$ ).

### 4.7.28 Determination of $\mathrm{pK}_{\mathrm{a}}$ values for $\left[\operatorname{dpypcp}(\mathrm{H})_{2}\right]^{\mathbf{2 +}}$

The $\mathrm{pK}_{\mathrm{a}}$ determinations were carried out with the kind assistance of Dr. Song Bin, a former postdoctoral fellow in the laboratory of Dr. Chris Orvig at UBC.

### 4.7.28.1 Materials

Water was deionised (Barnstead D8902 and D8904 cartridges) and distilled (Corning MP-1 Megapure still), and depleted in $\mathrm{CO}_{2}$ by boiling under Ar for 30 min . The concentration of the NaOH titrant was established to be $0.1094 \mathrm{~mol} \mathrm{~L}^{-1}$ by titration against potassium biphthalate.

### 4.7.28.2 Instrumentation

An automatic titration system controlled by an IBM compatible PC running "in-house" software written in QBasic, and consisting of a Metrohm 713 pH meter equipped with a Metrohm 6.0233.100 electrode and a model 665 Metrohm Dosimat autoburet ( 5 mL capacity, 0.005 mL accuracy), was used. Titrations were performed at 298 K in a waterjacketed vessel thermostatted by a Julabo UC circulating bath.

### 4.7.28.3 Procedure

A stock solution of dpypcp was made by dissolving the ligand ( $33.8 \mathrm{mg}, 7.64 \times 10^{-2}$ mmol) in a mixture of dil. $\mathrm{HCl}\left(10.0 \mathrm{~mL}, 0.1419 \mathrm{~mol} \mathrm{~L}^{-1}\right.$ by titration against standard $\mathrm{NaOH})$ and $\mathrm{H}_{2} \mathrm{O}(15.0 \mathrm{~mL})$. Solutions for titration were made by mixing 10.0 mL of the stock solution, $\mathrm{H}_{2} \mathrm{O}(35.0 \mathrm{~mL})$ and aq. $\mathrm{NaCl}\left(5.0 \mathrm{~mL}, 1.60 \mathrm{~mol} \mathrm{~L}^{-1}\right)$. It was necessary to add between $3-3.5 \mathrm{~mL}$ of $\mathrm{NaOH}\left(0.1094 \mathrm{~mol} \mathrm{~L}^{-1}\right)$ to this solution prior to each titration to raise the pH which was initially too low for accurate determination by the instrument. Computer-controlled titrations were performed by sequential addition via an autoburet of 0.05 mL aliquots of $\mathrm{NaOH}\left(0.1094 \mathrm{~mol} \mathrm{~L}^{-1}\right)$ to this mixture. After equilibration, the electrode potential at each addition was recorded by the computer and translated into a pH value; thus a plot of $\mathrm{pH} v s$. vol. NaOH added was obtained. To determine the $\mathrm{pK}_{\mathrm{a}}$ values, the plot was analysed using a Newton-Gauss non-linear least-squares curve-fitting program over the pH range $2.7-11.0$. The number of protons bound per ligand, $\bar{n}$, was calculated at each pH using the difference in vol. of NaOH added between a titration containing dpypcp and one in its absence; this number in mol divided by [dpypcp] gives $\bar{n}$.

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## 5 Attempted Catalytic Hydration of Maleic Acid

### 5.1 Introduction

To reiterate the point made in the General Introduction, the aqueous phase catalytic hydration of olefins (Scheme 5.1) takes the concept of atom economy to its highest level: the solvent is environmentally benign, and is a reactant in an addition, zero-waste reaction. In fact, the anti-Markovnikov addition of water to terminal olefins to produce linear alcohols has been cited as one of the ten remaining challenges for homogeneous catalysis. ${ }^{1}$ In principle, prochiral olefins could be asymmetrically hydrated to give optically pure alcohols.

## Scheme 5.1

$$
\mathrm{RCH}=\mathrm{CH}_{2}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{RCH}_{2} \mathrm{CH}_{2}(\mathrm{OH}) \text { and/or } \mathrm{RC} * \mathrm{H}(\mathrm{OH}) \mathrm{CH}_{3}
$$

There remains a dearth of transition metal complexes which are capable of bringing about this transformation. Aqueous solutions of chlororuthenate(II) catalyse the hydration of $\mathrm{CF}_{2} \mathrm{CF}_{2},{ }^{2}$ and $\mathrm{Cr}^{\mathrm{III}}$ and $\mathrm{Al}^{\mathrm{III}}$ complexes effect the hydration of maleic to malic acid. ${ }^{3,4}$ The report by Jensen and Trogler, which claimed that 1-hexene could be hydrated to 1 -hexanol by trans $-\mathrm{Pt}(\mathrm{H}) \mathrm{Cl}\left(\mathrm{PMe}_{3}\right)_{2},{ }^{5}$ was shown by Ramprasad et al. to be irreproducible. ${ }^{6}$ The literature to 1991 has been well reviewed by Xie, ${ }^{7}$ and since then there have been few developments.

Ganguly and Roundhill have found that complexes of the type $[\mathrm{Pd}(\mu-\mathrm{OH})(\mathrm{L})]_{2}{ }^{2+}$ ( $\mathrm{L}=$ dppe, dcype) are minimally active for the hydration of diethylmaleate in $\mathrm{H}_{2} \mathrm{O}$ /THF solution: both give about $14 \%$ conversion of diethylmaleate (dem) to diethylmalate (demOH) after 30 h at $140^{\circ} \mathrm{C}$, and significant quantities of diethylfumarate ( $17-19 \%$ ) and the hydrolysis products maleic acid (22-28 \%) and fumaric acid monoethyl ester ( $27 \%$ ) are also formed. ${ }^{8}$ These researchers have also demonstrated that the combination of $\mathrm{Na}_{2} \mathrm{PdCl}_{4}$ and $\mathrm{CuCl}_{2}$ is as active, giving $15 \%$ conversion of dem to demOH after 30 h
at $140^{\circ} \mathrm{C}$ (together with the isomerisation and hydrolysis products and, in this case, the oxidation product diethyl oxaloacetate). ${ }^{8}$

Bennett's group has observed what constitutes one step in one of several possible catalytic cycles: the insertion of an alkene into a $\mathrm{Pt}-\mathrm{OH}$ bond. ${ }^{9}$ Thus, dimethylmaleate reacts with cis- $(\mathrm{L}) \mathrm{PtMe}(\mathrm{OH}) \quad\left(\mathrm{L}=2 \mathrm{PPh}_{3}\right.$, dppe, dmpb) to give cis(L)PtMe(CH(CO2 Ce$\left.) \mathrm{CH}(\mathrm{OH})\left(\mathrm{CO}_{2} \mathrm{Me}\right)\right)$ (Scheme 5.2; only the coordinating P-atoms of the diphosphine ligand are shown). Moreover, these complexes reacted with aqueous acids $\left(\mathrm{HBF}_{4}\right.$ and $\left.\mathrm{HPF}_{6}\right)$ to give $\left[\operatorname{cis}-(\mathrm{L}) \mathrm{PtMe}\left(\mathrm{H}_{2} \mathrm{O}\right)\right]^{+}$and dmmOH , corresponding to an overall stoichiometric hydration of the olefin.

## Scheme 5.2



Important developments in the closely-related catalytic hydroamination reaction (e.g., addition of H and "NHR" across a double bond) have recently been reported by Hartwig and coworkers who used $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}$ for the hydroamination of styrene with aniline. ${ }^{10-13}$ This discovery, in addition to the similarity of calculated reaction enthalpies of olefin hydrations and hydroaminations, ${ }^{14}$ is almost certain to reinvigorate efforts in the search of the elusive olefin hydration catalyst.

### 5.2 Scope

This chapter reports the results for the attempted homogeneous, aqueous-phase, catalytic hydration of maleic acid (Scheme 5.3) using water-soluble $\mathrm{Pt}^{\mathrm{II}}, \mathrm{Pd}^{\text {II }}$ and $\mathrm{Ru}^{\text {II }}$ complexes of pyridyl- and anilinyldiphosphine ligands as catalyst precursors.

## Scheme 5.3



### 5.3 Results

The results for the attempted catalytic hydrations of maleic acid are given in Table 5.1.

Table 5.1. Product distributions for the attempted catalytic hydration of maleic acid ( $0.1 \mathrm{~mol} \mathrm{~L}^{-1}$ ) in water at $100^{\circ} \mathrm{C}$ using pyridyl- and anilinyldiphosphine complexes of platinum metals as catalyst precursors (substrate:catalyst = $100: 1$ ) according to Section 5.7.4. Percent conversions, which are equivalent to TONs, are reported for 24 h reaction times. Error is $\pm 1 \%$.

| Catalyst | \% maleic acid | \% fumaric acid | \% malic acid |
| :---: | :---: | :---: | :---: |
| None | 95 | 3 | 2 |
| $\mathrm{HCl}\left(1.2 \mathrm{~mol} \mathrm{~L}^{-1}\right)$ | 78 | 16 | 6 |
| $\mathrm{PdCl}_{2}(\text { dpype })^{\text {a,b,c }}$ | 95 | 3 | 2 |
| $\mathrm{PdBr}_{2}$ (dpype) ${ }^{\text {a,c }}$ | 95 | 3 | 2 |
| $\mathrm{PtCl}_{2}(\text { dpypcp })^{\text {a }}$ | 93 | 4 | 3 |
| $\left[\mathrm{Pt}(\text { dpype })_{2}\right] \mathrm{Cl}_{2}{ }^{\text {c }}$ | 92 | 4 | 4 |
| $\left[\mathrm{Pt}(\text { dpypcp })_{2}\right]^{\text {Cl }}{ }^{\text {c }}$ | 94 | 3 | 3 |
| $\mathrm{PdCl}_{2}$ (dmape) | 92 | 6 | 2 |
| $\mathrm{PdCl}_{2}\left(\mathrm{dmape}^{\text {d }}\right.$ ) $+\mathrm{SnCl}_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O}^{\mathrm{d}}$ | 90 | 8 | 2 |
| $\left[\mathrm{PdCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $)$ ]Cl | 88 | 6 | 6 |
| $\left[\operatorname{PdI}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{I}$ | 93 | 4 | 3 |
| $[\mathrm{PdCl}(P, N, S$-dmapmS $] \mathrm{Cl}$ | 85 | 8 | 7 |
| $\left[\mathrm{PtCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl}$ | 91 | 4 | 5 |
| $\begin{aligned} & {\left[\operatorname{PtCl}\left(P, P^{\prime}, N-\mathrm{dmapcp}\right)\right] \mathrm{Cl}+\mathrm{HCl}} \\ & (1.2 \mathrm{~mol} \mathrm{~L} \end{aligned}$ | 74 | 20 | 6 |
| $\mathrm{RuCl}_{2}\left(P, P^{\prime}, N, N^{\prime}\right.$-dmape $)$ | 95 | 3 | 2 |
| $\mathrm{I}^{\text {e }}$ | 13 | 87 | 0 |
| III ${ }^{\text {f }}$ | 28 | 71 | 1 |

${ }^{\text {a }}$ Not completely soluble at r.t. but dissolves at $100^{\circ} \mathrm{C}$.
${ }^{\mathrm{b}}$ Decomposes to metal during the course of the reaction.
${ }^{\text {c }}$ Complex characterised spectroscopically but not yet isolated in analytically pure form (see Section 4.7.12 for the Pt complexes).
${ }^{\mathrm{d}} \mathrm{Pd}: \mathrm{Sn}=1: 1$. Mixture not homogeneous.
${ }^{\mathrm{e}}$ See Section 5.7.1.
${ }^{\mathrm{f}}$ See Section 5.7.2.

### 5.4 Discussion

The only complexes whch showed even marginal activity for the hydration of maleic acid were $\left[\mathrm{PdCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl}$ and $[\mathrm{PdCl}(P, N, S$-dmapmS $)] \mathrm{Cl}$, both cationic complexes of Pd containing at least a $P, N$-bonded ligand. Although their activities are very low, they are superior to those of $[(\mathrm{L}) \mathrm{Pd}(\mu-\mathrm{OH})]_{2}{ }^{2+}$ which, in the hydration of dem in $\mathrm{THF} / \mathrm{H}_{2} \mathrm{O}$, are 2.6 and 2.9 mol malic acid $/ \mathrm{mol}$ catalyst for $\mathrm{L}=$ dppe and dcype, respectively, after 24 h at $120^{\circ} \mathrm{C}$, and 0 for both systems at $100^{\circ} \mathrm{C} .8^{8}$ Itaconic acid $\left(\mathrm{CH}_{2}=\mathrm{C}\left(\mathrm{CO}_{2} \mathrm{H}\right) \mathrm{CH}_{2} \mathrm{CO}_{2} \mathrm{H}\right)$ was also tested as a substrate with $\left[\mathrm{PdCl}\left(P, P^{\prime} N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl}$ as catalyst, but no hydration was observed showing that the internal position of the double bond is not the limiting factor in these reactions.

Although the addition of $\mathrm{SnCl}_{2}$ to chloro $\mathrm{Pt}^{\mathrm{II}}$-phosphine complexes has been shown to increase the interaction between metal and olefin, ${ }^{15}$ the $\mathrm{PdCl}_{2}$ (dmape) $/ \mathrm{SnCl}_{2}$ combination is no more effective a catalyst than the Pd complex alone, which itself shows no activity over that of the uncatalysed reaction. In addition, the $\left[\mathrm{PtCl}\left(P, P^{\prime}, N-\right.\right.$ dmapcp) $] \mathrm{Cl} / \mathrm{HCl}$ combination does not catalyse the hydration any more effectively than HCl alone, and also gives a comparable rate of isomerisation.

By analogy to the reaction of KOH with $\mathrm{PdCl}_{2}$ (dmape) in $\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{H}_{2} \mathrm{O}$ (Section 2.9.2.12), catalyst I probably contains the " $\mathrm{PdCl}(P, N$-dmapcpO)" fragment. Consistent with the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR data, II is probably $\left[\mathrm{Pd}\left(\mathrm{CH}_{3} \mathrm{CN}\right)\left(P, P^{\prime}, N\right.\right.$-dmape $\left.)\right]\left[\mathrm{NO}_{3}\right]_{2}$. Although their identities remain uncertain, I and II have been included in Table 5.1 because they are both effective olefin isomerisation catalysts, implying that there is an interaction between these complexes and the olefin. Once again, the active species are (likely) cationic Pd complexes containing at least a $P, N$-bound ligand.

### 5.5 Conclusions

Whereas a range of $\mathrm{Ru}, \mathrm{Pd}$ and Pt pyridyl- and anilinyldiphosphine complexes are soluble in water, none of them is an effective catalyst for the hydration of maleic acid. The compounds which appear to hold the most promise are cationic $\mathrm{Pd}^{\mathrm{II}}$ species containing a $P, N$-bonded ligand.

### 5.6 Recommendations for Future Work

The $C_{2}$-symmetric complex resulting from the reaction of KOH with $\mathrm{PtCl}_{2}$ (dmape) (Section 5.7.3) is probably the hydroxo-bridged $\mathrm{Pt}_{2}{ }^{\text {II }}$ complex $\left[\mathrm{Pt}(\mu-\mathrm{OH})_{2}\left(P, P^{\prime}{ }^{\prime}\right.\right.$ dmape) $]_{2}{ }^{2+}$, judging by the magnetic equivalence of the P -atoms and of the NMe groups; further work is necessary to confirm this, however. This compound reacts with maleic acid in acetone to form another species whose ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum shows 2 inequivalent P -atoms bound to Pt , possibly indicating $P, P^{\prime}, N$-bound dmape (Section 5.7.3). The ${ }^{1} \mathrm{H}$ NMR spectrum consists of broad peaks, and it was not possible to determine whether maleate had been inserted into the $\mathrm{Pt}-\mathrm{OH}$ bond or whether it had merely protonated the bridging ligand to form a compound like $\left[\mathrm{Pt}\left(\mathrm{OH}_{2}\right)\left(P, P^{\prime}, N\right.\right.$ dmape) $]^{2+}$. Elucidation of this reaction may give some insight into the possible steps involved in a catalytic hydration cycle by " $\mathrm{M}\left(P, P^{\prime}, N\right)^{n+\text { ", complexes. In addition, the }}$ exact nature of the olefin isomerisation catalysts I and II needs to be determined.

### 5.7 Experimental

### 5.7.1 Preparation of catalyst $I$, and attempted catalytic hydration protocol

To $\left[\mathrm{PdCl}\left(P, P^{\prime}, N\right.\right.$-dmapcp $\left.)\right] \mathrm{Cl}(54 \mathrm{mg}, 0.069 \mathrm{mmol})$ dissolved in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$ was added an aqueous solution of $\mathrm{KOH}\left(10 \mathrm{~mL}, 0.3 \mathrm{~mol} \mathrm{~L}^{-1}\right)$ under air. The two phase system was stirred for 25 min when the organic layer turned from yellow to orange. The $\mathrm{H}_{2} \mathrm{O}$ layer was removed and the $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ fraction was washed with successive portions of $\mathrm{H}_{2} \mathrm{O}$ $(2 \times 5 \mathrm{~mL})$. The $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ was removed in vacuo and the residue was dissolved in $\mathrm{H}_{2} \mathrm{O} / \mathrm{EtOH}$ (10:3 by vol.). The mixture was filtered through Celite 545 into a thick-walled glass bomb containing maleic acid ( $400 \mathrm{mg}, 3.44 \mathrm{mmol}$ ) and a magnetic stir bar. The vessel was evacuated and filled with Ar three times before being placed on an oil-bath at $95^{\circ} \mathrm{C}$ for 24 h . Analysis of the reaction solution was as outlined in Section 5.7.5.

### 5.7.2 Preparation of catalyst II

To $\mathrm{PdCl}_{2}$ (cod) $(99 \mathrm{mg}, 0.35 \mathrm{mmol})$ dissolved in $\mathrm{CH}_{3} \mathrm{CN}(10 \mathrm{~mL})$ was added $\mathrm{AgNO}_{3}$ $(120 \mathrm{mg}, 0.71 \mathrm{mmol})$; a white precipitate formed immediately. The slurry was stirred for 0.5 h and then filtered through Celite 545 . To the pale yellow filtrate was added dmape
( $202 \mathrm{mg}, 0.35 \mathrm{mmol}$ ). After 1 h , the volume of the solution was reduced in vacuo to $c a$. 1 mL and the product was afforded as a pale yellow powder by the addition of $\mathrm{Et}_{2} \mathrm{O}$ $(10 \mathrm{~mL})$. Yield: 220 mg ( $73 \%$ based on $\left[\mathrm{Pd}\left(\mathrm{CH}_{3} \mathrm{CN}\right)\left(P, P^{\prime}, N\right.\right.$-dmape $\left.\left.)\right]\left[\mathrm{NO}_{3}\right]_{2}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $81 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}, 300 \mathrm{~K}$ ): $\delta 22.4\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=4.3\right), 24.9\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=4.3\right)$.

### 5.7.3 Reaction of $\mathrm{PtCl}_{2}$ (dmape) with KOH followed by maleic acid

To $\mathrm{PtCl}_{2}$ (dmape) ( $22 \mathrm{mg}, 0.026 \mathrm{mmol}$ ) dissolved in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$ was added an aqueous KOH solution ( $10 \mathrm{~mL}, 1.0 \mathrm{~mol} \mathrm{~L}^{-1}$ ) under air. The two phase system was stirred overnight when the $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ layer became pale yellow. The $\mathrm{H}_{2} \mathrm{O}$ was removed and the organic fraction was washed with successive portions of $\mathrm{H}_{2} \mathrm{O}(3 \times 10 \mathrm{~mL})$ whereupon it was reduced to dryness in vacuo. The residue was taken up in $\mathrm{CDCl}_{3}$ and analysed by NMR spectroscopy. ${ }^{1} \mathrm{H}$ NMR ( $200 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 2.30\left(\mathrm{~s}, 24 \mathrm{H}, \mathrm{NCH}_{3}\right), 2.90$ (m, 4H, CH2), 7.0-8.1 (m, 16H, Ar). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(81 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta 31.0(\mathrm{~s}$, $\left.{ }^{1} J_{\mathrm{PPt}}=3680\right)$ :

The product from the previous reaction was dissolved in acetone ( 3 mL ) and maleic acid ( $4 \mathrm{mg}, 0.034 \mathrm{mmol}$ ) was added, causing the solution to change immediately from yellow to colourless. The solution was stirred overnight and then reduced to dryness in vacuo. The residue was dissolved in $\mathrm{CDCl}_{3}$ and analysed by NMR spectroscopy. ${ }^{1} \mathrm{H}$ NMR ( $200 \mathrm{MHz}, \mathrm{CDCl}_{3}, 300 \mathrm{~K}$ ): $\delta 2.0-3.6\left(\mathrm{br}, 28 \mathrm{H}, \mathrm{NCH}_{3}\right.$ and $\mathrm{CH}_{2}$ ), $6.8-8.2(\mathrm{br}, 16 \mathrm{H}$, Ar). A singlet at $\delta 6.1$ due to maleic acid was also apparent. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 121 MHz , $\left.\mathrm{CDCl}_{3}, 300 \mathrm{~K}\right): \delta 35.7\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=14,{ }^{1} J_{\mathrm{PPt}}=3620\right), 47.0\left(\mathrm{~d},{ }^{2} J_{\mathrm{PP}}=14,{ }^{1} J_{\mathrm{PPt}}=3420\right)$.

### 5.7.4 General protocol for the catalytic hydration of maleic acid

To a combination of maleic acid ( $116 \mathrm{mg}, 1.00 \mathrm{mmol}$ ) and the appropriate metal complex ( 0.01 mmol ) in a thick-walled glass bomb charged with a magnetic stir bar was added $\mathrm{H}_{2} \mathrm{O}(10 \mathrm{~mL})$. The solution was degassed by shaking the vessel while a vacuum was applied. Once the degassing was complete, $\operatorname{Ar}$ ( 1 atm ) was admitted. The glass bomb was immersed in a thermostatted oil-bath at $100^{\circ} \mathrm{C}$. After 24 h , a 3 mL aliquot was withdrawn. This was reduced to dryness on a rotatory evaporator and the residue was ground to a fine powder using a pestle and mortar. The powder ( 7 mg ) was dissolved in acetone- $\mathrm{d}_{6}(0.5 \mathrm{~mL})$ and analysed by ${ }^{1} \mathrm{H}$ NMR spectroscopy according to Section 5.7.5.

### 5.7.5 Determination of extent of hydration from ${ }^{1} \mathrm{H}$ NMR spectra

The proportions of maleic, fumaric and malic acids present in an acetone- $\mathrm{d}_{6}$ solution containing a mixture of the three were calculated using the ratios of the appropriate ${ }^{1} \mathrm{H}$ NMR peak integrations. Shown in Figure 5.1 is a representative spectrum. The following are the ${ }^{1} \mathrm{H}$ NMR ( 300 MHz , acetone- $\mathrm{d}_{6}, 300 \mathrm{~K}$ ) data for the 3 components. ${ }^{7}$ (Assignments for malic acid are given according to the Fischer projection in Figure 5.1)

Maleic acid: $\delta 6.40(\mathrm{~s}, 2 \mathrm{H}$, cis $-\mathrm{HOOCCH}=\mathrm{CHCOOH}$ ).
Fumaric acid: $\delta 6.80(\mathrm{~s}, 2 \mathrm{H}$, trans $-\mathrm{HOOCCH}=\mathrm{CHCOOH})$.
Malic acid: $\delta 4.52\left(\mathrm{dd}, 1 \mathrm{H}, \mathrm{HOOCCH}_{a}(\mathrm{OH}) \mathrm{CH}_{\mathrm{b}} \mathrm{H}_{\mathrm{c}} \mathrm{COOH},{ }^{3} J_{\mathrm{HaHb}}=7.2,{ }^{3} J_{\mathrm{HaHc}}=\right.$ 4.5), $2.75\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{HOOCCH}_{a}(\mathrm{OH}) \mathrm{CH}_{\mathrm{b}} \mathrm{H}_{\mathrm{c}} \mathrm{COOH},{ }^{3} J_{\mathrm{HaHb}}=7.2,{ }^{3} J_{\mathrm{HaHc}}=4.5,{ }^{2} J_{\mathrm{HbHc}}=\right.$ 15.9).


Figure 5.1 A sample ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, 300 \mathrm{~K}$ ) spectrum of an acetone- $\mathrm{d}_{6}$ solution containing maleic, fumaric and malic acids. $\mathrm{fa}=$ fumaric acid, $\mathrm{ma}=$ maleic acid. $\mathrm{H}_{\mathrm{a}}$ and $\mathrm{H}_{\mathrm{b}, \mathrm{c}}$ refer to the protons given in the Fischer projection of malic acid.

The area under the peaks due to fumaric and maleic acids, and the $H_{a}$ and $H_{b, c}$ protons of malic acid are denoted $A_{f a}, A_{m a}, A_{H a}$ and $A_{H b, c}$, respectively. As $H_{a}$
corresponds to 1 proton and $\mathrm{H}_{\mathrm{b}, \mathrm{c}}$ to 2, the total peak area due to the three acids is given either by:

$$
\begin{gathered}
\mathrm{A}_{\mathrm{TOT}}=\mathrm{A}_{\mathrm{fa}}+\mathrm{A}_{\mathrm{ma}}+2 \mathrm{~A}_{\mathrm{Ha}}, \text { or } \\
\mathrm{A}_{\mathrm{TOT}}=\mathrm{A}_{\mathrm{fa}}+\mathrm{A}_{\mathrm{ma}}+\mathrm{A}_{\mathrm{Ha}, \mathrm{~b}}
\end{gathered}
$$

In practice, the former of the above equations was used in subsequent calculations because the $H_{a}$ peak always fell in a region of the spectrum which was uncomplicated by peaks due to the catalyst. The percentages of each of the acids in solution are given by:

$$
\begin{aligned}
& \% \text { fumaric acid }=\mathrm{A}_{\mathrm{fa}} / \mathrm{A}_{\mathrm{TOT}} \times 100 \\
& \% \text { maleic acid }=\mathrm{A}_{\mathrm{ma}} / \mathrm{A}_{\mathrm{TOT}} \times 100 \\
& \% \text { malic acid }=2 \mathrm{~A}_{\mathrm{Ha}} / \mathrm{A}_{\mathrm{TOT}} \times 100
\end{aligned}
$$

By comparison of the relative concentrations (calculated by ${ }^{1} \mathrm{H}$ NMR peak ratios) to the actual relative concentrations for acetone- $\mathrm{d}_{6}$ solutions containing known masses of the three acids, the error in the technique was found by Xie to be $\pm 1 \% .^{7}$ All results were compared to those obtained for "blank" reactions, i.e., those run under identical conditions in the absence of metal complex.

### 5.8 References

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## A1 General Experimental Protocols

## A1.1 General Procedures

All procedures were conducted using standard Schlenk techniques under an $\operatorname{Ar}$ or $\mathrm{N}_{2}$ atmosphere unless otherwise noted. In some cases, an Ar-filled glovebox was used to handle particularly $\mathrm{O}_{2}$ - or $\mathrm{H}_{2} \mathrm{O}$-sensitive materials. All reactions were performed at r.t. (ca. $20-25^{\circ} \mathrm{C}$ ) unless otherwise specified.

## A1.2 Instrumentation

## A1.2.1 Nuclear magnetic resonance (NMR) spectroscopy

Six different NMR spectrometers were used in the course of this work. Spectrometer frequencies for ${ }^{1} \mathrm{H},{ }^{31} \mathrm{P}$ and ${ }^{13} \mathrm{C}$ for each instrument are given in Table A1.1. Residual solvent proton ( ${ }^{1} \mathrm{H}$, relative to external $\mathrm{SiMe}_{4} \delta 0.00$ ), external $\mathrm{P}(\mathrm{OMe})_{3}\left({ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}, \delta\right.$ 141.00 vs. external $85 \%$ aq. $\mathrm{H}_{3} \mathrm{PO}_{4}$ ), or solvent carbon ( ${ }^{13} \mathrm{C}, \delta 77.0$ relative to external $\mathrm{SiMe}_{4}$ ) were used as the reference. Downfield shifts were taken as positive. All $J$-values are given in Hz ; $\mathrm{s}=$ singlet, $\mathrm{d}=$ doublet, $\mathrm{t}=$ triplet, $\mathrm{m}=$ multiplet, $\mathrm{br}=$ broad, $\mathrm{p}=\mathrm{pseud}$.

Table A1.1 Spectrometer frequencies for ${ }^{1} \mathrm{H},{ }^{31} \mathrm{P}$ and ${ }^{13} \mathrm{C}$ for each of the NMR instruments used in the course of this work.

|  |  | Spectrometer Frequency (MHz) |  |
| :--- | :---: | :---: | :---: |
| Spectrometer | ${ }^{1} \mathrm{H}$ | ${ }^{31} \mathrm{P}$ | ${ }^{13} \mathrm{C}$ |
| Bruker AC200 | 200.13 | 81.02 | 50.32 |
| Bruker AV300 | 300.13 | 121.49 | 75.46 |
| Bruker AV400 | 400.13 | 161.98 | 100.61 |
| Bruker AM400 | 400.13 | 161.98 | 100.61 |
| Bruker AMX500 | 500.14 | 202.47 | 125.76 |
| Varian XL300 | 299.94 | 121.42 | 75.43 |

For variable temperature NMR experiments, the probe temperature was calibrated using MeOH. ${ }^{1}$ Some NMR experiments were conducted by Ms. Liane Darge, Ms. Marietta Austria, or Dr. Nick Burlinson, all of the UBC Chemistry Department.

## A1.2.2 X-ray crystallography

X-ray crystallographic analyses were performed either by the late Dr. Steven Rettig or Dr. Brian Patrick both of the UBC Chemistry Department, or by Dr. Victor Young of the University of Minnesota.

## A1.2.3 Elemental analysis

Elemental analyses were conducted using a Carlo Erba 1108 analyser by Mr. Peter Borda of the UBC Chemistry Department.

## A1.2.4 Ultraviolet-visible (UV-vis) spectroscopy

UV-vis spectra of coloured complexes were recorded on a Hewlett Packard 8452A diode array spectrophotometer and are reported as $\lambda_{\max }( \pm 2 \mathrm{~nm})\left[\varepsilon\left(\mathrm{L} \mathrm{mol}{ }^{-1} \mathrm{~cm}^{-1}\right)\right] ;$ sh $=$ shoulder.

## A1.2.5 Infra-red (IR) spectroscopy

IR spectra were recorded on either an ATI Mattson Genesis series or a BomemMichelson MB-100 FTIR spectrometer, scanning $500-4000 \mathrm{~cm}^{-1}$. Samples were prepared as KBr discs. IR data are reported as $v\left( \pm 4 \mathrm{~cm}^{-1}\right)$ (relative intensity); $\mathrm{s}=$ strong, $\mathrm{m}=$ medium, $\mathrm{w}=$ weak .

## A1.2.6 Conductivity

Conductivity measurements were made on approximately $10^{-3} \mathrm{~mol} \mathrm{~L}^{-1}$ solutions using a Serfass conductance bridge model RCM15B1 (Arthur H. Thomas Co. Ltd.) connected to a 3404 cell (Yellow Springs Instrument Co.) and are reported as $\Lambda_{M}\left( \pm 0.5 \mathrm{ohm}^{-1} \mathrm{~mol}^{-1}\right.$ $\mathrm{cm}^{2}$ ).

## A1.2.7 Gas chromatography (GC)

A Hewlett Packard 5890A gas chromatograph equipped with a $25 \mathrm{~m}-0.32 \mathrm{~mm} \mathrm{HP} 17$ column and an $\mathrm{H}_{2} /$ air flame ionisation detector (FID) was used. He was used as the carrier gas.

## A1.3 Materials

## A1.3.1 Gases

Gases were purchased from commercial sources and used without purification, except Ar (H.P.) and $\mathrm{N}_{2}$ (U.S.P.) which were dried by passing through $\mathrm{P}_{2} \mathrm{O}_{5}$ and anhydrous $\mathrm{CaSO}_{4}$, respectively.

## A1.3.2 Solvents

Reagent grade solvents (Fisher Scientific) were either distilled from $\mathrm{CaH}_{2}\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right.$, $\mathrm{CH}_{3} \mathrm{NO}_{2}$ ), $\mathrm{Na}\left(\mathrm{Et}_{2} \mathrm{O}\right.$, hexanes), $\mathrm{Mg} / \mathrm{I}_{2}(\mathrm{EtOH})$, or anhydrous $\mathrm{K}_{2} \mathrm{CO}_{3}$ (acetone) under $\mathrm{N}_{2}$. PhCN was stored over $\mathrm{CaSO}_{4}$. Other solvents were used as supplied. All deuterated solvents were purchased from Cambridge Isotope Laboratories. $\mathrm{CDCl}_{3}$, and $\mathrm{C}_{6} \mathrm{D}_{6}$ were dried over activated molecular sieves (Fisher: Type 4 $\AA, 4-8$ mesh), deoxygenated, and stored under $\mathrm{Ar} . \mathrm{CD}_{2} \mathrm{Cl}_{2}$ was stored under vacuum over $\mathrm{CaH}_{2}$. Other deuterated solvents $\left(\mathrm{CD}_{3} \mathrm{OD}, \mathrm{D}_{2} \mathrm{O}\right.$, acetone- $\mathrm{d}_{6}$, DMSO- $\mathrm{d}_{6}$ ) were used as supplied.

## A1.3.3 Reagents

Unless otherwise noted, reagents were purchased from commercial sources. and used without purification.

## A1.3.3.1 Metal complexes

Metal complex precursors were synthesised according to the literature procedures given in Table A1.2. NMR spectroscopic data for the complexes matched those given in the literature in all cases. $\mathrm{RuCl}_{3} \cdot \mathrm{xH}_{2} \mathrm{O}$ was obtained on loan from Johnson Matthey, Ltd. and Colonial Metals, Inc.

Table A1.2 Procedures used to synthesise metal complex precursors.

| Complex | Reaction | Reference |
| :---: | :---: | :---: |
| $\mathrm{PtCl}_{2}$ (cod) | $\mathrm{K}_{2} \mathrm{PtCl}_{4}+\operatorname{cod} \rightarrow \mathrm{PtCl}_{2}($ cod $)+2 \mathrm{KCl}$ | 2 |
| $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{4}$ | $\begin{aligned} & \mathrm{K}_{2} \mathrm{PtCl}_{4}+4 \mathrm{PPh}_{3}+2 \mathrm{KOH}+\mathrm{EtOH} \rightarrow \mathrm{Pt}^{2}\left(\mathrm{PPh}_{3}\right)_{4}+ \\ & 4 \mathrm{KCl}+\mathrm{H}_{2} \mathrm{O}+\mathrm{CH}_{3} \mathrm{CHO} \end{aligned}$ | 3 |
| $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{3}$ | $\mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{4} \rightarrow \mathrm{Pt}\left(\mathrm{PPh}_{3}\right)_{3}+\mathrm{PPh}_{3}$ | 3 |
| trans $-\mathrm{PdCl}_{2}(\mathrm{PhCN})_{2}$ | $\mathrm{PdCl}_{2}+2 \mathrm{PhCN} \rightarrow \mathrm{PdCl}_{2}(\mathrm{PhCN})_{2}$ | 4 |
| $\mathrm{PdCl}_{2}$ (cod) | $\mathrm{H}_{2} \mathrm{PdCl}_{4}+\operatorname{cod} \rightarrow \mathrm{PdCl}_{2}($ cod $)+2 \mathrm{HCl}$ | 2 |
| $\mathrm{PdCl}_{2}$ (nbd) | $\mathrm{PdCl}_{2}(\mathrm{PhCN})_{2}+\mathrm{nbd} \rightarrow \mathrm{PdCl}_{2}(\mathrm{nbd})+2 \mathrm{PhCN}$ | 5 |
| $\mathrm{PdCl}(\mathrm{Me})(\mathrm{cod})$ | $\begin{aligned} & \mathrm{PdCl}_{2}(\mathrm{cod})+\mathrm{SnMe}_{4} \rightarrow \mathrm{PdCl}(\mathrm{Me})(\mathrm{cod})+ \\ & \mathrm{SnCl}(\mathrm{Me})_{3} \end{aligned}$ | 6 |
| $\begin{aligned} & {[\mathrm{Pd}(\mu-\mathrm{Cl})(\mathrm{MeO}-} \\ & \mathrm{cod})]_{2} \end{aligned}$ | $\begin{aligned} & 2 \mathrm{PdCl}_{2}(\mathrm{cod})+2 \mathrm{NaOMe} \rightarrow[\mathrm{Pd}(\mu-\mathrm{Cl})(\mathrm{MeO}- \\ & \operatorname{cod})]_{2}+2 \mathrm{NaCl} \end{aligned}$ | 7 |
| $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}$ | $\begin{aligned} & 2 \mathrm{PdCl}_{2}+\mathrm{N}_{2} \mathrm{H}_{4}+8 \mathrm{PPh}_{3} \rightarrow 2 \mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}+4 \mathrm{HCl} \\ & +\mathrm{N}_{2} \end{aligned}$ | 8 |
| $\mathrm{Pd}_{2}(\mathrm{dba})_{3} \cdot \mathrm{CHCl}_{3}$ | $\begin{aligned} & 2 \mathrm{PdCl}_{2}+3 \mathrm{dba}+2 \mathrm{MeOH}+4 \mathrm{NaOAc} \rightarrow \\ & \mathrm{Pd}_{2}(\mathrm{dba})_{3}+2 \mathrm{H}_{2} \mathrm{CO}+4 \mathrm{NaCl}+4 \mathrm{HOAc} \end{aligned}$ | 9 |
| $\mathrm{RuCl}_{2}\left(\mathrm{PPh}_{3}\right)_{3}$ | $\begin{aligned} & 2 \mathrm{RuCl}_{3}+7 \mathrm{PPh}_{3}+\mathrm{H}_{2} \mathrm{O} \rightarrow 2 \mathrm{RuCl}_{2}\left(\mathrm{PPh}_{3}\right)_{3}+ \\ & \mathrm{OPPh}_{3}+2 \mathrm{HCl} \end{aligned}$ | 10 |
| $\left[\mathrm{Rh}(\mu-\mathrm{Cl})(\mathrm{CO})_{2}\right]_{2}$ | $2 \mathrm{RhCl}_{3}+6 \mathrm{CO} \rightarrow\left[\mathrm{Rh}(\mu-\mathrm{Cl})(\mathrm{CO})_{2}\right]_{2}+2 \mathrm{COCl}_{2}$ | 11 |
| $[\mathrm{Rh}(\mu-\mathrm{Cl})(\operatorname{cod})]_{2}$ | $\begin{aligned} & 2 \mathrm{RhCl}_{3}+2 \mathrm{EtOH}+2 \operatorname{cod} \rightarrow[\mathrm{Rh}(\mu-\mathrm{Cl})(\operatorname{cod})]_{2}+2 \\ & \mathrm{CH}_{3} \mathrm{CHO}+4 \mathrm{HCl} \end{aligned}$ | 12,13 |

## A1.3.3.2 Organic compounds

On one occasion, 2-bromopyridine was stirred with NaOH pellets overnight and distilled from CaO to remove $\mathrm{H}_{2} \mathrm{O}$ and then degassed by 3 freeze-pump-thaw cycles to remove $\mathrm{O}_{2}$, but this was found not to enhance significantly the yields of the pyridyldiphosphine ligand syntheses. The ligand dpype was made according to the procedure by Baird et al. ${ }^{14}$ The precursor to the cyclopentane-bridged diphosphine ligands, 1,2bis(dichlorophosphino)cyclopentane, was made by a literature procedure ${ }^{15}$ and kindly donated by previous researchers in this group Drs. Richard Schutte and Kenneth MacFarlane.

The physical state of samples of 2-bromoaniline purchased from Aldrich was variable. This compound is a white crystalline solid at r.t., but on two occasions was delivered as a red viscous liquid; the pure compound was separated by sublimation. $\mathrm{N}, \mathrm{N}$ -
dimethyl-2-bromoaniline was made via methylation of the pure compound with dimethylsulphate according to a literature procedure. ${ }^{16}$

Dimethyl- and diethylmaleate and dimethylfumarate were degassed by 3 freeze-pump-thaw cycles prior to use.

## A1.4 References

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## A2 Crystal Structure Data for Dmape



Figure A2.1 ORTEP representation of dmape (50 \% ellipsoids).

Table A2.1 EXPERIMENTAL DETAILS

| A. Crystal Data |  |
| :---: | :---: |
| Empircal formula | $\mathrm{C}_{34} \mathrm{H}_{44} \mathrm{~N}_{4} \mathrm{P}_{2}$ |
| Formula weight | 570.7 |
| Crystal colour, habit | colourless, irregular |
| Crystal dimensions | $0.20 \times 0.40 \times 0.45 \mathrm{~mm}$ |
| Crystal system | triclinic |
| Lattic type | primitive |
| Lattice parameters | $\begin{aligned} & \mathrm{a}=8.1849(4) \AA, \mathrm{b}=15.5001(14) \AA, \mathrm{c}=19.882(2) \AA \\ & \alpha=73.501(4)^{\circ}, \beta=81.0524(13)^{\circ}, \gamma=79.7046(9)^{\circ} \\ & \mathrm{V}=2364.9(3) \AA^{\circ} \end{aligned}$ |
| Space group | $\mathrm{P}(-1)$ (\#2) |
| Z value | 3 |
| $\mathrm{D}_{\text {calc }}$ | $1.202 \mathrm{~g} \mathrm{~cm}^{-3}$ |
| $\mathrm{F}_{000}$ | 918.00 |
| $\mu(\mathrm{MoK} \alpha)$ | $1.67 \mathrm{~cm}^{-1}$ |
| B. Intensity Measurements |  |
| Diffractometer | Rigaku/ADSC CCD |
| Radiation | MoK $\alpha$ ( $\lambda=0.71069 \AA$ ) graphite monochromated |
| Detector aperture | $94 \mathrm{~mm} \times 94 \mathrm{~mm}$ |
| Data images | 462 exposures of 9.0 s |
| $\phi$ oscillation range ( $\chi=-90$ ) | 0.0-190.0 ${ }^{\circ}$ |
| $\omega$ oscillation range ( $\chi=-90$ ) | -23.0- $18.0^{\circ}$ |
| Detector position | $38.883(6) \mathrm{mm}$ |
| Detector swing angle | $-10.0{ }^{\circ}$ |
| $2 \theta_{\text {max }}$ | $60.1^{\circ}$ |
| Number of reflections measured | Total: 21881 |
|  | Unique: $10698\left(\mathrm{R}_{\text {int }}=0.047\right)$ |
| Corrections | Lorentz-polarization |
|  | Absorption/decay/scaling (correction factors: $0.8288-1.000$ ) |
| C. Structure Solution and Refinement |  |
| Structure solution | Direct methods (SIR 97) |
| Refinement | Full-matrix least-squares |
| Function minimized | $\Sigma \omega\left(\mathrm{F}_{0}{ }^{2}-\mathrm{F}_{\mathrm{c}}{ }^{2}\right)^{2}$ |
| Least squares weights | $\omega=1 /\left(\sigma^{2} \mathrm{~F}_{0}{ }^{2}\right)$ |
| p-factor | 0.0000 |
| Anomalous dispersion | All non-hydrogen atoms |
| Number of observations | 10698 |
| Number of variables | 541 |
| Reflection/parameter ratio | 19.77 |
| Residuals: $\mathrm{R}, \mathrm{R}_{\mathrm{w}}$ | 0.077, 0.083 |
| Goodness of fit indicator | 1.41 |
| Number of observations ( $\mathrm{I}>3 \sigma(\mathrm{I})$ ) | 6421 |
| Residuals (on F, $\mathrm{I}>3 \sigma\left(\mathrm{I}\right.$ ) : $\mathrm{R}, \mathrm{R}_{\mathrm{W}}$ | 0.041, 0.039 |
| Max shift/error in final cycle | 0.0007 |
| Maximum peak in final difference map | $0.43 e^{-} \AA^{-3}$ |
| Minimum peak in final difference map | -0.43 $e^{-} \AA^{-3}$ |

A. Crystal Data

Formula weight
Crystal colour, habit
Crystal dimensions
Crystal system
Lattic type
Lattice parameters

Space group
$Z$ value
$\mathrm{D}_{\text {cale }}$
$\mu(\mathrm{MoK} \alpha)$
B. Intensity Measurements

Diffractometer
Radiation
Detector aperture
Data images
$\phi$ oscillation range ( $\chi=-90$ )
$\omega$ oscillation range ( $\chi=-90$ )
Detector position
Detector swing angle
Number of reflections measured

Corrections

## C. Structure Solution and Refinement

Structure solution
Refinement
Function minimized
Least squares weights
p-factor
Anomalous dispersion
Number of observations
Reflection/parameter ratio
Residuals: $\mathrm{R}, \mathrm{R}_{\mathrm{w}}$
Goodness of fit indicator
Number of observations (I $>3 \sigma(\mathrm{I})$ )
Residuals (on F, I > $3 \sigma(\mathrm{I})$ ): R, $\mathrm{R}_{\mathrm{W}}$
Max shift/error in final cycle
Maxımum peak in final difference map
Minimum peak in final difference map
19.77
$\mathrm{C}_{34} \mathrm{H}_{44} \mathrm{~N}_{4} \mathrm{P}_{2}$ 570.7
$0.20 \times 0.40 \times 0.45$
triclinic
primitive
$\mathrm{a}=8.1849(4) \AA, \mathrm{b}=15.5001(14) \AA, \mathrm{c}=19.882(2) \AA$
$\alpha=73.501(4)^{\circ}, \beta=81.0524(13)^{\circ}, \gamma=79.7046(9)^{\circ}$
P(-1) (\#2)
3
$1.202 \mathrm{~g} \mathrm{~cm}^{-3}$
$1.67 \mathrm{~cm}^{-1}$

Rigaku/ADSC CCD
MoK $\alpha(\lambda=0.71069 \AA$ ) graphite monochromated
$94 \mathrm{~mm} \times 94 \mathrm{~mm}$
462 exposures of 9.0 s
$0.0-190.0^{\circ}$
$-23.0-18.0^{\circ}$
$38.883(6) \mathrm{mm}$
$60.1^{\circ}$
Total: 21881
Unique: $10698\left(\mathrm{R}_{\text {int }}=0.047\right)$
Lorentz-polarization
Absorption/decay/scaling
(correction factors: 0.8288-1.000)

Direct methods (SIR 97)
Full-matrix least-squares
$\Sigma \omega\left(\mathrm{F}_{0}{ }^{2}-\mathrm{F}_{\mathrm{c}}{ }^{2}\right)^{2}$
$\omega=1 /\left(\sigma^{2} \mathrm{~F}_{0}{ }^{2}\right)$
0.0000

All non-hydrogen atoms
10698
1.41

6421
$0.041,0.039$
0.0007
$-0.43 e^{-} \AA^{-3}$

$$
\begin{array}{lcl}
\text { Table A2.2 } & \text { Atamic coordinates and } \mathrm{B}_{\text {iao }} / \mathrm{B}_{\text {af }} \\
& & y \\
\text { atom } & \mathrm{x} & \mathrm{y} \\
\mathrm{P}(1) & 0.02079(6) & 0.23272(3) \\
\mathrm{P}(2) & 0.21478(6) & 0.34224(3) \\
\mathrm{P}(3) & 0.30000(6) & 0.12088(4) \\
\mathrm{N}(1) & 0.0183(2) & 0.03231(11) \\
\mathrm{N}(2) & -0.2253(2) & 0.39293(10) \\
\mathrm{N}(3) & 0.4020(2) & 0.49925(11) \\
\mathrm{N}(4) & -0.0218(2) & 0.29899(11) \\
\mathrm{N}(3) & 0.1320(2) & 0.04114(12) \\
\mathrm{N}(6) & 0.0784(2) & 0.29114(11) \\
\mathrm{C}(1) & 0.1143(2) & 0.30917(12) \\
\mathrm{C}(2) & 0.1456(2) & 0.26527(12) \\
\mathrm{C}(3) & 0.2012(2) & 0.14443(13) \\
\mathrm{C}(4) & 0.1753(2) & 0.05270(13) \\
\mathrm{C}(5) & 0.3127(3) & -0.01446(14) \\
\mathrm{C}(6) & 0.4744(3) & 0.0066(2) \\
\mathrm{C}(7) & 0.5013(2) & 0.09608(15) \\
\mathrm{C}(8) & 0.3660(2) & 0.16316(13) \\
\mathrm{C}(9) & -0.0098(3) & -0.05983(15) \\
\mathrm{C}(10) & -0.0873(3) & 0.0574(2) \\
\mathrm{C}(11) & 0.0171(2) & 0.30131(12) \\
\mathrm{C}(12) & -0.1060(2) & 0.37690(12) \\
\mathrm{C}(13) & -0.1116(2) & 0.43291(13) \\
\mathrm{C}(14) & 0.0054(3) & 0.41449(15) \\
\mathrm{C}(15) & 0.1246(3) & 0.33915(15)
\end{array}
$$

    distance
    $1.375(3)$
$1.379(3)$
$1.418(2)$
$1.386(3)$
$1.384(3)$
$1.395(3)$
$1.392(3)$
$1.372(3)$

㤩
Table A2.3 Bond Lengtbs( $A$ ) (continued)

产


$1.378(3)$
$1.381(3)$
旁
1.392(3)
* Symmetry operation: 1-x, -y, 2-z (here and elsewhere).


岛 든 순



Table A2.3 Bond Lengths (A)







|  | 范 |  | $\begin{aligned} & \widetilde{y_{0}^{2}} \\ & \text { N: } \end{aligned}$ | $\begin{aligned} & \text { © } \\ & \stackrel{\rightharpoonup}{*} \\ & \stackrel{3}{3} \end{aligned}$ | $\begin{aligned} & \text { !} \\ & \stackrel{0}{3} \\ & \hline \end{aligned}$ | $\begin{aligned} & \text { ⿻⼷ㄴ } \\ & \stackrel{\leftrightarrow}{\mathbf{Q}} \end{aligned}$ |  | ज | $\begin{aligned} & \text { ভ্ড匕 } \\ & \stackrel{\infty}{y} \end{aligned}$ |  | $\begin{aligned} & \text { 틍 } \\ & \stackrel{2}{3} \end{aligned}$ | $\begin{aligned} & \stackrel{\Xi}{5} \\ & \stackrel{\rightharpoonup}{\Xi} \end{aligned}$ | $\begin{aligned} & \text { ⿹ㅡㄹ } \\ & \stackrel{\rightharpoonup}{0} \\ & \stackrel{y}{9} \end{aligned}$ | $\begin{aligned} & \text { ভ్〒゙ } \\ & \underset{\sim}{6} \end{aligned}$ | $\begin{aligned} & \text { ভ্তu } \\ & \text { N్త } \end{aligned}$ | $\begin{aligned} & \text { Ex } \\ & \text { 区ug } \end{aligned}$ | $\begin{aligned} & \text { © } \\ & \text { © } \end{aligned}$ |  | $\begin{aligned} & \text { 흥 } \\ & \stackrel{\oplus}{7} \end{aligned}$ | 5 <br>  <br>  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 辰 | 苛 | 芘 | $\frac{9}{0}$ |  | $0$ | 苞 | \％ | 朢 | 픙 | \％ | $\stackrel{\text { ers }}{0}$ | $\stackrel{\pi}{0}$ | 9 | $\stackrel{\bar{\circ}}{0}$ | 产 | $\stackrel{\widehat{\Xi}}{\mathbf{\nabla}}$ | $\frac{\overline{5}}{0}$ | $\frac{\text { 棌 }}{0}$ | $\stackrel{\overline{5}}{0}$ | 霏 墨 |
|  | $\stackrel{5}{5}$ |  | $\stackrel{y}{0}$ | 응 | 赑 | $\stackrel{\pi}{0}$ | $\stackrel{\stackrel{\rightharpoonup}{\Xi}}{6}$ | $\stackrel{E}{5}$ | $\overline{\oplus ్ ర 斤 ~}$ | 骨 | 僉 | 骨 | 寓 | $\stackrel{\mathscr{F}}{0}$ | 合 | $\stackrel{\text { 銤 }}{ }$ | $\frac{\stackrel{\rightharpoonup}{4}}{0}$ | $\stackrel{\stackrel{\rightharpoonup}{5}}{0}$ | $\stackrel{\text { 需 }}{ }$ | $\frac{9}{0}$ | $$ |
|  | $\frac{5}{3}$ | $\bar{\Xi}$ | $\bar{\aleph}$ | $\frac{\overline{5}}{z}$ | 읃 | 要 | $\overline{0}$ | 춘 | $\stackrel{\rightharpoonup}{Z}$ |  | $\frac{\widehat{4}}{6}$ | 봉 | 空 | $\stackrel{\overline{e n}}{0}$ | $\frac{\stackrel{\rightharpoonup}{2}}{2}$ | $\stackrel{\mathrm{E}}{6}$ | $\stackrel{\bar{m}}{0}$ | $\stackrel{ल}{\curvearrowleft}$ | 要 | © | 要 突 |



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## A3 Crystal Structure Data for Dmapcp



Figure A3.1 ORTEP representation of dmapcp (50 \% ellipsoids).
Table A3.2 Atomic coordinates ( $\mathrm{A} \times 10^{\wedge} 4$ ) and equivalent isotropic
U (eq) is defined as one third of the trace of the orthogonalized

Table A3.1 Crystal data and structure refinement

| Empirical formula | C37 H48 N4 F 2 |
| :---: | :---: |
| Formula weight | 610.73 |
| Tempesature | 180(1) K |
| Wavelength | 0.71069 A |
| Diffractometer | Rigaku/ADSC CCD |
| Crystal system, space group | orthorhombic. P212121 |
| Unit cell dimensions | $\begin{array}{ll} \mathrm{a}=11.9757(10) \mathrm{A} & \text { alpha }=90 \mathrm{deg} \\ \mathrm{~b}=14.9163(2) \mathrm{A} & \text { beta }=90 \mathrm{deg} . \\ \mathrm{c}=19.8124(5) \mathrm{A} & \text { gamma }=90 \mathrm{deg} . \end{array}$ |
| Volume | $3539.2(3)$ A^3 $^{\text {a }}$ |
| z, Calculated density | 4. $1.146 \mathrm{Mg} / \mathrm{m}^{\wedge} 3$ |
| Absorption coefficient | $0.153 \mathrm{mma}^{\wedge}-1$ |
| $F(000)$ | 1312 |
| Crystal size | $0.40 \times 0.25 \times 0.20 \mathrm{~mm}$ |
| Theta range for data collection | 1.99 to 30.52 deg . |
| Index ranges | $-10<=h<=16,-21<=k<=17,-23<=1<=27$ |
| Reflections collected / unique | $9864 / 9864[\mathrm{R}$ (int) $=0.0620]$ |
| Completeness to 2 theta $=30.00$ | 98.98 |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9700 and 0.9413 |
| Refinement method | Full-matrix least-squares on Fa2 |
| Data / restraints / parameters | 9864 / $0 / 389$ |
| Goodness-of-fit on $\mathrm{F}^{\wedge} 2$ | 1.199 |
| Final R indices [I>2sigma(I)] | $\mathrm{R} 1=0.0453, \mathrm{wR2}=0.0668$ |
| R indices (all data) | $\mathrm{RI}=0.0942, \mathrm{wR2}=0.0705$ |
| Absolute structure parameter | $0.00(19)$ |
| Largest diff. peak and hole | 0.366 and -0.426 e. $\mathrm{A}^{\wedge}-3$ |



Table A3.3 Bond lengths [A] and angles [deg]



A4 Crystal Structure Data for $\left[\mathbf{P t C l}\left(P, P^{\prime}, N-\right.\right.$ dmapep)]Cl•1.46 $\mathrm{H}_{2} \mathrm{O} \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$


Figure A4.1 ORTEP representation of $\left[\operatorname{PtCl}\left(P, P^{\prime}, N \text {-dmapcp }\right)\right]^{+}(50 \%$ ellipsoids $)$.

Appendix 4: Crystal Structure Data for [ $\mathrm{PtCl}(\mathrm{P}, \mathrm{P} ', \mathrm{~N}-$ dmapcp $)] \mathrm{Cl} \cdot 1.46 \mathrm{H}_{2} \mathrm{O} \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$


| Table A4.1 |
| :--- |
| Empirical Formula |
| Formula Weight |
| Crystal Color, Habit |
| Crystal Dimensions |
| Crystal Systern |
| Lattice Type |
| Lattice Parameters |
|  |
| Space Group |
| Z value |
| Dcaic <br> Fooo <br> $\mu($ MoKa $)$ <br> Radfaactometer <br> Detector Aperture <br> Data Images |

g

| atom | x | $y$ | $z$ | $\mathrm{B}_{\text {eq }}$ |
| :---: | :---: | :---: | :---: | :---: |
| C(9) | -0.0278(6) | 0.5698(4) | 0.3085(4) | 3.89(15) |
| C(10) | 0.1058(5) | 0.5483(4) | 0.3063(5) | 4.1(2) |
| C(11) | 0.1648(4) | 0.4534(4) | 0.3033(4) | 2.88(12) |
| C(12) | -0.1766(4) | 0.2782(4) | 0.3915(4) | 2.88(12) |
| C(13) | -0.2143(4) | 0.3793(4) | 0.2315(4) | 3.13(13) |
| C(14) | $0.2015(3)$ | 0.1676(3) | 0.4081(3) | 1.48(10) |
| C(15) | 0.2856(4) | 0.1830(4) | 0.4616(4) | 2.55(12) |
| C(16) | $0.3290(5)$ | 0.1026(5) | 0.5354(4) | 4.0(2) |
| C(17) | 0.2868(5) | $0.0116(4)$ | 0.5599(4) | 4.2(2) |
| C(18) | $0.1973(5)$ | -0.0042(4) | 0.5111(4) | 3.22(13) |
| C(19) | 0.1576(4) | 0.0751(3) | 0.4349(3) | 1.95(10) |
| C(20) | 0.4579(5) | 0.2871(5) | 0.4448(5) | 4.5(2) |
| C(21) | $0.2344(5)$ | 0.3377(5) | 0.5005(5) | 4.4(2) |
| C(22) | 0.1773(3) | $0.1206(3)$ | 0.0523(3) | 1.50(10) |
| C(23) | 0.1922(4) | 0.2120(3) | -0.0215(3) | 2.06(10) |
| C(24) | $0.1904(4)$ | 0.2129(4) | -0.1142(4) | 2.61(12) |
| C(25) | $0.1705(4)$ | 0.1282(4) | -0.1336(4) | 2.94(13) |
| C(26) | $0.1534(4)$ | $0.0386(4)$ | -0.0622(4) | 2.61(12) |
| C(27) | 0.1581(4) | 0.0356(3) | 0.0299(3) | 2.11(11) |
| C(28) | 0.3058(5) | 0.3559(4) | -0.0636(4) | 3.16(12) |
| C(29) | 0.0839(5) | 0.3691(4) | $0.0061(4)$ | 4.01(13) |
| C(30) | 0.1749(4) | -0.0196(3) | 0.2428(3) | 1.41(9) |
| C(31) | 0.2840(4) | -0.0923(3) | 0.2549(3) | 1.79(10) |
| C(32) | 0.2709(5) | -0.1894(4) | 0.3123(4) | 2.60(12) |



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| atom | $x$ | y | 2 | $\mathrm{B}_{\text {eq }}$ | oce |
| :---: | :---: | :---: | :---: | :---: | :---: |
| C（33） | 0．1523（5） | －0．2167（4） | 0．3599（4） | 3．03（13） |  |
| C（34） | 0．0432（4） | －0．1476（4） | $0.3467(4)$ | 2．73（12） |  |
| C（35） | 0．0528（4） | －0．0488（3） | 0．2895（4） | 2．18（11） |  |
| C（36） | 0．4591（4） | －0．1056（4） | 0．1263（4） | 3．32（13） |  |
| C（37） | 0．5017（5） | －0．0873（4） | 0．2715（4） | 3．80（14） |  |
| C（38） | 0．1771（11） | 0．6825（9） | 0．0586（9） | 4．0（3） | 0.522 |
| C（38a） | 0．3189（14） | 0．6571（11） | 0．1203（13） | 7．2（5） | 0.478 |







Table A4.3 Bond Lengths $(\dot{A})$ (continued)




Table A4.4 Bond Angles( ${ }^{\circ}$ )


| atom |
| :--- |
| $\mathrm{C}(26)$ |
| $\mathrm{C}(30)$ |
| $\mathrm{C}(32)$ |
| $\mathrm{C}(34)$ |
|  |



## A5 Crystal structure data for $\mathrm{PtCl}_{2}\left(P, P^{\prime}\right.$-dmape $) \cdot \mathbf{C H}_{2} \mathbf{C l}_{2}$



Figure A5.1 ORTEP representation of $\mathrm{PtCl}_{2}\left(P, P^{\prime}\right.$-dmape) (50 \% ellipsoids).

Appendix 5: Crystal Structure Data for $\mathrm{PtCl}_{2}\left(\mathrm{P}, \mathrm{P}^{\prime}-\right.$ dmape $) \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$

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\begin{aligned}
& \text { Table A5.1 } \\
& \text { Empirical Formula } \\
& \text { Formula Weight } \\
& \text { Crystal Color, Habit } \\
& \text { Crystal Dimensions } \\
& \text { Crystal System } \\
& \text { Lattice Type } \\
& \text { Lattice Parameters } \\
& \\
& \hline \text { Space Group } \\
& \text { Z value . } \\
& D_{\text {cate }} \\
& \text { Fooo } \\
& \hline \mu(\text { MoK } \alpha) \\
& \hline \text { Diffractometer } \\
& \text { Radiation } \\
& \text { Detector Aperture } \\
& \text { Data Images } \\
& \phi \text { oscillation Range }(x=0)
\end{aligned}
$$



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\text { Table A5. } 2 \text { Atomic coordinates and } \mathrm{B}_{\text {ioo }} / \mathrm{B}_{\text {ep }}
$$


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Table A5．2 Atomic coordinates and $\mathrm{B}_{\text {iso }} / \mathrm{B}_{\text {eq }}$（continued）

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\underset{0}{2} \\
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Table A5. 4 Bond Angles $\left({ }^{\circ}\right)$







Table A5. 3 Bond Lengths( $(\boldsymbol{A})$











## A6 Crystal Structure Data for $[\mathbf{P d C l}(\text { dmape } O)]_{2}\left[\mathrm{PF}_{6}\right]_{2} \cdot \mathbf{4} \mathbf{C D C l}_{3}$



Figure A6.1 ORTEP representation of $[\mathrm{PdCl}(\text { dmapeO })]_{2}{ }^{2+}(50 \%$ ellipsoids $)$.



| Cryatal Data |  |
| :---: | :---: |
| Empirical formula | $\mathrm{C}_{36} \mathrm{H}_{45} \mathrm{Cl}_{7} \mathrm{P}_{6} \mathrm{~N}_{4} \mathrm{OP}_{3} \mathrm{Pd}$ |
| Crystal Habit, color | Irregular block, pale yellow |
| Crystal size | $0.20 \times 0.10 \times 0.10 \mathrm{~mm}$ |
| crystal system | Triclinic |
| space group | pi |
|  | $a=12.8710(3) \AA \alpha=72.938(1)^{\circ}$ |
|  | $b=14.0672(3) A \quad \beta=68.222(1)^{\circ}$ |
|  | $c=15.4779(4) \& \quad \gamma=73.376(2)^{\circ}$ |
| volume | 2437.8(1) $\mathrm{A}^{3}$ |
| 2 | 2 |
| Fornula weight | 1112.23 |
| Density (calculated) | $1.515 \mathrm{mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.919 \mathrm{~mm}^{-1}$ |
| F(000) | 1124 |
| Data Collection |  |
| Diffractometer | Siemens Smart platform CCD |
| Yavelength | 0.71073 A |
| тemperacure | 173 (2) K |
| $\theta$ range for data collection | 1.45 to $25.00^{\circ}$ |
| Index ranges | $-13 \leq h \leq 15,-15 \leq k \leq 16,0 \leq 1 \leq 18$ |
| Reflections collected | 1676316763 |
| Independent reflections | $8168\left(\mathrm{R}_{\text {int }}=0.0639\right)$ |
| Solution and Refinement |  |
| system used | Shelxtl-v5.0 |
| Solution | Direct methods |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting scheme | $\begin{aligned} & w=\left[\sigma^{2}\left(\mathrm{~F}_{0}^{2}\right)+(\mathrm{AP})^{2}+(\mathrm{BP})\right]^{-1}, \text { where } P= \\ & \left.\left(\mathrm{F}^{2}+2 \mathrm{FC}^{2}\right)\right) / 3, A=0.086, \text { and } B=0.0 \end{aligned}$ |
| Absorption correction | SADABS (Sheldrick, 1996) |
| Max. and min. transmission | 1.000 and 0.697 |
| Data / restraints / parameters | 8168 / 42/531 |
| R indices ( $\mathrm{I} \times 20$ ( I ) 5134 ) | R1 $=0.0710$, wR2 $=0.1563$ |
| R indices (all data) | R1 $=0.1179, w R 2=0.1768$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.960 |
| Largest diff. peak and hole | 1.328 and $-0.900 \mathrm{e}^{-3}$ |



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|  | $x$ | $y$ | $z$ | $\mathrm{U}(\mathrm{eq})$ | sOF |
| :--- | :--- | :--- | :--- | :--- | :--- |
| $\mathrm{C}(36)$ | $4489(12)$ | $1673(11)$ | $2849(9)$ | $171(5)$ | 1 |
| $\mathrm{Cl}(5)$ | $3774(5)$ | $1368(6)$ | $2311(3)$ | $252(4)$ | 1 |
| $\mathrm{Cl}(6)$ | $3729(3)$ | $2725(6)$ | $3336(5)$ | $253(3)$ | 1 |
| $\mathrm{Cl}(7)$ | $4889(5)$ | $665(6)$ | $3776(5)$ | $245(3)$ | 1 |

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## A7 Crystal Structure Data for $\mathbf{P d C l}_{\mathbf{2}}(\mathbf{P}, \mathbf{N}$-dmapm)



Figure A7.1 ORTEP representation of $\mathrm{PdCl}_{2}(P, N$-dmapm) ( $50 \%$ ellipsoids).

| $\begin{aligned} & \stackrel{\circ}{\dot{1}} \\ & \dot{O} \\ & \underset{1}{1} \end{aligned}$ |  | $\begin{aligned} & \text { O} \\ & \stackrel{4}{4} \\ & \hline 1 \end{aligned}$ | $\begin{aligned} & \circ \\ & \stackrel{\circ}{8} \\ & 0 \end{aligned}$ |  |  | C. Structure Solution and Refinement |  |  |  |  | $\begin{aligned} & \mathbf{\circ} \\ & \hline \mathbf{O} \\ & 0 \end{aligned}$ |  | $\stackrel{8}{\underset{\sim}{\circ}}$ | $\stackrel{9}{8}$ | $\begin{aligned} & \infty \\ & \infty \\ & \infty \end{aligned}$ | $\begin{aligned} & \mathbf{0} \\ & 0 \\ & 0 \\ & \hdashline \\ & \text { דib } \\ & 0 \end{aligned}$ | $\begin{aligned} & \infty \\ & \infty \\ & 0 \end{aligned}$ | $\overline{0}$ | $\stackrel{\infty}{\underset{\sim}{n}}$ | $\begin{aligned} & \text { N} \\ & \text { - } \\ & \text { - } \\ & \text { 웅 } \end{aligned}$ | $\begin{aligned} & \pi \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | $\underset{\sim}{\stackrel{\circ}{E}}$ | No. of Reflections Measured |  |  |  |  |  | Least Squares Weights | $\begin{aligned} & \text { 范 } \\ & \text { H } \\ & \hline \end{aligned}$ |  | $\text { No. Observations ( } \mathrm{I}>0.00 \sigma(\mathrm{I}) \text { ) }$ |  |  |  |  |  |  |  |  |  |


Table A7.1

| Empirical Formula |
| :--- |
| Formula Weight |
| Crystal Color, Habit |
| Crystal Dimensions |
| Crystal System |
| Lattice Type |
| Lattice Parameters |
| Space Group |
| Z value |
| Dealc |
| Foco |
| $\mu($ MoK $\alpha)$ |
| Difractometer |
| Radiation |
| Detector Aperture |
| Data Images |
| $\phi$ oscillation Range $(x=0)$ |




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Table A7．2


| atom | $x$ | y | 2 | $\mathrm{B}_{\text {eq }}$ |
| :---: | :---: | :---: | :---: | :---: |
| H(31) | 0.4332 | 0.4784 | 0.4060 | 3.0779 |
| H(32) | 0.3268 | 0.4319 | 0.4232 | 3.0779 |
| H(33) | 0.6466 | 0.1723 | 0.5054 | 1.9621 |
| H(34) | 0.7367 | 0.0659 | 0.5378 | 2.6065 |
| H(35) | 0.7507 | -0.0093 | 0.4179 | 3.1273 |
| H(36) | 0.6926 | 0.0242 | 0.2672 | 2.7300 |
| H(37) | 0.7252 | 0.1892 | 0.1673 | 3.2525 |
| H(38) | 0.6009 | 0.2157 | 0.1193 | 3.2525 |
| H(39) | 0.6472 | 0.2342 | 0.2227 | 3.2525 |
| $\mathrm{H}(40)$ | 0.5510 | 0.0457 | 0.1546 | 4.0991 |
| H(41) | 0.5429 | 0.1028 | 0.0784 | 4.0991 |
| H(42) | 0.6671 | 0.0757 | 0.1259 | 4.0991 |






Table A7.2


| Table A7.3 | Bond Lengths $(A)$ |  |  |  |  | Table A7.3 | Bond Lengths ( $\dot{A}$ ) |  |  |  | distance |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| atom | atom | distance | atom | atom | distance | atom | atom | distance | atom | atom |  |
| $\mathrm{Pd}(1)$ | Cl(1) | 2.3041 (6) | $\mathrm{Pd}(1)$ | $\mathrm{Cl}(2)$ | 2.3812(6) | C(2) | H(1) | 0.98 | C(3) | H(2) | 0.98 |
| Pd(1) | P(1) | 2.1798(6) | $\mathrm{Pd}(1)$ | N(1) | 2.132(2) | C(4) | H(3) | 0.98 | C(5) | H(4) | 0.98 |
| $\mathrm{P}(1)$ | C(1) | 1.801(2) | $P(1)$ | C(9) | $1.806(2)$ | C(7) | H(5) | 0.98 | C(7) | H(6) | 0.98 |
| $\mathbf{P}(1)$ | C(17) | 1.824(2) | $P(2)$ | C(17) | 1.873(2) | C(7) | H(7) | 0.98 | C(8) | H(8) | 0.98 |
| P (2) | C(18) | 1.847(2) | $\mathrm{P}(2)$ | C(26) | $1.845(2)$ | C(8) | H(9) | 0.98 | C(8) | H(10) | 0.98 |
| N(1) | C(6) | 1.481(3) | N(1) | C(7) | 1.492(4) | C(10) | H(11) | 0.98 | C(11) | $\mathrm{H}(12)$ | 0.98 |
| N(1) | C(8) | 1.490(3) | N(2) | C(14) | 1.440(4) | C(12) | H(13) | 0.98 | C(13) | H(14) | 0.98 |
| $\mathrm{N}(2)$ | C(15) | 1.470 (3) | N(2) | $\mathrm{C}(16)$ | 1.470(4) | C(15) | H(15) | 0.98 | C(15) | H(16) | 0.98 |
| N(3) | C(23) | 1.435(3) | N(3) | C(24) | 1.467(3) | C(15) | H(17) | 0.98 | C(16) | H(18) | 0.98 |
| N(3) | C(25) | 1.453(3) | N(4) | C(31) | 1.415(4) | C(16) | H(19) | 0.98 | C(16) | H(20) | 0.98 |
| N(4) | C(32) | 1.459(4) | N(4) | C(33) | 1.460(4) | C(17) | $\mathrm{H}(21)$ | 0.98 | $\mathrm{C}(17)$ | $\mathrm{H}(22)$ | 0.98 |
| C(1) | C(2) | 1.401(3) | C(1) | C(6) | 1.385(3) | C(19) | H(23) | 0.98 | C(20) | H(24) | 0.98 |
| C(2) | C(3) | 1.383(4) | C(3) | C(4) | 1.381(4) | C(21) | H(25) | 0.98 | C(22) | H(26) | 0.98 |
| C(4) | C(5) | 1.385(4) | C(5) | C(6) | 1.395(3) | C(24) | H(27) | 0.98 | C(24) | H(28) | 0.98 |
| C(9) | C(10) | 1.391(4) | C(9) | C(14) | 1.402(3) | C(24) | H(29) | 0.98 | C(25) | H(30) | 0.98 |
| C(10) | C(11) | 1.385(4) | C(11) | C(12) | 1.377(5) | C(25) | H(31) | 0.98 | C(25) | H(32) | 0.98 |
| C(12) | C(13) | 1.385(5) | C(13) | C(14) | 1.398(4) | C(27) | H(33) | 0.98 | C(28) | H(34) | 0.98 |
| C(18) | C(19) | 1.401(3) | C(18) | C(23) | 1.402(3) | C(29) | H(35) | 0.98 | C(30) | H(36) | 0.98 |
| C(19) | C(20) | 1.394(3) | C(20) | C(21) | 1.377(4) | C(32) | H(37) | 0.98 | C(32) | H(38) | 0.98 |
| C(21) | C(22) | 1.392(4) | C(22) | C(23) | 1.399(3) | C(32) | H(39) | 0.98 | C(33) | H(40) | 0.98 |
| C(26) | C(27) | 1.398(4) | C(26) | C(31) | 1.415(3) | C(33) | H(41) | 0.98 | C(33) | H(42) | 0.98 |
| C(27) | C(28) | 1.392(3) | C(28) | C(29) | 1.378(4) |  |  |  |  |  |  |
| C(29) | C(30) | 1.383(4) | C(30) | C(31) | $1.408(4)$ |  |  |  |  |  |  |




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Table A7．4 Bond Angles $\left({ }^{\circ}\right)$（continued） 
  
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Bond Angles（ ${ }^{\circ}$ ）   

## A8 Crystal Structure Data for $\mathbf{P d}_{2} \mathbf{C l}_{\mathbf{2}}(\mathbf{d m a p m}) \cdot \mathbf{2} \mathbf{C H C l}_{3}$



Figure A8.1 ORTEP representation of $\mathrm{Pd}_{2} \mathrm{Cl}_{2}$ (dmapm) (50 \% ellipsoids).

Table A8. 1 Experimental details

| Empirical Formula | C33 H42 | Cl2 N4 P2 Pd | 2 (C | H | Cl3) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Formula Weight |  |  |  |  | 79.12 |
| Crystal System |  |  | Mono | nocl | linic |
| Space group |  | C2/c |  | (No. | . 15) |
| $\mathrm{a}, \mathrm{b}, \mathrm{c}$ [ $\AA$ ] 4 | 44.988 (4) | 9.984 (2) |  | . 531 | 31 (4) |
| alpha, beta, gamma [deg] | 90 | 122.730(10) |  |  | 90 |
| V [Å] |  |  |  |  | 69 (3) |
| Z |  |  |  |  | 8 |
| D(obs), D(calc) [g/ $\mathrm{cm}^{3}$ ] |  |  | 0.000, | , 1. | 1.547 |
| F (000) |  |  |  |  | 4320 |
| Mu (MoKa) [/mm] |  |  |  |  | 1.335 |
| Crystal Size [mm] |  | 0.03 x | 0.08 x | x | 0.25 |
| Data | a Collect |  |  |  |  |
| Temperature (K) |  |  |  |  | 198 |
| Radiation [ ${ }_{\text {a }}$ ] |  | MoKa |  |  | 71070 |
| Theta Min-Max [Deg] |  |  | 3.1, | , 2 | 23.0 |
| Dataset |  | 9: 49 ; -10: | 10 ; | -26 | 6: 26 |
| Tot., Uniq. Data, R (int) |  | 29756, | 6419, | 0 | 0.109 |
| Observed data [I > 2.0 sigma(I)] |  |  |  |  | 3341 |
|  | finement |  |  |  |  |
| Nref, Npar |  |  | 6419 | 9, | 460 |
| R, wR, S |  | 0.0600, | 0.0850 | 0, 1 | 1.39 |
| $\left.\mathrm{w}=\backslash \mathrm{S}^{\wedge} 2^{\wedge}\left(\mathrm{FO}^{\wedge} 2^{\wedge}\right)\right]^{\prime}$ |  |  |  |  |  |
| Max. and Av. Shift/Error |  |  | 0.00 | 00, 0 | 0.00 |
| Min. and Max. resd. dens. [e/ $\dot{A}^{3}$ ] |  |  | -1.36 | 6, 3 | 3.25 |

Table A8.2 Final Coordinates and Equivalent Isotropic Displacement parameters ( $\AA^{2}$ ) of the non-Hydrogen Atoms.

| Atom | x | Y | z | $\mathrm{U}(\mathrm{eq})$ [ A$]$ |
| :---: | :---: | :---: | :---: | :---: |
| Pd1 | 0.36711 (3) | 0.31833 (9) | 0.86120 (5) | 0.0193 (3) |
| Pd2 | 0.34242 (3) | 0.11232 (9) | 0.79054 (5) | 0.0193 (3) |
| Clı | 0.33950 (10) | 0.2935 (3) | $0.9207(2)$ | 0.0364 (14) |
| Cl2 | $0.37000(10)$ | -0.0319(3) | 0.8814 (2) | 0.0366 (14) |
| P1 | 0.38928 (9) | 0.3373 (3) | 0.8027 (2) | 0.0219 (12) |
| P2 | 0.31898 (9) | 0.2477 (3) | 0.7075 (2) | $0.0179(12)$ |
| N1 | 0.3939 (3) | $0.5130(10)$ | 0.9055 (5) | 0.021 (4) |
| N2 | 0.4581 (3) | 0.2490 (10) | 0.9138 (5) | 0.032 (4) |
| N3 | 0.3291 (3) | -0.0540(10) | 0.7184 (5) | $0.029(4)$ |
| N4 | 0.2503 (3) | 0.1441 (9) | 0.6740 (5). | 0.024 (4) |
| C1 | $0.4119(3)$ | 0.5680 (10) | 0.8766 (6) | 0.022 (4) |
| C2 | 0.4275 (4) | 0.6950 (10) | 0.8955 (7) | 0.034 (5) |
| C3 | 0.4454 (5) | 0.746 (2) | 0.8682 (8) | 0.059 (6) |
| C4 | 0.4470 (4) | 0.682 (2) | 0.8223 (9) | 0.065 (6) |
| C5 | $0.4292(5)$ | 0.553 (2) | 0.8011 (7) | 0.053 (6) |
| C6 | 0.4118 (3) | 0.4960 (10) | 0.8286 (6) | 0.025 (5) |
| C7 | 0.3658 (4) | 0.6070 (10) | 0.8942 (9) | 0.057 (6) |
| C8 | 0.4190 (4) | 0.4890 (10) | 0.9767 (7) | 0.035 (5) |
| C9 | 0.4511 (3) | 0.1880 (10) | 0.8540 (7) | $0.032(5)$ |
| C10 | 0.4746 (4) | 0.105 (2) | 0.8529 (8) | $0.051(6)$ |
| C11 | 0.4667 (5) | $0.050(2)$ | 0.7950 (10) | 0.069 (8) |
| C12 | 0.4354 (5) | 0.078 (2) | 0.7389 (9) | 0.071 (8) |
| C13 | 0.4118 (4) | 0.163 (2) | $0.7389(7)$ | 0.044 (5) |
| C14 | 0.4192 (4) | $0.2200(10)$ | 0.7968 (6) | 0.034 (5) |
| C15 | 0.4568 (5) | 0.153 (2) | 0.9566 (8) | 0.053 (6) |
| C16 | $0.4908(4)$ | 0.327 (2) | 0.9479 (8) | 0.059 (6) |
| C17 | 0.3530 (3) | $0.3660(10)$ | $0.7181(6)$ | 0.027 (4) |
| C18 | 0.3140 (4) | $0.0000(10)$ | 0.6526 (6) | 0.028 (5) |
| C19 | 0.3038 (4) | -0.0890(10) | 0.6005 (7) | 0.036 (5) |
| C20 | 0.2907 (4) | -0.040(2) | 0.5393 (7) | 0.040 (5) |
| C21 | 0.2865 (4) | $0.099(2)$ | 0.5279 (6) | 0.036 (5) |
| C22 | 0.2955 (3) | 0.1870 (10) | 0.5770 (6) | 0.025 (4) |
| C23 | 0.3088 (3) | $0.1390(10)$ | 0.6408 (6) | 0.018 (4) |
| C24 | 0.3619 (4) | -0.1290(10) | 0.7395 (7) | 0.036 (5) |
| C25 | 0.3034 (4) | -0.1460(10) | 0.7222 (7) | 0.047 (5) |
| C26 | 0.2479 (3) | 0.2830 (10) | 0.6594 (6) | 0.020 (4) |
| C27 | 0.2167 (3) | 0.3540 (10) | 0.6323 (6) | 0.029 (5) |
| C28 | 0.2160 (4) | $0.4900(10)$ | 0.6199 (6) | 0.033 (5) |
| C29 | 0.2448 (4) | $0.5560(10)$ | 0.6319 (6) | 0.029 (5) |
| C30 | 0.2771 (4) | 0.4860 (10) | 0.6589 (6) | 0.027 (5) |
| C31 | 0.2790 (3) | $0.3490(10)$ | 0.6736 (6) | 0.021 (4) |
| C32 | 0.2460 (5) | $0.1180(10)$ | 0.7273 (8) | 0.054 (6) |
| C33 | 0.2257 (4) | $0.0670(10)$ | $0.6161(7)$ | 0.045 (6) |
| Cl3 | $0.43250(10)$ | 0.1527 (5) | 1.0891 (2) | 0.082 (2) |
| Cl4 | 0.36890 (10) | 0.0133 (6) | 1.0558 (2) | $0.0759(19)$ |
| Cl5 | 0.42490 (10) | -0.1241(5) | 1.0545 (3) | 0.085 (2) |
| C34 | 0.4024 (4) | $0.030(2)$ | 1.0403 (7) | 0.045 (5) |
| Cl6 | 0.19310 (10) | -0.0673 (4) | 0.4581 (2) | 0.0633 (17) |
| Cl7 | 0.12130 (10) | -0.1357(5) | $0.3662(2)$ | 0.086 (2) |
| Cl8 | 0.1385 (2) | 0.1055 (5) | 0.4436 (2) | 0.0779 (19) |
| C35 | $0.1509(4)$ | -0.061(2) | 0.4441 (8) | $0.050(6)$ |

Table A8.3 Bond distances ( $\AA$ )

| Atom | Atom | Distance | Atom | Atom | Distance |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Pd1 | Pd2 | 2.5272 (14) | N4 | C33 | 1.461 (17) |
| Pd1 | Cl1 | 2.386 (5) | N4 | C26 | $1.422(14)$ |
| Pd1 | P1 | 2.154(5) | N4 | C32 | 1.45 (2) |
| Pd1 | N1 | 2.235 (11) | C1 | C2 | 1.401(16) |
| Pd2 | $\mathrm{Cl2}$ | 2.364 (4) | C1 | C6 | 1.378(18) |
| Pd2 | P2 | 2.183 (4) | C2 | C3 | 1.39 (3) |
| Pd2 | N3 | $2.259(10)$ | C3 | C4 | 1.33 (3) |
| Cl3 | C34 | 1.736 (19) | C4 | C5 | 1.46 (3) |
| Cl4 | C34 | 1.75 (2) | C5 | C6 | 1.40(3) |
| Cl5 | C34 | 1.77(2) | C9 | C10 | 1.35 (3) |
| Cl6 | C35 | 1.74 (2) | C9 | C14 | 1.40 (2) |
| Cl7 | C35 | $1.797(18)$ | C10 | C11 | 1.38 (3) |
| Cl8 | C35 | 1.75 (2) | C11 | C12 | 1.36(3) |
| P1 | C17 | 1.841(13) | C12 | C13 | 1.36 (3) |
| P1 | C6 | 1.801(12) | C13 | C14 | 1.39 (2) |
| P1 | C14 | 1.848 (17) | C18 | C19 | 1.414 (18) |
| P2 | C31 | 1.825 (14) | C18 | C23 | 1.411(14) |
| P2 | C17 | 1.837 (14) | C19 | C20 | 1.37 (2) |
| P2 | C23 | 1.804(12) | C20 | C21 | 1.41(3) |
| N1 | C8 | $1.500(18)$ | C21 | C22 | 1.36 (2) |
| N1 | C1 | 1.44 (2) | C22 | C23 | 1.423(17) |
| N1 | C7 | 1.48 (2) | C26 | C31 | 1.41 (2) |
| N2 | C9 | 1.457 (18) | C26 | C27 | 1.38 (2) |
| N2 | C16 | 1.46 (2) | C27 | C28 | 1.388(14) |
| N2 | C15 | 1.45 (2) | C28 | C29 | 1.34 (2) |
| N3 | C18 | 1.474 (16) | C29 | C30 | 1.41 (2) |
| N3 | C24 | 1.48 (2) | C30 | C31 | 1.405(14) |
| N3 | C25 | 1.52 (2) | C2 | H2 | 0.9755 |
| C3 | H3 | 0.9844 | C20 | H20 | 0.9768 |
| C4 | H4 | 0.9782 | C21 | H21 | 0.9787 |
| C5 | H5 | 0.9810 | C22 | H22 | 0.9762 |
| C7 | H7C | 0.9789 | C24 | H24A | 0.9805 |
| C7 | H7A | 0.9796 | C24 | H24C | 0.9818 |
| C7 | H7B | 0.9800 | C24 | H24B | 0.9809 |
| C8 | H8A | 0.9774 | C25 | H25A | 0.9790 |
| C8 | H8B | 0.9823 | C25 | H25B | 0.9812 |
| C8 | H8C | 0.9823 | C25 | H25C | 0.9806 |
| C10 | H10 | 0.9813 | C27 | H27 | 0.9797 |
| C11 | H11 | 0.9823 | C28 | H28 | 0.9782 |
| C12 | H12 | 0.9799 | C29 | H29 | 0.9798 |
| C13 | H13 | 0.9798 | C30 | H30 | 0.9777 |
| C15 | H15A | 0.9814 | C32 | H32C | 0.9778 |
| C15 | H15C | 0.9812 | C32 | H32A | 0.9799 |
| C15 | H15B | 0.9787 | C32 | H32B | 0.9805 |
| C16 | H16C | 0.9825 | C33 | H33C | 0.9771 |
| C16 | H16A | 0.9789 | C33 | H33A | 0.9826 |
| C16 | H16B | 0.9804 | C33 | н33 В | 0.9753 |
| C17 | H17A | 0.9786 | C34 | H34 | 0.9808 |
| C17 | H17B | 0.9790 | C35 | H35 | 0.9811 |
| C19 | H19 | 0.9758 |  |  |  |

Table A8.4 Bond angles ( ${ }^{\circ}$ )

| Atom | Atom | Atom | Angle | Atom | Atom | Atom | Angle |
| :--- | :--- | :--- | ---: | :--- | :--- | :--- | :--- |
| Pd2 | Pd1 | C11 | $98.85(10)$ | C1 | N1 | C8 | $111.3(13)$ |
| Pd2 | Pd1 | P1 | $78.74(10)$ | C7 | N1 | C8 | $110.5(12)$ |
| Pd2 | Pd1 | N1 | $164.3(3)$ | C9 | N2 | C15 | $112.5(11)$ |
| C11 | Pd1 | P1 | $176.79(16)$ | C9 | N2 | C16 | $113.7(13)$ |
| C11 | Pd1 | N1 | $96.6(4)$ | C15 | N2 | C16 | $111.1(13)$ |
| P1 | Pd1 | N1 | $85.7(4)$ | Pd2 | N3 | C18 | $111.0(7)$ |
| Pd1 | Pd2 | C12 | $92.12(9)$ | Pd2 | N3 | C24 | $107.9(8)$ |
| Pd1 | Pd2 | P2 | $86.99(10)$ | Pd2 | N3 | C25 | $106.6(9)$ |
| Pd1 | Pd2 | N3 | $165.4(4)$ | C18 | N3 | C24 | $110.5(13)$ |
| C12 | Pd2 | P2 | $177.8(2)$ | C18 | N3 | C25 | $111.9(12)$ |
| C12 | Pd2 | N3 | $94.2(3)$ | C24 | N3 | C25 | $108.8(10)$ |
| P2 | Pd2 | N3 | $86.2(3)$ | C26 | N4 | C32 | $112.0(10)$ |
| Pd1 | P1 | C6 | $102.5(5)$ | C26 | N4 | C33 | $110.8(10)$ |
| Pd1 | P1 | C14 | $128.0(5)$ | C32 | N4 | C33 | $112.5(13)$ |
| Pd1 | P1 | C17 | $108.5(5)$ | N1 | C1 | C2 | $119.7(12)$ |
| C6 | P1 | C14 | $106.9(7)$ | N1 | C1 | C6 | $118.6(10)$ |
| C6 | P1 | C17 | $104.3(5)$ | C2 | C1 | C6 | $121.6(14)$ |
| C14 | P1 | C17 | $104.5(6)$ | C1 | C2 | C3 | $119.2(15)$ |
| Pd2 | P2 | C17 | $108.7(4)$ | C2 | C3 | C4 | $122.8(18)$ |
| Pd2 | P2 | C23 | $103.4(4)$ | C3 | C4 | C5 | $117.1(19)$ |
| Pd2 | P2 | C31 | $128.9(5)$ | C4 | C5 | C6 | $122.0(16)$ |
| C17 | P2 | C23 | $107.4(7)$ | P1 | C6 | C1 | $120.1(11)$ |
| C26 | C2 | C2 | P2 | C31 | C31 | C27 | C26 |

Appendix 8: Crystal Structure Data for $\mathrm{Pd}_{2} \mathrm{Cl}_{2}($ dmapm $) \cdot 2 \mathrm{CHCl}_{3}$

| Atom | Atom | Atom | Angle | Atom | Atom | Atom | Angle |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| C26 | C31 | C30 | 118.5(13) | C14 | C13 | H13 | 120.28 |
| C1 | C2 | H2 | 120.28 | N2 | C15 | H15A | 109.54 |
| N2 | C15 | H15B | 109.79 | H24A | C24 | H24C | 109.44 |
| N2 | C15 | H15C | 109.65 | H24B | C24 | H24C | 109.53 |
| H15A | C15 | H15B | 109.42 | N3 | C25 | H25A | 109.41 |
| H15A | C15 | H15C | 109.17 | N3 | C25 | H25B | 109.62 |
| H15B | C15 | H15C | 109.25 | N3 | C25 | H25C | 109.51 |
| N2 | C16 | H16A | 109.50 | H25A | C25 | H25B | 109.41 |
| N2 | C16 | H16B | 109.56 | H25A | C25 | H25C | 109.52 |
| N2 | C16 | H16C | 109.65 | H25B | C25 | H25C | 109.36 |
| H16A | C16 | H16B | 109.42 | C26 | C27 | H27 | 119.56 |
| H16A | C16 | H16C | 109.35 | C28 | C27 | H27 | 120.14 |
| H16B | C16 | H16C | 109.35 | C27 | C28 | H28 | 119.13 |
| P1 | C17 | H17A | 111.20 | C29 | C28 | H28 | 118.90 |
| P1 | C17 | H17B | 111.14 | C28 | C29 | H29 | 120.35 |
| P2 | C17 | H17A | 110.90 | C30 | C29 | H29 | 120.45 |
| P2 | C17 | H17B | 110.88 | C29 | C30 | H30 | 120.01 |
| H17A | C17 | H17B | 109.73 | C31 | C30 | H30 | 119.60 |
| C18 | C19 | H19 | 120.03 | N4 | C32 | H32A | 109.45 |
| C20 | C19 | H19 | 119.82 | N4 | C32 | H32B | 109.36 |
| C19 | C20 | H20 | 120.05 | N4 | C32 | H32C | 109.40 |
| C21 | C20 | H20 | 119.91 | H32A | C32 | H32B | 109.39 |
| C20 | C21 | H21 | 119.43 | H32A | C32 | H32C | 109.58 |
| C22 | C21 | H21 | 119.52 | H32B | C32 | H32C | 109.65 |
| C21 | C22 | H22 | 119.91 | N4 | C33 | H3 3A | 109.09 |
| C23 | C22 | H22 | 119.96 | N4 | C33 | H33B | 109.56 |
| N3 | C24 | H24A | 109.52 | N4 | C33 | H33C | 109.38 |
| N3 | C24 | H24B | 109.45 | H33A | C33 | H33B | 109.53 |
| N3 | C24 | H24C | 109.43 | H33A | C33 | H33C | 109.23 |
| H24A | C24 | H24B | 109.47 | H33B | C33 | H33C | 110.03 |
| Cl3 | C34 | Cl4 | 111.1(10) | Cl6 | C35 | Cl7 | 107.3(10) |
| Cl3 | C34 | C15 | 109.1(10) | Cl6 | C35 | Cl8 | $110.2(11)$ |
| Cl4 | C34 | Cl5 | 110.0(11) | Cl7 | C35 | Cl 8 | 109.7(10) |
| Cl3 | C34 | H34 | 109.09 | Cl6 | C35 | H35 | 109.86 |
| Cl4 | C34 | H34 | 108.82 | Cl7 | C35 | H35 | 109.91 |
| Cl5 | C34 | H34 | 108.65 | Cl 8 | C35 | H35 | 109.87 |

## A9 Crystal Structure Data for $\mathbf{P t C l}_{\mathbf{2}}$ (dpype) $\cdot \mathbf{C H}_{\mathbf{2}} \mathbf{C l}_{\mathbf{2}}$



Figure A9.1 ORTEP representation of $\mathrm{PtCl}_{2}$ (dpype) $\cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$ ( $50 \%$ ellipsoids).

Table A9.1 Full Crystallographic Data

| A. Crystal Data |  |
| :---: | :---: |
| Empircal formula | $\mathrm{C}_{23} \mathrm{H}_{22} \mathrm{~N}_{4} \mathrm{Cl}_{4} \mathrm{P}_{2} \mathrm{Pt}$ |
| Formula weight | 753.30 |
| Crystal colour, habit | colourless, irregular |
| Crystal dimensions | $0.30 \times 0.40 \times 0.50 \mathrm{~mm}$ |
| Crystal system | monoclinic |
| Lattic type | primitive |
| Number of reflections used | 25 (20.9-30.6 ${ }^{\circ}$ ) |
| for unit cell determination ( $2 \theta$ range) |  |
| Omega scan peak width at half height | $0.31{ }^{\circ}$ |
| Lattice parameters | $\begin{aligned} & a=8.452(2) \AA, b=16.351(4) \AA, c=19.794(2) \AA \\ & \beta=97.49(1)^{\circ} \\ & V=2712.1(8) \AA^{3} \end{aligned}$ |
| Space group | $\mathrm{P} 2_{1} / \mathrm{n}$ |
| Z value | 4 |
| $\mathrm{D}_{\text {calc }}$ | $1.845 \mathrm{~g} \mathrm{~cm}^{-3}$ |
| $\mathrm{F}_{000}$ | 1456 |
| $\mu(\mathrm{MoK} \alpha)$ | $56.85 \mathrm{~cm}^{-1}$ |
| B. Intensity Measurements |  |
| Diffractometer | Rigaku AFC65 |
| Radiation | MoK $\alpha(\lambda=0.71069 \AA$ ) |
| Take-off angle | $6.0^{\circ}$ |
| Detector aperture | 6.0 mm horizontal 6.0 mm vertical |
| Crystal to detector distance | 285 mm |
| Temperature | $21.0{ }^{\circ} \mathrm{C}$ |
| Scan type | $\omega-2 \theta$ |
| Scan rate | $16.0{ }^{\circ} \mathrm{min}^{-1}$ (in $\omega$ ) up to 9 scans |
| Scan width | $(1.10+0.35 \tan \theta)^{\circ}$ |
| $2 \theta_{\text {max }}$ | $55^{\circ}$ |
| Number of reflections measured | Total: 6864 |
|  | Unique: $6432\left(\mathrm{R}_{\text {int }}=0.043\right)$ |
| Corrections | Lorentz-polarization |
|  | Absorption |
|  | (trans. factors: 0.783-1.000) |
|  | Decay ( 16.32 \% decline) |
|  | Secondary extinction (coefficient: $6.2(15) \times 10^{-7}$ ) |
| C. Structure Solution and Refinement |  |
| Structure solution | Patterson methods (DIRDIF92 PATTY) |
| Refinement | Full-matrix least-squares |
| Function minimized | $\Sigma \omega\left(\left\|\mathrm{F}_{0}\right\|-\left\|\mathrm{F}_{\mathrm{c}}\right\|\right)^{2}$ |
| Least squares weights | $\omega=1 /\left(\sigma^{2} \mathrm{~F}_{0}\right)$ |
| p -factor | 0.0000 |
| Anomalous dispersion | All non-hydrogen atoms |
| Number of observations | 3913 |
| Number of variables | 308 |
| Reflection/parameter ratio | 12.70 |
| Residuals: $\mathrm{R}, \mathrm{R}_{\mathrm{w}}$ | 0.031, 0.029 |
| Goodness of fit indicator | 1:54 |
| Max shift/error in final cycle | 0.0008 |
| Maximum peak in final difference map | $0.99 e^{-} \AA^{-3}$ (near Pt) |
| Minimum peak in final difference map | -0.95 $e^{-} \AA^{-3}$ |

A. Crystal Data

Empircal formula
Crystal colour, habit
Crystal dimensions
Crystal system
Lattic type
Number of reflections used
for unit cell determination ( $2 \theta$ range)
Omega scan peak width at half height
Lattice parameters

Space group
Z value
$\mathrm{D}_{\text {calt }}$
$\mu(\mathrm{MoK} \alpha)$
B. Intensity Measurements

Diffractometer
Radiation
Take-off angle
Detector aperture
Crystal to detector distance
Temperature
Scan type
Scan rate
Scan width
$2 \theta_{\text {max }}$
Number of reflections measured
Corrections

## C. Structure Solution and Refinement

Structure solution
nem
imized
p-factor
Anomalous dispersion
Number of observations
Number of variables
Reflection/parameter ratio
Residuals: $\mathrm{R}, \mathrm{R}_{\mathrm{w}}$
Max shift/error in final cycle
Maximum peak in final difference map
Minimum peak in final difference map
$\mathrm{C}_{23} \mathrm{H}_{22} \mathrm{~N}_{4} \mathrm{Cl}_{4} \mathrm{P}_{2} \mathrm{Pt}$
753
$0.30 \times 0.40 \times 0.50 \mathrm{~mm}$
monoclinic
primitive
$25\left(20.9-30.6^{\circ}\right)$
$0.31^{\circ}$
$\mathrm{a}=8.452(2) \AA, \mathrm{b}=16.351(4) \AA, \mathrm{c}=19.794(2) \AA$
$\beta=97.49(1)^{\circ}$
$\mathrm{V}=2712.1(8) \AA^{3}$
$\mathrm{P} 2_{1} / \mathrm{n}$
4

1456
$56.85 \mathrm{~cm}^{-1}$

## Rigaku AFC65

$\operatorname{MoK} \alpha(\lambda=0.71069 \AA)$
$6.0^{\circ}$
6.0 mm horizontal
.0 mm vertical
285 mm
$\omega-2 \theta$
$16.0^{\circ} \mathrm{min}^{-1}$ (in $\omega$ ) up to 9 scans
$(1.10+0.35 \tan \theta)^{\circ}$
$55^{\circ}$
Total: 6864
Unique: $6432\left(\mathrm{R}_{\text {int }}=0.043\right)$
Lorentz-polarization
Absorption
Decay ( $16.32 \%$ decline)
Secondary extinction
(coefficient: $6.2(15) \times 10^{-7}$ )
Patterson methods (DIRDIF92 PATTY)
$\Sigma \omega\left(\left|\mathrm{F}_{0}\right|-\left|\mathrm{F}_{\mathrm{c}}\right|\right)^{2}$
$\omega=1 /\left(\sigma^{2} \mathrm{~F}_{0}\right)$
All non-hydrogen atoms
3913
308
12.70
0.031, 0.029
0.0008
$0.99 e^{-} \AA^{-3}$ (near Pt)
$-0.95 e^{-} \AA^{-3}$

Table A9.2 Atomic coordinates

| atom | $\mathbf{x}$ | $\mathbf{y}$ | $\mathbf{z}$ | $\mathbf{B}_{\text {eq }}$ |
| :--- | :--- | :--- | :--- | :--- |
| $\mathrm{Pt}(1)$ | $0.15065(3)$ | $0.21171(1)$ | $0.18786(1)$ | $2.219(5)$ |
| $\mathrm{Cl}(1)$ | $-0.0670(2)$ | $0.19385(10)$ | $0.10162(8)$ | $3.32(4)$ |
| $\mathrm{Cl}(2)$ | $-0.0235(2)$ | $0.2437(1)$ | $0.26723(8)$ | $4.41(4)$ |
| $\mathrm{Cl}(3)$ | $-0.0748(3)$ | $0.4591(2)$ | $0.1630(2)$ | $11.1(1)$ |
| $\mathrm{Cl}(4)$ | $-0.431(3)$ | $0.4237(2)$ | $0.1207(1)$ | $7.64(7)$ |
| $\mathrm{P}(1)$ | $0.3595(2)$ | $0.229(1)$ | $0.26692(8)$ | $2.57(4)$ |
| $\mathrm{P}(2)$ | $0.3243(2)$ | $0.18388(10)$ | $0.11661(8)$ | $2.42(3)$ |
| $\mathrm{N}(1)$ | $0.3006(7)$ | $0.0936(3)$ | $0.3383(3)$ | $4.2(2)$ |
| $\mathrm{N}(2)$ | $0.5678(7)$ | $0.3322(4)$ | $0.3243(3)$ | $4.6(2)$ |
| $\mathrm{N}(3)$ | $0.4153(7)$ | $0.0288(4)$ | $0.1192(3)$ | $4.9(2)$ |
| $\mathrm{N}(4)$ | $0.4044(7)$ | $0.2246(3)$ | $-0.0050(3)$ | $4.0(1)$ |
| $\mathrm{C}(1)$ | $0.529697)$ | $0.1746(4)$ | $0.2358(3)$ | $3.0(1)$ |
| $\mathrm{C}(2)$ | $0.5265(7)$ | $0.1961(4)$ | $0.1604(3)$ | $3.0(1)$ |
| $\mathrm{C}(3)$ | $0.3333(7)$ | $0.1728(4)$ | $0.3466(3)$ | $2.7(1)$ |
| $\mathrm{C}(4)$ | $0.3338(8)$ | $0.211(4)$ | $0.4081(3)$ | $3.8(2)$ |
| $\mathrm{C}(5)$ | $0.2955(10)$ | $0.1659(5)$ | $0.4620(3)$ | $5.1(2)$ |
| $\mathrm{C}(6)$ | $0.2956(10)$ | $0.0865(5)$ | $0.4538(4)$ | $5.2(2)$ |
| $\mathrm{C}(7)$ | $0.2632(9)$ | $0.0524(4)$ | $0.3918(4)$ | $4.7(2)$ |
| $\mathrm{C}(8)$ | $0.4231(7)$ | $0.3269(4)$ | $0.2887(3)$ | $2.9(1)$ |
| $\mathrm{C}(9)$ | $0.3310(9)$ | $0.3936(4)$ | $0.2692(3)$ | $4.0(2)$ |
| $\mathrm{C}(10)$ | $0.391(1)$ | $0.469(5)$ | $0.2859(4)$ | $5.6(2)$ |
| $\mathrm{C}(11)$ | $0.538(1)$ | $0.4766(5)$ | $0.3217(4)$ | $5.4(2)$ |
| $\mathrm{C}(12)$ | $0.6217(10)$ | $0.4076(5)$ | $0.3401(4)$ | $5.8(2)$ |
| $\mathrm{C}(13)$ | $0.3171(7)$ | $0.0807(4)$ | $0.0832(3)$ | $2.8(1)$ |
| $\mathrm{C}(14)$ | $0.2148(9)$ | $0.0576(4)$ | $0.0276(3)$ | $4.1(2)$ |
| $\mathrm{C}(15)$ | $0.218(1)$ | $-0.0218(5)$ | $0.0049(4)$ | $5.2(2)$ |
| $\mathrm{C}(16)$ | $0.320(1)$ | $-0.0758(4)$ | $0.0389(4)$ | $5.2(2)$ |
| $\mathrm{C}(17)$ | $0.415(1)$ | $-0.0486(5)$ | $0.0973(5)$ | $6.2(2)$ |
| $\mathrm{C}(18)$ | $0.3127(7)$ | $0.2493(4)$ | $0.0410(3)$ | $2.9(1)$ |
| $\mathrm{C}(19)$ | $0.2189(9)$ | $0.3180(4)$ | $0.0331(4)$ | $4.0(2)$ |
| $\mathrm{C}(20)$ | $0.2205(9)$ | $0.3646(4)$ | $-0.0246(4)$ | $4.8(2)$ |
| $\mathrm{C}(21)$ | $0.3108(10)$ | $0.3399(5)$ | $-0.0723(3)$ | $4.8(2)$ |
| $\mathrm{C}(22)$ | $0.4005(10)$ | $0.2701(4)$ | $-0.0602(4)$ | $4.8(2)$ |
| $\mathrm{C}(23)$ | $-0.228(1)$ | $0.3920(5)$ | $0.1686(4)$ | $6.8(3)$ |
|  |  |  |  |  |

$\mathrm{B}_{e q}=8 / 3 \pi^{2}\left(U_{11}\left(a a^{*}\right)^{2}+U_{22}\left(b b^{*}\right)^{2}+U_{33}\left(c c^{*}\right)^{2}+2 U_{12} a a^{*} b b^{*} \cos \gamma+2 U_{13} a a^{*} c c^{*} \cos \beta+\right.$ $\left.2 U_{23} b b^{*} c c^{*} \cos \alpha\right)$

Table A9.3 Bond Lengths ( $\AA$ )

| atom | atom | distance | atom | atom | distance |
| :--- | :--- | :--- | :--- | :--- | :--- |
| $\mathrm{P}(1)$ | $\mathrm{C}(1)$ | $2.359(2)$ | $\mathrm{P}(1)$ | $\mathrm{Cl}(2)$ | $2.348(2)$ |
| $\mathrm{Pt}(1)$ | $\mathrm{P}(1)$ | $2.209(2)$ | $\mathrm{Pt}(1)$ | $\mathrm{P}(2)$ | $2.211(2)$ |
| $\mathrm{Cl}(3)$ | $\mathrm{C}(23)$ | $1.712(9)$ | $\mathrm{Cl}(4)$ | $\mathrm{C}(24)$ | $1.730(9)$ |
| $\mathrm{P}(1)$ | $\mathrm{C}(1)$ | $1.817(6)$ | $\mathrm{P}(1)$ | $\mathrm{C}(3)$ | $1.816(6)$ |
| $\mathrm{P}(1)$ | $\mathrm{C}(8)$ | $1.819(7)$ | $\mathrm{P}(2)$ | $\mathrm{C}(2)$ | $1.824(6)$ |
| $\mathrm{P}(2)$ | $\mathrm{C}(13)$ | $1.810(6)$ | $\mathrm{P}(2)$ | $\mathrm{C}(18)$ | $1.832(6)$ |
| $\mathrm{N}(1)$ | $\mathrm{C}(3)$ | $1.329(8)$ | $\mathrm{N}(1)$ | $\mathrm{C}(7)$ | $1.327(8)$ |
| $\mathrm{N}(2)$ | $\mathrm{C}(8)$ | $1.333(8)$ | $\mathrm{N}(2)$ | $\mathrm{C}(12)$ | $1.338(9)$ |
| $\mathrm{N}(30$ | $\mathrm{C}(13)$ | $1.327(8)$ | $\mathrm{N}(3)$ | $\mathrm{C}(17)$ | $1.338(9)$ |
| $\mathrm{N}(4)$ | $\mathrm{C}(18)$ | $1.334(7)$ | $\mathrm{N}(4)$ | $\mathrm{C}(22)$ | $1.319(8)$ |
| $\mathrm{C}(1)$ | $\mathrm{C}(2)$ | $1.531(8)$ | $\mathrm{C}(3)$ | $\mathrm{C}(4)$ | $1.370(8)$ |
| $\mathrm{C}(4)$ | $\mathrm{C}(5)$ | $1.370(9)$ | $\mathrm{C}(5)$ | $\mathrm{C}(6)$ | $1.34(1)$ |
| $\mathrm{C}(6)$ | $\mathrm{C}(7)$ | $1.354(10)$ | $\mathrm{C}(8)$ | $\mathrm{C}(9)$ | $1.365(8)$ |
| $\mathrm{C}(9)$ | $\mathrm{C}(10)$ | $1.371(9)$ | $\mathrm{C}(10)$ | $\mathrm{C}(11)$ | $1.35(1)$ |
| $\mathrm{C}(11)$ | $\mathrm{C}(12)$ | $1.36(1)$ | $\mathrm{C}(13)$ | $\mathrm{C}(14)$ | $1.362(8)$ |
| $\mathrm{C}(14)$ | $\mathrm{C}(15)$ | $1.375(9)$ | $\mathrm{C}(15)$ | $\mathrm{C}(16)$ | $1.35(1)$ |
| $\mathrm{C}(15)$ | $\mathrm{C}(16)$ | $1.39(1)$ | $\mathrm{C}(18)$ | $\mathrm{C}(19)$ | $1.371(9)$ |
| $\mathrm{C}(19)$ | $\mathrm{C}(20)$ | $1.375(9)$ | $\mathrm{C}(20)$ | $\mathrm{C}(21)$ | $1.350(10)$ |
| $\mathrm{C}(21)$ | $\mathrm{C}(22)$ | $1.374(10)$ |  |  |  |

Table A9.4 Bond Angles $\left({ }^{\circ}\right)$

| atom | atom | atom | angle | atom | atom | atom | angle |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $\mathrm{Cl}(1)$ | $\mathrm{Pt}(1)$ | $\mathrm{Cl}(2)$ | $90.80(6)$ | $\mathrm{Cl}(1)$ | $\mathrm{Pt}(1)$ | $\mathrm{P}(1)$ | $177.19(6)$ |
| $\mathrm{Cl}(1)$ | $\mathrm{Pt}(1)$ | $\mathrm{P}(2)$ | $91.87(6)$ | $\mathrm{Cl}(2)$ | $\mathrm{Pt}(1)$ | $\mathrm{P}(1)$ | $91.18(6)$ |
| $\mathrm{Cl}(2)$ | $\mathrm{Pt}(1)$ | $\mathrm{P}(2)$ | $177.25(6)$ | $\mathrm{P}(1)$ | $\mathrm{Pt}(1)$ | $\mathrm{P}(2)$ | $86.176)$ |
| $\mathrm{Pt}(1)$ | $\mathrm{P}(1)$ | $\mathrm{C}(1)$ | $108.6(2)$ | $\mathrm{Pt}(1)$ | $\mathrm{P}(1)$ | $\mathrm{C}(3)$ | $113.7(2)$ |
| $\mathrm{Pt}(1)$ | $\mathrm{P}(1)$ | $\mathrm{C}(8)$ | $115.4(2)$ | $\mathrm{C}(1)$ | $\mathrm{P}(1)$ | $\mathrm{C}(3)$ | $106.9(3)$ |
| $\mathrm{C}(1)$ | $\mathrm{P}(1)$ | $\mathrm{C}(8)$ | $105.3(3)$ | $\mathrm{C}(3)$ | $\mathrm{P}(1)$ | $\mathrm{C}(8)$ | $106.4(3)$ |
| $\mathrm{Pt}(1)$ | $\mathrm{P}(2)$ | $\mathrm{C}(2)$ | $109.5(2)$ | $\mathrm{Pt}(1)$ | $\mathrm{P}(2)$ | $\mathrm{C}(13)$ | $115.5(2)$ |
| $\mathrm{Pt}(1)$ | $\mathrm{P}(2)$ | $\mathrm{C}(18)$ | $115.6(2)$ | $\mathrm{C}(2)$ | $\mathrm{P}(2)$ | $\mathrm{C}(13)$ | $105.1(3)$ |
| $\mathrm{C}(2)$ | $\mathrm{P}(2)$ | $\mathrm{C}(13)$ | $105.7(3)$ | $\mathrm{C}(13)$ | $\mathrm{P}(2)$ | $\mathrm{C}(18)$ | $104.5(3)$ |
| $\mathrm{C}(3)$ | $\mathrm{N}(1)$ | $\mathrm{C}(7)$ | $117.6(6)$ | $\mathrm{C}(8)$ | $\mathrm{N}(2)$ | $\mathrm{C}(12)$ | $116.4(2)$ |
| $\mathrm{C}(13)$ | $\mathrm{N}(3)$ | $\mathrm{C}(17)$ | $117.0(6)$ | $\mathrm{C}(18)$ | $\mathrm{N}(4)$ | $\mathrm{C}(22)$ | $116.2(6)$ |
| $\mathrm{P}(1)$ | $\mathrm{C}(1)$ | $\mathrm{C}(2)$ | $108.5(4)$ | $\mathrm{P}(2)$ | $\mathrm{C}(2)$ | $\mathrm{C}(1)$ | $109.5(4)$ |
| $\mathrm{P}(1)$ | $\mathrm{C}(3)$ | $\mathrm{N}(1)$ | $112.3(5)$ | $\mathrm{P}(1)$ | $\mathrm{C}(3)$ | $\mathrm{C}(4)$ | $125.4(4)$ |
| $\mathrm{N}(1)$ | $\mathrm{C}(3)$ | $\mathrm{C}(4)$ | $122.1(6)$ | $\mathrm{C}(3)$ | $\mathrm{C}(4)$ | $\mathrm{C}(5)$ | $118.2(7)$ |
| $\mathrm{C}(4)$ | $\mathrm{C}(5)$ | $\mathrm{C}(6)$ | $120.1(7)$ | $\mathrm{C}(5)$ | $\mathrm{C}(6)$ | $\mathrm{C}(7)$ | $118.6(7)$ |
| $\mathrm{N}(1)$ | $\mathrm{C}(7)$ | $\mathrm{C}(6)$ | $123.3(7)$ | $\mathrm{P}(1)$ | $\mathrm{C}(8)$ | $\mathrm{N}(2)$ | $114.1(5)$ |
| $\mathrm{P}(1)$ | $\mathrm{C}(8)$ | $\mathrm{C}(9)$ | $122.7(5)$ | $\mathrm{N}(2)$ | $\mathrm{C}(8)$ | $\mathrm{C}(9)$ | $123.2(6)$ |
| $\mathrm{C}(8)$ | $\mathrm{C}(9)$ | $\mathrm{C}(10)$ | $118.7(7)$ | $\mathrm{C}(9)$ | $\mathrm{C}(10)$ | $\mathrm{C}(11)$ | $119.0(7)$ |
| $\mathrm{C}(10)$ | $\mathrm{C}(11)$ | $\mathrm{C}(12)$ | $119.2(7)$ | $\mathrm{N}(2)$ | $\mathrm{C}(12)$ | $\mathrm{C}(11)$ | $123.5(7)$ |


| atom | atom | atom | angle | atom | atom | atom | angle |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $\mathrm{P}(2)$ | $\mathrm{C}(13)$ | $\mathrm{N}(3)$ | $114.3(5)$ | $\mathrm{P}(2)$ | $\mathrm{C}(13)$ | $\mathrm{C}(14)$ | $122.8(5)$ |
| $\mathrm{N}(3)$ | $\mathrm{C}(13)$ | $\mathrm{C}(14)$ | $122.9(6)$ | $\mathrm{C}(13)$ | $\mathrm{C}(14)$ | $\mathrm{C}(15)$ | $119.3(7)$ |
| $\mathrm{C}(14)$ | $\mathrm{C}(15)$ | $\mathrm{C}(16)$ | $119.4)$ | $\mathrm{C}(15)$ | $\mathrm{C}(16)$ | $\mathrm{C}(17)$ | $117.8(7)$ |
| $\mathrm{N}(3)$ | $\mathrm{C}(17)$ | $\mathrm{C}(16)$ | $123.4(8)$ | $\mathrm{P}(2)$ | $\mathrm{C}(18)$ | $\mathrm{N}(4)$ | $114.0(5)$ |
| $\mathrm{P}(2)$ | $\mathrm{C}(18)$ | $\mathrm{C}(19)$ | $122.7(5)$ | $\mathrm{N}(4)$ | $\mathrm{C}(18)$ | $\mathrm{C}(19)$ | $123.3(6)$ |
| $\mathrm{C}(18)$ | $\mathrm{C}(19)$ | $\mathrm{C}(20)$ | $118.76)$ | $\mathrm{C}(19)$ | $\mathrm{C}(20)$ | $\mathrm{C}(21)$ | $118.9(7)$ |
| $\mathrm{C}(20)$ | $\mathrm{C}(21)$ | $\mathrm{C}(22)$ | $118.5(7)$ | $\mathrm{N}(4)$ | $\mathrm{C}(22)$ | $\mathrm{C}(21)$ | $124.4(7)$ |
| $\mathrm{Cl}(3)$ | $\mathrm{C}(23)$ | $\mathrm{Cl}(4)$ | $111.9(5)$ |  |  |  |  |

## A10 Crystal Structure Data for $\left[\mathrm{Pt}_{\mathbf{2}}(\mathrm{dpype})_{2} \mathbf{A g}_{4}\left(\mathbf{N O}_{3}\right)_{\mathbf{8}}\left(\mathbf{H}_{\mathbf{2}} \mathbf{O}\right)_{\mathbf{2}}\right]_{n}$



Figure A10.1 ORTEP representation of the repeating unit of $\left.\left[\mathrm{Pt}_{2} \text { (dpype) }\right)_{2} \mathrm{Ag}_{4}\left(\mathrm{NO}_{3}\right)_{8}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]_{n}(33 \%$ ellipsoids).

Appendix 10: Crystal Structure Data for $\left[\mathrm{Pt}_{2}(\text { dpype })_{2} \mathrm{Ag}_{4}\left(\mathrm{NO}_{3}\right)_{8}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]_{n}$

$$
\begin{aligned}
& w \text { oscillation Range ( } \chi=-90.0 \text { ) } \\
& \text { Detcctor Position } \\
& \text { Detector Swing Angle } \\
& 2 \theta_{\text {nus }} \\
& \text { No. of Reflections Measured } \\
& \text { Corrections }
\end{aligned}
$$

$$
\begin{aligned}
& \text { Table A10.1 } \\
& \text { Empirical Formula } \\
& \text { Formula Weight } \\
& \text { Crystal Color, Habit } \\
& \text { Crystal Dimensions } \\
& \text { Crystal System } \\
& \text { Lattice Type } \\
& \text { Lattice Parameters } \\
& \\
& \text { Space Group } \\
& \text { Z vaiue } \\
& D_{\text {calc }} \\
& \text { Fooo } \\
& \mu(\text { MoK } \alpha) \\
& \hline \text { Radiation } \\
& \text { Detector Aperture } \\
& \text { Data Images } \\
& \phi \text { soscillation Range }(\chi=-90)
\end{aligned}
$$

| 涊 | $\underset{i}{\underset{i}{5}}$ | $\underset{\sim}{\underset{\sim}{x}}$ | $\underset{\underset{\sim}{c}}{\underset{\sim}{\widetilde{c}}}$ | $\underset{\sim}{\underset{\sim}{\leftrightarrows}}$ | $\stackrel{\overparen{c}}{\underset{\sim}{\mathrm{O}}}$ | $\stackrel{\widehat{G}}{\stackrel{\rightharpoonup}{0}}$ | $\stackrel{\stackrel{\rightharpoonup}{\circ}}{\stackrel{\rightharpoonup}{\circ}}$ |  | $\underset{\underset{i}{C}}{\stackrel{\rightharpoonup}{4}}$ | $\underset{\substack{\mathrm{N}}}{\stackrel{\rightharpoonup}{\mathrm{~N}}}$ | $\stackrel{\stackrel{\ominus}{6}}{\stackrel{\rightharpoonup}{\circ}}$ | $\begin{gathered} \widehat{\infty} \\ \underset{\sim}{\infty} \end{gathered}$ | $\underset{\sim}{\underset{\sim}{x}}$ | $\underset{\sim}{\underset{\sim}{\omega}}$ | $\stackrel{\widehat{G}}{\underset{\sim}{6}}$ | $\underset{\sim}{\mathrm{N}}$ | $\underset{\sim}{\stackrel{Y}{\mathrm{~N}}}$ | $\stackrel{\stackrel{\rightharpoonup}{\odot}}{\stackrel{\rightharpoonup}{\circ}}$ | $\underset{\sim}{\stackrel{\rightharpoonup}{\mathrm{N}}}$ | $\underset{\substack{\mathrm{O}}}{\substack{0}}$ | $\underset{\underset{\sim}{\infty}}{\stackrel{\rightharpoonup}{\infty}}$ | $\stackrel{\text { en }}{\stackrel{6}{6}}$ | $\underset{\substack{\underset{\sim}{c}}}{\substack{\text { re}}}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $N$ |  | $\widehat{10}$ 0 0 0 0 |  |  |  |  | $\begin{aligned} & 0 \\ & \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \end{array} \end{aligned}$ | © ⿹ㅡㄴ 0 | 5 <br> 0 <br> 8 <br> 0 <br> 0 <br> 0 | $\begin{aligned} & \overparen{65} \\ & \stackrel{0}{0} \\ & \stackrel{0}{0} \\ & \stackrel{1}{0} \end{aligned}$ | © $\stackrel{7}{7}$ $\underset{6}{5}$ | 6 <br>  <br>  | $\begin{gathered} \underset{1}{E} \\ \substack{\text { O} \\ \hline 8} \end{gathered}$ |  | 10 0 0 0 0 0 | 粊 |  |  | $\begin{aligned} & \text { B } \\ & \text { Co } \\ & \text { C } \\ & \hline 0 \end{aligned}$ |  |  |  | © <br> 0 <br> $\infty$ <br> $\infty$ <br> $\underset{0}{\infty}$ |  |
| － |  |  |  | E O． B O | $\begin{aligned} & \text { E} \\ & \stackrel{0}{\circ} \\ & \text { H } \\ & 0 . \end{aligned}$ |  |  |  |  | $\stackrel{\underset{\sim}{\infty}}{\stackrel{\infty}{\leftrightarrows}}$ | 6 <br> $\substack{6 \\ \multirow{1}{N}{0 \\ 0}\\ 0 \\ 0}$ |  | $\begin{aligned} & \stackrel{6}{8} \\ & \stackrel{0}{0} \\ & \substack{\infty \\ 0} \end{aligned}$ | $\begin{aligned} & \underset{-}{\underset{\sim}{E}} \\ & \stackrel{\infty}{\infty} \end{aligned}$ |  | $\stackrel{\infty}{\underset{N}{*}}$ | $\stackrel{\infty}{\stackrel{\infty}{0}}$ | $\stackrel{\overparen{\infty}}{\underset{\sim}{7}}$ | $\stackrel{\substack{\infty \\ \underset{\sim}{c}}}{\substack{2}}$ |  | $\widehat{5}$ N 10 10 0 | $\begin{aligned} & \stackrel{3}{3} \\ & \stackrel{3}{3} \\ & 03 \\ & 0 \end{aligned}$ |  |  |
| $\times$ |  |  |  | $\frac{\stackrel{\infty}{\mathbb{O}}}{\underset{\sim}{\underset{~}{4}}}$ | $\infty$ <br> $\stackrel{\infty}{\infty}$ <br>  | $\stackrel{i}{\infty}$ | 읖 $\stackrel{0}{0}$ $\stackrel{-}{0}$ |  |  | $\begin{aligned} & \underset{O}{O} \\ & \stackrel{0}{7} \\ & \underset{\sim}{0} \end{aligned}$ | $\begin{aligned} & \stackrel{\rightharpoonup}{\Xi} \\ & \stackrel{\rightharpoonup}{9} \\ & \stackrel{y}{0} \\ & \hline \end{aligned}$ | $\begin{aligned} & \underset{\sim}{C} \\ & \stackrel{N}{5} \\ & \stackrel{0}{6} \end{aligned}$ | $\begin{aligned} & \text { 会 } \\ & \underset{0}{2} \end{aligned}$ | ت － － － |  |  |  | $\Xi$ <br>  <br>  | $\begin{aligned} & \frac{0}{7} \\ & \frac{6}{6} \\ & \underset{0}{6} \end{aligned}$ | O． 0 0 0 0 0 | E $\stackrel{0}{6}$ $\underset{0}{1}$ |  | $\begin{aligned} & \stackrel{0}{0} \\ & \stackrel{0}{0} \\ & \text { 0} \\ & 0 \\ & 0 \end{aligned}$ |  |
| $\underset{\substack{5 \\ \hline}}{\square}$ | $\stackrel{E}{B}$ | $\frac{\infty}{z}$ | $3$ | © | $\widehat{0}$ | $\underset{U}{\mathbb{U}}$ | $\stackrel{S}{6}$ | $\stackrel{\omega}{6}$ | $\stackrel{E}{\Xi}$ | $\stackrel{\infty}{\infty}$ | $\stackrel{\ominus}{\circlearrowleft}$ | $\stackrel{\ddot{0}}{\ddot{0}}$ | $\underset{U}{3}$ | $\underset{U}{\mathrm{E}}$ | $\stackrel{\overparen{O}}{0}$ | $\underset{\Xi}{\Xi}$ | $\stackrel{29}{3}$ | $\stackrel{9}{0}$ | $E$ | $\stackrel{\infty}{\circlearrowright}$ | $\underset{O}{\ddot{O}}$ | - | $\frac{-}{6}$ | S B E |


five
 13
00
0
0
$\vdots$
0

| Table A10．2 atom | Atomic coordinates and $\mathrm{Beq}_{\text {eq }}$ |  |
| :---: | :---: | :---: |
|  | x | $y$ |
| Pt．（1） | 0.47345 （3） | 0．58466（3） |
| $\mathrm{Ag}(1)$ | $0.33193(8)$ | 0．67590（7） |
| $\mathrm{Ag}(2)$ | $0.06506(11)$ | 0．55562（9） |
| $\mathrm{P}(1)$ | 0．2881（2） | 0．5679（2） |
| P （2） | 0．4073（2） | 0．4828（2） |
| O（1） | $0.1098(11)$ | $0.6941(9)$ |
| O（2） | $0.1505(10)$ | 0．6652（8） |
| O（3） | －0．0287（9） | 0.6667 （8） |
| $\mathrm{O}(4)$ | 0．3745（9） | 0．8614（8） |
| O（5） | 0．4374（9） | $0.7718(7)$ |
| O（6） | 0．4911（8） | $0.9300(6)$ |
| O（7） | 0.1487 （12） | $0.5598(12)$ |
| $\bigcirc(8)$ | 0．2939（14） | $0.5882(11)$ |
| $\bigcirc(9)$ | $0.3114(15)$ | 0．6134（13） |
| O（10） | －0．1819（15） | 0．5881（9） |
| O（11） | －0．0672（11） | $0.7005(12)$ |
| O（12） | －0．2375（13） | 0.7445 （11） |
| O（13） | －0．077（2） | 0．6849（12） |
| $\mathrm{N}(1)$ | 0．3546（7） | 0．4146（6） |
| N（2） | 0．2444（8） | 0．7390（6） |
| N（3） | 0．4670（7） | 0．3153（6） |
| $\mathrm{N}(4)$ | $0.5631(8)$ | 0．4472（7） |
| N （5） | $0.0775(10)$ | 0．6747（8） |
| N（6） | 0．4338（8） | 0．8541（8） |

Table A10.3

$$
\begin{aligned}
& \text { gths }(\bar{A})^{*} \\
& \text { distance } \\
& 2.7690(7) \\
& 2.234(2) \\
& 2.131(7) \\
& 2.552(10) \\
& 2.282(8) \\
& 2.436(12) \\
& 2.642(11) \\
& 2.378(13) \\
& 2.83(2) \\
& 1.848(10) \\
& 1.805(11) \\
& \hline 1.840(10) \\
& 1.237(13) \\
& \hline 1.227(14) \\
& \hline 1.215(12) \\
& 1.24(2) \\
& 1.22(2) \\
& 1.204(14) \\
& 1.308(11) \\
& 1.335(13) \\
& 1.403(11) \\
& 1.318(12) \\
& \hline 1.539(13) \\
& 1.380(14)
\end{aligned}
$$

$$
\text { Bond Lengths }(A)^{*} \text { (continued) }
$$

* Here and elsewhere, superscripts refer to symmetry operations:

$$
\begin{aligned}
& \text { distance } \\
& 1.398(14) \\
& 1.32(2) \\
& 1.365(14) \\
& 1.352(15) \\
& 1.376(15) \\
& 1.33(2)
\end{aligned}
$$

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\stackrel{\widehat{E}}{\bar{Z}}
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    anglc
    $115.3(3)$
$99.9(4)$
$116.9(4)$
$112.2(3)$
$104.0(4)$
$107.0(4)$
$109.2(8)$
$105.0(8)$
$88.9(7)$
$105.1(11)$
$89.8(10)$
$123.4(6)$
$121.5(8)$
$111.8(7)$
$126.3(6)$
$116.4(8)$
$111.2(7)$
$121.7(12)$
$118.1(12)$
$118.9(11)$
$118.9(16)$
$121.2(19)$
$120.4(14)$
$110.4(7)$


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Bond Angles( $0^{\circ}$ )


Table A10.4
Table A10.4 Bond Angles $\left(^{\circ}\right.$ ) (continucd)

| atom | atom | atom | angle | atom | atom | atom | angle | atorn | atora | atom | angle | atom | atom | atom | angle |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Pt}(1)^{\text {a }}$ | $\mathrm{Pt}(1)$ | $\mathrm{P}(1)$ | 85.09(6) | $\mathrm{Pt}(1)^{\text {a }}$ | Pt (1) | P (2) | 91.18(7) | $\mathrm{Pt}_{(1)}$ | $\mathrm{P}(1)$ | C(1) | 109.2(3) | $\mathrm{Pt}(1)$ | $\mathrm{P}(1)$ | C (3) | 115.3(3) |
| $\mathrm{Pt}(\mathrm{I})^{\text {a }}$ | $\mathrm{Pt}(1)$ | $\mathrm{N}(1)$ | 93.3 (2) | $\mathrm{Pt}(1)^{\text {a }}$ | $\mathrm{Pt}(1)$ | N(3) | 90.1(2) | $\mathrm{Pt}(1)$ | $\mathrm{P}(1)$ | C(8) | 115.5(4) | $\mathrm{C}(1)$ | $\mathrm{P}(1)$ | C(3) | 99.9(4) |
| $\mathrm{P}(1)$ | $\mathrm{Pt}(1)$ | P (2) | 84.47(9) | $\mathrm{P}(1)$ | Pt(1) | $N(1)^{\text {a }}$ | 173.3(2) | C (1) | $\mathrm{P}(1)$ | $\mathrm{C}(8)$ | 108.9(5) | C(3) | $\mathrm{P}(1)$ | $\mathrm{C}(8)$ | 106.9(4) |
| P(1) | $\mathrm{Pt}(1)$ | $\mathrm{N}(3)^{\text {a }}$ | 94.8(2) | P (2) | $\mathrm{Pt}(1)$ | $\mathrm{N}(1)^{\mathrm{a}}$ | $89.0(2)$ | $\mathrm{Pt}_{(1)}$ | $\mathrm{P}(2)$ | C(2) | 108.1(3) | $\mathrm{Pt}(1)$ | P (2) | C (13) | 112.2(3) |
| $\mathrm{P}(2)$ | $\mathrm{Pt}(1)$ | $N(3)^{4}$ | 178.5(2) | $\mathrm{N}(1)$ | Pt (1) | $N(3)^{\circ}$ | $91.8(3)$ | $\mathrm{Pt}_{(1)}$ | $\mathrm{P}(2)$ | C(18) | 118.1(3) | $\mathrm{C}(2)$ | $\mathrm{P}(2)$ | C(13) | 104.0(4) |
| O(1) | $\mathrm{Ag}(1)$ | $\mathrm{O}(4)$ | 90.5(4) | 0 (1) | Ag(1) | O(5) | 95.8(3) | C(2) | $\mathrm{P}(2)$ | C(18) | 106.5 (4) | C(13) | $\mathrm{P}(2)$ | C(18) | 107.0(4) |
| O(1) | $\mathrm{Ag}(1)$ | $\mathrm{N}(2)$ | 79.3(3) | O(1) | $\mathrm{Ag}^{\text {(1) }}$ | $N(4)^{n}$ | 114.3(3) | $\mathrm{Ag}_{(1)}$ | O(1) | $N(5)$ | 123.3(9) | $\mathrm{Ag}^{(2)}$ | $\bigcirc(2)$ | N(5) | 109.2(8) |
| $\bigcirc(4)$ | $\mathrm{Ag}(1)$ | O(5) | 45.3(3) | O(4) | Ag(i) | $\mathrm{N}(2)$ | $88.2(3)$ | $\mathrm{Ag}(1)$ | $\bigcirc(4)$ | $\mathrm{Ag}_{(2)}{ }^{\text {c }}$ | $154.8(4)$ | $\mathrm{Ag}(1)$ | O(4) | N(6) | 105.0(8) |
| $O(4)$ | $\mathrm{Ag}(1)$ | $N(4)^{a}$ | 116.1(3) | $O$ (5) | Ag(1) | N(2) | 133.5(3) | $\mathrm{Ag}(2)^{\text {c }}$ | O(4) | $\mathrm{N}(6)$ | 93.8(7) | Ag(1) | $\mathrm{O}(5)$ | $\stackrel{N}{(6)}$ | 88.9(7) |
| 0 (5) | Ag(1) | $N(4){ }^{\text {a }}$ | 73.0(3) | $N(2)$ | $\mathrm{Ag}_{\mathrm{g}}(1)$ | $\mathrm{N}(4)^{\text {a }}$ | $150.8(3)$ | $\mathrm{Ag}(2)^{\text {c }}$ | 0 (6) | $N(6)$ | 98.6(6) | $\mathrm{Ag}(2)$ | O(7) | $N(7)$ | 105.1(11) |
| 0 (2) | $\mathrm{Ag}(2)$ | $\bigcirc$ O(3) | 44.7(3) | $\mathrm{O}(2)$ | $\mathrm{AgF}_{\mathrm{g}} \mathbf{( 2 )}$ | 0 (4) ${ }^{\text {b }}$ | $110.2(4)$ | $\mathrm{Ag}(2)$ | $0(8)$ | $N(7)$ | $86.9(11)$ | $\mathrm{Ag}^{(2)}$ | O(10) | $N(8)$ | 89.8(10) |
| $O(2)$ | Ag(2) | $\mathrm{O}(6)^{\text {b }}$ | 87.5(3) | $\mathrm{O}(2)$ | $\mathrm{Ag}(2)$ | O(7) | 118.8(4) | $\mathrm{Ag}(2)$ | O(11) | N(8) | 99.6(9) | $\mathrm{Pt}(1)^{\text {e }}$ | $\mathrm{N}(1)$ | $C_{(3)}$ | 123.4(6) |
| $O(2)$ | $\mathrm{Ag}(2)$ | O(8) | 77.9(4) | O(2) | $\mathrm{Ag}_{5}(2)$ | $0(10)$ | 112.2(4) | $\mathrm{Pt}(1)^{\text {a }}$ | $N(1)$ | C (7) | 114.3(6) | $\mathrm{C}(3)$ | $\mathrm{N}(1)$ | C(7) | $121.5(8)$ |
| O (2) | $\mathrm{Ag}(2)$ | O(11) | 95.9(4) | O(3) | $\mathrm{Ag}(2)$ | $\mathrm{O}(4)^{\text {b }}$ | 115.1(3) | $\mathrm{Ag}_{\mathrm{g}}(1)$ | N(2) | C(8) | 128.0(7) | Ag(1) | $\mathrm{N}(2)$ | C(12) | 111.8(7) |
| $O(3)$ | $\mathrm{Ag}(2)$ | $\mathrm{O}(6)^{\text {b }}$ | 68.7(3) | $\bigcirc$ (3) | $\mathrm{Ag}(2)$ | $\bigcirc(7)$ | 149.9(4) | $\mathrm{C}(8)$ | $N(2)$ | C(12) | 117.1(9) | $\mathrm{Pt}_{\mathrm{t}}(1)^{\text {a }}$ | $\mathrm{N}(3)$ | C(13) | 126.3(6) |
| $O(3)$ | Ag(2) | $\mathrm{O}(8)$ | 122.0(3) | $\mathrm{O}(3)$ | Ag(2) | O(10) | 70.6(3) | $\mathrm{Pt}(1)^{\text {a }}$ | $N(3)$ | $\mathrm{C}(17)$ | 117.2(6) | $\mathrm{C}(13)$ | $\mathrm{N}(3)$ | C(17) | 116.4(8) |
| $\mathrm{O}(3)$ | $\mathrm{Ag}(2)$ | O(11) | 78.1(3) | $\mathrm{O}(4)^{\text {b }}$ | $\mathrm{Ag}(2)$ | $\mathrm{O}(6)^{\text {b }}$ | 48.7(3) | ${\operatorname{Ag}(1)^{\text {a }}}^{\text {a }}$ | $\mathrm{N}(4)$ | C(18) | 132.667 | $\mathrm{Ag}(1)^{9}$ | $\mathrm{N}(4)$ | $\mathrm{C}(22)$ | 111.2(7) |
| $O(4)^{\text {b }}$ | $\mathrm{Ag}(2)$ | O(7) | 93.6(4) | $\mathrm{O}(4)^{\text {b }}$ | $\mathrm{Ag}(2)$ | $\mathrm{O}(8)$ | 87.7(4) | C(18) | N(4) | C(22) | 116.3(9) | O(1) | $\mathrm{N}(\mathrm{5})$ | O(2) | 121.7(12) |
| $\mathrm{O}(4)^{\text {b }}$ | $\mathrm{Ag}(2)$ | O(10) | 114.3(3) | $\mathrm{O}(4)^{6}$ | $\mathrm{Ag}(2)$ | O(11) | 152.8(3) | O(1) | $\mathrm{N}(5)$ | O (3) | 120.2(12) | $\mathrm{O}(2)$ | $\mathrm{N}(5)$ | $\mathrm{O}(3)$ | 118.1(12) |
| $0(6)^{\text {b }}$ | $\mathrm{Ag}(2)$ | 0 (7) | 141.3(4) | $0(6)^{\text {b }}$ | $\mathrm{Ag}(2)$ | $\mathrm{O}(8)$ | 125.3(4) | O(4) | N(6) | O (5) | 119.1(11) | O(4) | $\mathrm{N}(6)$ | O(6) | 118.9(11) |
| $0(6)^{\text {b }}$ | $\mathrm{Ag}^{(2)}$ | O(10) | 86.0(3) | $0(6)^{\text {b }}$ | $\mathrm{Ag}(2)$ | O(11) | 128.3(3) | O(5) | $\mathrm{N}(6)$ | O (6) | 122.0(10) | $\mathrm{O}(7)$ | ${ }^{\kappa}(7)$ | O(8) | 118.9(16) |
| $O(7)$ | $\mathrm{Ag}(2)$ | O (8) | 46.7(4) | $\mathrm{O}(7)$ | $\mathrm{Ag}(2)$ | $\bigcirc(10)$ | 106.74) | O(7) | $\mathrm{N}(7)$ | $\bigcirc$ O(9) | 119.4(19) | O(8) | $\mathrm{N}(7)$ | O(9) | 121.2(19) |
| $\mathrm{O}(7)$ | $\mathrm{Ag}(2)$ | O(11) | 79.8(4) | O (8) | $\mathrm{Ag}(2)$ | O(11) | 105.7(4) | O(10) | $\mathrm{N}(8)$ | $\mathrm{O}(11)$ | 120.0(15) | O(10) | $\mathrm{N}(8)$ | O(12) | 120.4(14) |
| O(8) | Ag(2) | $\mathrm{O}(10)$ | 148.3(4) | $\mathrm{O}(10)$ | $\operatorname{Ag}(2)$ | $0(11)$ | 45.1(3) | O(11) | $\mathrm{N}(8)$ | $\mathrm{O}(12)$ | 119.5(14) | P (1) | C(1) | C (2) | 110.4(7) |

## A11 Crystal structure data for $\mathbf{P t I}_{2}(\mathbf{d p y p c p}) \cdot \mathbf{0 . 1 8} \mathbf{C H}_{\mathbf{2}} \mathbf{C l}_{\mathbf{2}}$



Figure A11.1 ORTEP representation of $\mathrm{PtI}_{2}$ (dpypcp) ( $50 \%$ ellipsoids).


Table A11.1


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$\phi$ oscillation Range ( $x=-90$ )
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| Table A11.2 | Atomic coordin | and $\mathrm{B}_{\text {eq }}$ |  |  |
| :---: | :---: | :---: | :---: | :---: |
| atom | x | $y$ | $z$ | $\mathrm{B}_{\text {eq }}$ |
| $\mathrm{Pt}(1)$ | 0.42762(2) | 0.278203(14) | 0.26502(2) | 1.754(6) |
| $\mathrm{Pt}(2)$ | 0.08576(2) | 0.738399 (14) | 0.24230(2) | 1.849(6) |
| I(1) | 0.37277(3) | 0.15347(3) | 0.21376(4) | 3.440(14) |
| $\mathrm{I}(2)$ | 0.54719(3) | 0.22341 (3) | 0.37865(3) | $2.661(12)$ |
| I(3) | $0.13837(3)$ | 0.86071(3) | 0.30458(4) | 3.041(13) |
| 1(4) | -0.03263(3) | $0.79664(3)$ | 0.13023 (3) | $3.208(13)$ |
| $\mathrm{Cl}(1)$ | 0.5849(8) | 0.4676(5) | 0.0256(6) | 26.6(6) |
| $\mathrm{P}(1)$ | 0.46796(11) | 0.38443(9) | 0.31229(11) | 1.73(4) |
| $\mathrm{P}(2)$ | 0.33444 (11) | 0.33097(9) | 0.16764(11) | 1.86(4) |
| $\mathrm{P}(3)$ | 0.04569(11) | 0.63345(10) | 0.19145(11) | 2.10(4) |
| P(4) | 0.18559(11) | 0.68281(9) | 0.33235(11) | 1.88(4) |
| $\mathrm{N}(1)$ | 0.3955(4) | 0.4139(3) | 0.4093(4) | 2.46(15) |
| N(2) | 0.6075(4) | 0.4629(3) | 0.3552(4) | 2.41(15) |
| $N(3)$ | 0.1739(4) | 0.3552(4) | 0.1049(4) | 3.5(2) |
| N(4) | 0.3842(4) | 0.3388(4) | 0.0506(4) | 3.2(2) |
| N(5) | 0.0587(4) | 0.5601(4) | 0.0746(4) | 3.6(2) |
| $N(6)$ | -0.0858(4) | 0.6070(4) | 0.2236(5) | 4.3(2) |
| N(7) | 0.3195 (4) | 0.6827(3) | 0.2973(3) | $2.05(14)$ |
| N(8) | 0.2387(4) | 0.6682(3) | 0.4801(4) | 2.7(2) |
| C(1) | 0.3912(4) | 0.4443(4) | 0.2541(4) | 2.2(2) |
| C(2) | 0.3658(4) | 0.4225(4) | $0.1757(5)$ | 2.4(2) |
| C(3) | 0.3064(5) | 0.4826(4) | 0.1331 (5) | 2.9(2) |
| C(4) | 0.3469(5) | 0.5475(4) | 0.1787(5) | 3.4(2) |
| C(5) | $0.4069(5)$ | 0.5228(4) | 0.2532(5) | 2.9(2) |

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Atomic coordinates and $\mathrm{B}_{e q}$（continued）


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\times \quad
\end{array}
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\begin{aligned}
& \text { distance } \\
& 1.355(10) \\
& 1.365(14) \\
& 1.373(10) \\
& 1.320(14) \\
& 1.547(10) \\
& 1.564(10) \\
& 1.519(13) \\
& 1.386(11) \\
& 1.388(13) \\
& 1.426(12) \\
& 1.337(15) \\
& 1.390(10) \\
& 1.368(11) \\
& 1.374(11) \\
& 1.401(11)
\end{aligned}
$$

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| A11.4 Bond Angles( ${ }^{\circ}$ ) |  |  |  |  |  |  |  | Table A11.4 Bond Angles $\left({ }^{\circ}\right)$ (continued) |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| atom | atom | atom | angle | atom | atom | atom | angle | atom | atom | atom | angle | atom | atom | atom | angle |
| I(1) | $\mathrm{Pt}(1)$ | I(2) | 91.43(2) | I(1) | $\mathrm{Pt}(1)$ | $\mathrm{P}(1)$ | 176.18(5) | P (2) | C(2) | C(3) | 122.6(5) | C(1) | C(2) | C(3) | 103.5(0) |
| I(1) | $\mathrm{Pt}(1)$ | P (2) | 92.08(5) | I(2) | $\mathrm{Pt}(1)$ | $\mathrm{P}(1)$ | 88.98(5) | C(2) | C(3) | C(4) | 102.1(6) | C(3) | C(4) | C(5) | 108.1(6) |
| I(2) | $\mathrm{Pt}(1)$ | $\mathbf{P}(2)$ | 175.07(5) | $\mathrm{P}(1)$ | $\mathrm{Pt}(1)$ | P(2) | 87.75(7) | C(1) | C(5) | C(4) | 104.5(6) | $\mathrm{P}(1)$ | C(6) | $\mathrm{N}(1)$ | 113.4(6) |
| I(3) | $\mathrm{Pt}(2)$ | I(4) | $92.38(2)$ | I(3) | $\mathrm{Pt}(2)$ | $\mathrm{P}(3)$ | 178.01(5) | $\mathrm{P}(1)$ | C(6) | C(7) | 122.5(5) | N(1) | C(6) | C(7) | 124.0(7) |
| I(3) | $\mathrm{Pt}(2)$ | $\mathrm{P}(4)$ | 91.17(5) | 1(4) | $\mathrm{Pt}(2)$ | $P(3)$ | 89.38(5) | C(6) | C(7) | C(8) | 117.4(6) | C(7) | C(8) | C(9) | 119.2(8) |
| I(4) | $\mathrm{Pt}(2)$ | P(4) | 176.15(5) | $\mathrm{P}(3)$ | $\mathrm{Pt}(2)$ | P(4) | 87.05(7) | C(8) | C(9) | C(10) | 118.6(8) | N(1) | C(10) | C(9) | 125.1(7) |
| $\mathrm{Pt}(1)$ | $\mathrm{P}(1)$ | C(1) | 105.5(2) | $\mathrm{Pt}(1)$ | $\mathrm{P}(1)$ | C(6) | 116.1(2) | $\mathrm{P}(1)$ | C(11) | N(2) | 117.6(5) | $\mathrm{P}(1)$ | C(11) | C(12) | 118.0(6) |
| $\mathrm{Pt}(1)$ | $\mathrm{P}(1)$ | C(11) | 114.3(2) | C(1) | $\mathrm{P}(1)$ | C(6) | 105.5(3) | N(2) | C(11) | C(12) | 124.3(6) | C(11) | C(12) | C(13) | 116.8(8) |
| C(1) | $\mathrm{P}(1)$ | C(11) | 106.9(3) | C(6) | $\mathrm{P}(1)$ | C(11) | 107.8(3) | C(12) | C(13) | C(14) | 119.9(8) | C(13) | C(14) | C(15) | 118.8(7) |
| $\mathrm{P}_{\mathrm{t}}(1)$ | $P(2)$ | C(2) | 104.8(3) | Pt(1) | $\mathrm{P}(2)$ | C(16) | 115.7(3) | N(2) | C(15) | C(14) | 123.8(8) | $\mathrm{P}(2)$ | C(16) | N(3) | 115.0(6) |
| $\mathrm{Pt}(1)$ | P (2) | C(21) | 117.2(2) | C(2) | $\mathrm{P}(2)$ | C(16) | 109.3(3) | P(2) | C(16) | C(17) | 121.2(6) | N(3) | $\mathrm{C}(16)$ | C(17) | 123.8(7) |
| C(2) | $\mathrm{P}(2)$ | C(21) | 105.1(4) | C(16) | $\mathrm{P}(2)$ | C(21) | 104.1(3) | C(16) | C(17) | C(18) | 118.9(9) | C(17) | C(18) | C(19) | 118.2(8) |
| $\mathrm{Pt}(2)$ | $\mathrm{P}(3)$ | C(26) | 106.6(3) | $\mathrm{Pt}(2)$ | $\mathrm{P}(3)$ | C(31) | 110.2(3) | C(18) | C(19) | C(20) | 119.3(7) | N(3) | C(20) | C(19) | 122.8(9) |
| $\mathrm{Pt}(2)$ | $\mathrm{P}(3)$ | C(36) | 117.5(3) | C(26) | $\mathrm{P}(3)$ | C(31) | 107.1(4) | $\mathrm{P}(2)$ | C(21) | N(4) | 113.9(6) | $\mathrm{P}(2)$ | C(21) | C(22) | 122.6(6) |
| C(26) | P(3) | C(36) | 102.5(4) | C(31) | $\mathrm{P}(3)$ | C(36) | 112.1(4) | N(4) | C(21) | $\mathrm{C}(22)$ | 123.5(7) | C(21) | C(22) | C(23) | 118.2(8) |
| $\mathrm{Pt}(2)$ | $\mathrm{P}(4)$ | C(27) | 106.1(3) | $\mathrm{Pt}(2)$ | P (4) | C(41) | 116.6(3) | C(22) | C(23) | C(24) | 120.5(9) | C(23) | C(24) | C(25) | 117.8(9) |
| $\mathrm{Pt}(2)$ | P(4) | C(46) | 114.6(2) | C(27) | P (4) | C(41) | 103.1(3) | N(4) | C(25) | C(24) | 125.1(8) | $\mathrm{P}(3)$ | C(26) | C(27) | 107.0(5) |
| C(27) | P (4) | C(46) | 106.7(3) | C(41) | P (4) | C(46) | 108.6(3) | P (3) | C(26) | C(30) | 124.6(6) | C(27) | C(26) | C(30) | 101.6(6) |
| C(6) | $\mathrm{N}(1)$ | C(10) | 115.6(7) | C(11) | N(2) | C(15) | 116.4(7) | P(4) | C(27) | C(26) | 109.3(5) | P(4) | $\mathrm{C}(27)$ | C(28) | 122.1(6) |
| C(16) | $\mathrm{N}(3)$ | C(20) | 117.0(8) | C(21) | $\mathrm{N}(4)$ | C(25) | 114.7(7) | C(26) | C(27) | C(28) | 102.3(6) | C(27) | $\because \mathrm{C}(28)$ | C(29) | 104.7(7) |
| C(31) | N(5) | C(35) | 117.3(8) | C(36) | N(6) | C(40) | 116.8(9) | C(28) | C(29) | C(30) | 106.7(6) | C(26) | C(30) | C(29) | 105.0(7) |
| C(41) | N(7) | C(45) | 116.5(6) | C(46) | N(8) | C(50) | 117.3 (6) | $\mathrm{P}(3)$ | C(31) | N(5) | 117.1(6) | $\mathrm{P}(3)$ | C(31) | C(32) | 120.2(7) |
| $\mathrm{P}(1)$ | C(1) | C(2) | 110.1(5) | P(1) | C(1) | C(5) | 122.3(6) | $\mathrm{N}(5)$ | C(31) | C(32) | 122.6(7) | C(31) | C(32) | C(33) | 118.9(8) |
| C(2) | C(1) | C(5) | 104.9(6) | $P(2)$ | C(2) | C(1) | 109.4(5) | C(32) | C(33) | C(34) | 118.9(9) | C(33) | C(34) | C(35) | 118.2(8) |


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## A12 Crystal Structure Data for $\left[\mathbf{P t}_{\mathbf{2}}(\mathbf{d p y p c p})_{2} \mathbf{A g}_{6}\left(\mathbf{N O}_{3}\right)_{10}\right]_{n}$



Figure A12.1 ORTEP representation of the repeating unit of $\left[\mathrm{Pt}_{2}(\mathrm{dpypcp})_{2} \mathrm{Ag}_{6}\left(\mathrm{NO}_{3}\right)_{10}\right]_{n}$ ( $33 \%$ ellipsoids).




|  | $\mathbf{x}$ | $y$ | 2 | $\mathrm{U}(\mathrm{eq})$ |
| :---: | :---: | :---: | :---: | :---: |
| C(45) | 10019 (10) | 3582 (8) | 6687(7) | 47(3) |
| C(90) | 5634 (10) | -5417(14) | 4440(10) | 71 (5) |
| C(91) | 5814 (11) | -6139(9) | 4715 (14) | 99 (8) |
| C(92) | 4601 (9) | -1467(14) | 3769 (9) | 68 (5) |
| C(93) | 4338 (15) | -782(16) | 3852 (17) | 143(12) |
| C(94) | 7002 (8) | -3523(7) | 2831(6) | 33 (2) |
| C(95) | 6296 (10) | -3711(9) | 2379 (8) | 60 (4) |
| C(96) | 7012 (9) | -4652 (9) | 7468 (8) | 49 (3) |
| C(97) | 6785 (9) | -4539 (8) | 8096 (7) | 46 (3) |
| C (98) | 8568(8) | -5027(6) | 4745 (7) | $38(2)$ |
| C (99) | 8951(12) | -5026(8) | 4172 (9) | 64 (4) |

Bond lengths $[\AA]$ and angles [deg]
Table A12.3 Bond lengths [ $\AA \mathrm{A}]$ and angles [deg]

Table A12.2 Atomic coordinates ( $A \times 10^{\wedge} 4$ ) and equivalent isotropic displacement parameters $A \operatorname{As}$ one third of the trace of the orthogonalized Uij tensor.

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Table A12.3 Bond lengths [ A ] and angles [deg]

## A13 Crystal structure data for $\operatorname{Pt}\left(\boldsymbol{\eta}^{2}-\mathrm{dmf}\right)($ dpypcp $) \cdot 2 \mathbf{C D C l}_{3}$



Figure A13.1 ORTEP representation of $\operatorname{Pt}\left(\eta^{2}-\mathrm{dmf}\right)(\mathrm{dpypcp})$ ( $50 \%$ ellipsoids).

Appendix 13: Crystal Structure Data for Pt $\left(\eta^{2}-d m f\right)(d p y p c p) \cdot 2 \mathrm{CDCl}_{3}$
$-23.0-17.8^{\circ}$
$39.23(1) \mathrm{mm}$
$-10.0^{\circ}$
$60.1^{\circ}$
Total: 35186
Unique: $9896\left(\right.$ R $\left._{\text {int }}=0.042\right)$
Lorentr-polarization
Absorption/decay/scaling
(corr. factors: $0.5115-1.0000)$
Patterson Methods (DIRDIF92 PATTY) Full-matrix least-squares $w=\frac{1}{\sigma^{2}\left(F^{2}\right)}$
0.0000 0.0000
 $\stackrel{\text { 8 }}{\circ}$ $\stackrel{\text { a }}{\text { N }}$
 $\stackrel{\text { T }}{\sim}$ $0.029 ; 0.023$
0.002
$0.67 e^{-} / \dot{A}^{3}$
$-0.52 e^{-} / \dot{A}^{3}$


 No. Observations No. Variables Residuals (on $F^{2}$, all data): R; Rw Goodness of Fit Indicator
No. Observations (I>3 (1)) Residuals (on $\mathrm{F}, \mathrm{I}>3 \sigma(\mathrm{I})$ ): $\mathrm{R} ; \mathrm{Rw}$ Max Shift/Error in Final Cycle Maximum peak in Final Diff. Map Minimum peak in Final Diff. Map
EXPERIMENTAL DETAILS

$\mathrm{V}=3890.4(4) \dot{A}^{3}$


 Rigaku/ADSC CCD
MoKa $(\lambda=0.71069 A)$
graphite monochromated
$94 \mathrm{~mm} \times 94 \mathrm{~mm}$
769 exposures of 16.0 seconds
$0.0-190.2^{\circ}$

Space Group
Z value
$\mathrm{D}_{\text {calc }}$
$\mathrm{F}_{000}$
$\mu(\mathrm{MoK} \alpha)$




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\text { Table A13.2 Atomic coordinates and } \mathrm{B}_{\text {eq }} \text { (continued) }
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Table A13.3 Bond Lengths $(\dot{A})$ (continued)






This is not the end. It is not even the beginning of the end.
But it is, perhaps, the end of the beginning.

- Winston Churchill
(On the victory in Egypt)
Speech at the Mansion House
November $10^{\text {th }}, 1942$


[^0]:    ${ }^{\text {a }}$ Both peaks due to a are singlets.
    ${ }^{\mathrm{b}}$ Both peaks due to $\mathbf{b}$ are doublets.

[^1]:    ${ }^{\mathbf{a}}$ All peaks due to $\mathbf{b}-\mathbf{e}$ are doublets.

[^2]:    ${ }^{\text {a }}$ Measured at r.t., and using a 121 MHz spectrometer, unless otherwise indicated.
    ${ }^{\mathrm{b}}$ Single numbers represent singlets; comma-separated values signify pairs of doublets. Where there is more than one product, each appears on a separate line.
    ${ }^{c}$ Measured using an 81 MHz spectrometer.
    ${ }^{\mathrm{d}}$ Measured using a 202 MHz spectrometer. Unlocked acquisition.
    ${ }^{e}$ Measured at 220 K .

[^3]:    * Superscripts refer to symmetry operations: (a) $1-x, 1-y, 1-z$ (b) $1 / 2-x, y-1 / 2,3 / 2-z \alpha$.

[^4]:    ${ }^{a}$ Measured in $\mathrm{CDCl}_{3}$.
    ${ }^{b}$ The fumarate diesters give two configurational diastereomers when bonded to rac-" $\operatorname{Pt}(\mathrm{dpypcp}) "$.
    ${ }^{c}$ Measured in $\mathrm{C}_{6} \mathrm{D}_{6}$.
    ${ }^{d} \mathrm{Pt}(\mathrm{dpypcp})\left(\eta^{2}\right.$-dem $)$ has chemically inequivalent P -atoms as shown in Chart 4.6. ${ }^{2} J_{\mathrm{PP}}=13 \mathrm{~Hz}$.

[^5]:    Symmetry transformations used to generate equivalent atoms:

