PHOSPHINOAMIDE LIGANDS FOR THE SYNTHESIS OF EARLY TRANSITION METAL ORGANOMETALLIC COMPLEXES

by

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Abstract

Early transition metal hydrides are currently of great interest; they are intermediates in catalytic processes, and have demonstrated ability to activate small molecules. While these complexes are traditionally supported by cyclopentadienyl-type ancillary ligands, current efforts are focused on alternative architectures. In particular, chelating mixed-donor ancillary ligands are currently employed for the synthesis of metal hydride complexes. Bidentate phosphinoamide ligands ([ArNP′Pr₂]⁻ where Ar = 3,5-dimethylphenyl) were used herein for the synthesis of scandium, yttrium and zirconium organometallic complexes that were characterized using NMR spectroscopy and X-ray diffraction techniques.

Mixed phosphinoamide-alkyl yttrium complexes were generated in solution as a mixture of products from reaction of ArNHP′Pr₂ with Y(CH₂SiMe₃)₃(THF)₂. Using the same methodology, (ArNHP′Pr₂)₂Sc(CH₂SiMe₃)(THF) was prepared and reaction with H₂ or PhSiH₃ gave the ligand redistribution product (ArNHP′Pr₂)₃Sc(THF), along with insoluble materials. A ferrocene-linked diphosphinoamide ligand was developed ([fc(NP′Pr₂)]²⁻ where fc = 1,1’-ferrocenyl) and employed for the synthesis of a discandium dihydride complex which is bridged by both hydride and phosphinoamide ligands. Because of the insolubility of this discandium dihydride subsequent attempted reactions with CO, alkenes and alkynes were unsuccessful.

Triphosphinoamide zirconium complexes (ArNHP′Pr₂)₂ZrX (X = Cl, Et, CH₂Ph, BH₄, PHPPh) were prepared and proved to be poor precursors for the synthesis of a zirconium hydride complex. The ferrocene-linked diphosphinoamide ligand was used in the synthesis of zirconium organometallic complexes, fc(NP′Pr₂)₂ZrR₂ (R = Me, CH₂Ph, CH₂′Bu, ′Bu). While these dialkyl zirconium complexes were unreactive with respect to H₂, they have been shown to undergo
insertion of (2,6-dimethylphenyl)isocyanide to generate the expected iminoacyl complexes. The reactivity of the iminoacyl complexes has been examined and a thermally induced 1,2-hydrogen shift reaction was observed for the benzyl-substituted iminoacyl, to generate an amidoalkene complex; the kinetics of the transformation were studied and deuterium isotopic labelling experiments revealed a primary isotope effect for the migrating hydrogen.

The electrochemical oxidation of ferrocene-linked diphosphinoamide scandium and zirconium complexes was examined using cyclic-voltammetry; irreversible oxidation of the ferroceny1 diphosphinoamide ligand in these complexes was observed.
Preface

Chapter 2 is based on work reported in two publications: [Halcovitch, N.R.], Fryzuk, M.D. *Dalton Trans.* **2012**, *41*, 1524; [Halcovitch, N.R.], Fryzuk M.D. *Organometallics* **2013**, ASAP, doi: 10.1021/om400353h. The latter publication also reports some data found in Chapter 5. I performed all experiments, data collection and was the major contributor to the writing of these manuscripts, with significant input from Prof. Fryzuk.

The cyclic voltammetry data collected and the DFT computations in Chapter 5 were performed in collaboration with Dr. J.M. Lauzon.
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<table>
<thead>
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<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>( \alpha )</td>
<td>refers to (or hydrogen atoms on) carbon adjacent the metal center</td>
</tr>
<tr>
<td>1 Å</td>
<td>( 10^{-10} ) meters</td>
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<tr>
<td>( \beta )</td>
<td>refers to (or hydrogen atoms on) 2\textsuperscript{nd} carbon from the metal center</td>
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<tr>
<td>( \delta )</td>
<td>chemical shift in NMR spectroscopy, given in parts per million</td>
</tr>
<tr>
<td>( E_{1/2} )</td>
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<tr>
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<td>( J )</td>
<td>scalar coupling constant in NMR spectroscopy</td>
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<tr>
<td>( \kappa )</td>
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<tr>
<td>( \eta )</td>
<td>denotes number of atoms (all same element) bonding to the metal center</td>
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<tr>
<td>( T_1 )</td>
<td>decay constant of spin magnetization (in z-direction) in NMR spectroscopy</td>
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<td>( \mu )</td>
<td>defines atom(s) bridging multiple metal centers</td>
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### List of abbreviations

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List of new compounds

2.1

2.2

2.3

Ar = 3,5-dimethylphenyl

2.4

2.5

2.6

Ar = 3,5-dimethylphenyl

2.7

2.8

2.9

2.10
Acknowledgements

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Foreward

*Coordination chemistry* is a field of inorganic chemistry in which researchers use molecules containing specific donor atoms, referred to as *ligands*, to bind to a transition metal ion resulting in a *coordination complex*. One area of coordination chemistry is *organometallic chemistry*, which is concerned with coordination complexes that contain metal-carbon bonds; this area has a long history that can be traced back to the 19th century. More recently, coordination complexes containing zirconium-carbon bonds have been pursued due to the work of Ziegler and Natta who developed a commercial process for the polymerization of alkenes. Their discoveries ultimately resulted in the award of the Nobel Prize in Chemistry in 1963 and have had broad implications due to the ubiquitous use of the polymers as plastics in modern day life. While polymerization is not the focus of all organozirconium research, it is an important application that has motivated work in this field. The studies herein report on the synthesis of organometallic complexes of zirconium, scandium and yttrium with ligands containing nitrogen and phosphorus donor atoms called *phosphinoamides*, which contain a phosphine attached directly to a primary amine.

The initial goal was to employ the phosphinoamide transition metal complexes to activate and bind N₂. When N₂ can be induced to bind as a ligand in a coordination complex, its fundamental reactivity can be studied. While achievement of this objective was elusive, a number of novel organometallic complexes were synthesized. Such complexes typically find applications as catalysts in fields such as polymerization, or for petrochemical applications like alkene functionalization (changing hydrocarbons to give them desirable properties). In these studies the phosphinoamide organometallic derivatives were used to examine fundamental
reactions at the metal-carbon bond. Examples include carbon-carbon bond formation from reacting isocyanides with organozirconium complexes and alkane formation from the reaction of an organoscandium complex with H2.

Initial research goals are sometimes not met, largely because research can be unpredictable. The examination of phosphinoamide complexes herein is of fundamental interest because understanding the role of the ligand in the behavior of the metal complex may help other researchers design systems for the aforementioned applications in the future. The following section offers detailed descriptions of relevant scientific literature and will be best understood by readers with some chemistry background.
1 Early transition metal hydrides and ligand design

1.1 Early transition metal hydrides

1.1.1 Overview

Transition metal alkyl and hydride complexes are central to organometallic chemistry. They are intermediates in catalytic processes and have been used for applications such as small molecule activation and alkene polymerization. These two compound classes are related because transition metal hydride complexes are often synthesized directly from metal alkyl complexes and H₂; also, the alkyl complexes can be prepared via migratory insertion of alkenes into metal hydrides. For molecules containing early transition metals, such as zirconocene complexes,¹ ² the former transformation follows a σ-bond metathesis mechanism as shown in Scheme 1.1. The mechanism requires an empty orbital at the metal center and a suitably polarized metal-carbon bond. The products are the hydrocarbon and the metal hydride complex. For group III metals PhSiH₃, is often used interchangeably with H₂ and it is proposed to react similarly via a σ-bond metathesis mechanism.³ For the early transition metals, hydride complexes are typically multimetallic due to the propensity for the hydride ligands to bridge two Lewis acidic metal centers. It should be noted that oxidative addition of H₂ may also be considered as a possible mechanism for this transformation; however, this usually is more applicable to (the electron rich) late transition metal alkyl derivatives.
Scheme 1.1: The σ-bond metathesis mechanism of hydrogenation (L = ligand, M = early transition metal, R = alkyl group).

Initial success in the synthesis of early transition metal hydrides stemmed from employing cyclopentadienyl-based ligands. This research area remains active, but current interest generally lies in the development of alternative ancillary ligands. In particular, the Fryzuk group has focused on the synthesis of mixed-donor chelating ligands, which will be discussed more thoroughly in Section 1.2. The following sections offer a survey of metal hydride complexes supported by non-cyclopentadienyl frameworks with a focus on synthesis, structure and ancillary ligand type.

1.1.2 Scandium and yttrium hydride complexes

The use of nitrogen-containing ligands, in particular amido (R\(_2\)N\(^-\)) ligands, for the early transition metals has spurred a “post-metallocene era”\(^6\). Indeed most non-cyclopentadienyl ligands found to stabilize Sc or Y hydride species typically contain N-donor atoms in a chelating array.

Two examples of a dianionic ligand set have been used successfully to support yttrium hydrides contain two amido donors linked by a binaphthyl 1.1\(^7\) or an ethylene 1.2\(^8\) unit (Figure 1.1).
Complexes (1.1)YR(THF) (R = Me, CH(SiMe$_3$)$_2$) were synthesized and combined with PhSiH$_3$ to produce PhSiRH$_2$ and the diyttrium complex [(1.1)Y(THF)]$_2$(µ-H)$_2$ containing two bridging hydride ligands.$^7$ In a similar fashion 1.3 undergoes reaction with H$_2$ to give a diyttrium complex 1.4 as the major product, however the unusual trimetallic complex 1.5 was also isolated from the reaction mixture as a minor product, as shown in Scheme 1.2.$^8$

**Figure 1.1:** Two dianionic diamido ligand sets used to support yttrium hydrides.
Additionally, amidinate and guanidinate ligands that have chelating arrays containing N-donors, and also charge delocalization over the N-C-N fragment have been employed (Figure 1.2). Chelating diamidinates 1.6, and unlinked amidinate 1.7 and guanidinate ligands 1.8 have been used to support diyttrium hydride complexes. Diamidinate 1.6 does not chelate to a single yttrium center but instead acts as a bridging ligand, forming bimetallic complexes. Complex (μ-
$1.6_2(YCH_2SiMe_3)_2$ reacts with phenylsilane to give $(\mu-1.6)_2Y_2(\mu-H)_2$ with concomitant formation of PhSiH$_2$CH$_2$SiMe$_3$. The amidinate ligand 1.7 ($R = SiMe_3$) has been used to support bimetallic hydride complexes of the form $((1.7)_2M)_2(\mu-H)_2$; these complexes were synthesized both for Sc, and Y.

Figure 1.2: Nitrogen-based chelating ligands used for Sc and Y hydride synthesis.

Amidinate ligand 1.7 ($R = 2,6-$Pr$_2$C$_6$H$_3$) has also been employed for the synthesis of a cationic yttrium hydride derivative (Scheme 1.3). Hydrogenation of the cationic yttrium alkyl compound 1.9 in THF results in a monomeric hydride complex 1.10, which when solubilized in chlorobenzene, aggregates to a bimetallic structure 1.11. This result is noteworthy because monomeric hydride complexes of yttrium are rare.

Scheme 1.3: Cationic yttrium hydride complexes supported by 1.7 (adapted from ref 12)
In addition to amidinates, guanidinate ligands 1.8 containing an electron-donating amine-group attached at the carbon atom of the chelate have been utilized. Complexes of the form [(1.8)₂Y]₂(µ-H)₂ were obtained from the parent (1.8)₂YCH₂SiMe₃ and phenylsilane. When isopropyl-substituted 1.8 is used the yttrium hydride complex was shown to be a highly active catalyst for ethylene polymerization. Interestingly, when the cyclohexyl derivative of 1.8 was employed for the synthesis of the complexes [(1.8)₂M]₂(µ-H)₂ (M = Y, Lu), and solutions of the two bimetallic species were mixed, heterobimetallic Y-Lu hydride complexes were observed, demonstrating an equilibrium between monometallic and bimetallic complexes in solution.

![Figure 1.3](image.png)

**Figure 1.3**: Monoanionic nitrogen-based chelating ligands.

The related monoanionic nitrogen-based chelates shown in Figure 1.3 have been employed to generate monosubstituted yttrium complex 1.15. Subsequent reaction of 1.15 with H₂ gives an unusual mixed alkyl-hydride cluster complex 1.16, as shown in Scheme 1.4. Additionally, it has been shown that the mixed alkyl-hydride cluster can be selectively protonated at the alkyl-group to give a cationic hydride cluster: [(1.12)Y]₃(THF)₃(µ-H)₂][B(C₆F₅)₄].
Scheme 1.4: A mixed alkyl-hydride yttrium cluster supported by 1.12 (adapted from ref 16)

In contrast to the dialkyl complexes supported by 1.12, reaction of (1.13)H and Y(CH₂SiMe₃)₃(THF)₂ resulted in generation of the monoalkyl derivatives 1.17 and 1.18 shown in Figure 1.4. The C-H activation at the ortho position of the phenyl ring, or of the ortho-methyl substituent, generates the N,N,C-chelate. The complexes shown both undergo reaction with PhSiH₃ to give the bimetallic hydride complexes [(1.13)Y(THF)]₂(µ-H)₂ that retain the ligand Y-C bond.¹⁸

Figure 1.4: NNC-donor ligands, derived from 1.13, in yttrium alkyl complexes.
Complexes using ligand 1.14 (Figure 1.3) in addition to a bulky anilido donor can support yttrium hydrides, (1.14)\(Y(\text{NH-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)(\text{CH}_2\text{SiMe}_3)\) reacts with PhSiH\(_3\) to give bimetallic \([1.14]Y(\text{NH-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)]_2(\mu-\text{H})_2\).\(^{19}\)

Mixed-donor chelates have garnered interest and two examples of N,O bidentate chelating ligands (Figure 1.5) have been successfully employed for the synthesis of yttrium hydrides. Hydrogenation of (1.19)\(2Y\text{CH(SiMe}_3\text{)}_2\) in THF led to formation of \([1.19]_2Y(\mu-\text{H})_2\) in approximately 10 % conversion, as determined by NMR spectroscopy.\(^{20}\) The metal hydride species could not be isolated due to further transformation to give the disproportionation product (1.19)\(_3Y\).

![Figure 1.5: NO-donor ligands for the synthesis of Y hydride complexes.](image)

Successful isolation of a yttrium hydride complex using salicylaldiminate (1.20) was reported in 2002.\(^{21}\) Complex 1.21 undergoes reaction with H\(_2\) to give the expected bimetallic product 1.22 as shown in Scheme 1.5. The addition of donor solvent to the bimetallic complex 1.22 results in the formation of a Lewis-base adduct 1.23, wherein the hydride has migrated to the carbon of the imine moiety in the ligand backbone. Interestingly, when the analogous scandium complex (1.20)\(_2\text{ScCH}_2\text{SiMe}_2\text{Ph}\) is exposed to H\(_2\) the hydride ligand apparently
migrates immediately to the salicylaldiminate backbone, giving a complex analogous to 1.23 (but without the neutral donors: L).

Various yttrium hydride cluster complexes have been synthesized using the ligands shown below in Figure 1.6. The tris(pyrazole)borate ligands 1.24 have demonstrated that the nuclearity of the molecules is dependent on both solvent choice and steric bulk of the ligand set.\(^{22}\) Indeed, complexes \((1.24)\text{Y}(\text{CH}_2\text{SiMe}_3)_{2}\) \((R = R' = \text{''Pr})\) react with \(\text{H}_2\) at relatively high pressures (75 atm) to give trinuclear complexes of the form \([([1.24]\text{Y})_{3}(\mu-\text{H})_6]\), while tetranuclear

---

**Scheme 1.5:** Hydride migration to a salicylaldiminate-backbone (adapted from ref 21)
complexes \([\text{1.24}]Y_4(\mu-H)_8 (R = R' = \text{Me})\) are obtained with less stericly demanding ligands.\(^{23}\)

These complexes have demonstrated remarkable reactivity towards CO; when the trinuclear yttrium cluster is used the disassembly of two CO molecules and formation of a propenolate-moiety was observed.\(^{23}\)

Figure 1.6: Monoanionic ligands to support high nuclearity metal hydride clusters.

A cyclen-derived ancillary ligand has been used to synthesize a yttrium hydride cluster. \((\text{1.25})Y(\text{CH}_2\text{SiMe}_3)_2\) reacts with PhSiH\(_3\) to give \([\text{(1.25)}Y)_3(\mu-H)_6\).\(^{24}\) The trinuclear species is stable in solution, and while no evidence for mononuclear or bimetallic species is observed the complex is quite active for the hydrosilation of alkenes with PhSiH\(_3\) at 60 °C.

In a manner analogous to that described with the cyclen-based ligand, reaction of \text{1.27} with H\(_2\) (10 atm) yields the trinuclear yttrium hydride complex \text{1.28} (Scheme 1.6).\(^{25}\) A cationic trinuclear complex \text{1.29} can be synthesized by protonation of one of the hydride ligands. In addition, hydrogenation of a mixture of \text{1.27} and [Et\(_3\)NH][BPh\(_4\)] (in a 2:1 ratio) generates the bimetallic complex \text{1.30} as shown in Scheme 1.6.
The examination of ligand designs used for the synthesis of Sc and Y hydride complexes reveals a range of chelating ligands. One trend that is apparent is the incorporation of nitrogen-based donors in the chelating ligand arrays. All the aforementioned metal hydrides were synthesized from reaction of metal alkyl complexes with H\(_2\) or PhSiH\(_3\). This stands in contrast to the hydride complexes of Zr and Hf, which can be synthesized \textit{via} a wide range of methods.
1.1.3 Zirconium and hafnium hydride complexes

The previous section detailed a variety of Sc, Y complexes used to support metal hydrides, which showed a high degree of sophistication in terms of ligand design. In contrast, there are fewer examples of group IV hydride complexes that are not based on the cyclopentadienyl framework. Consequently, these examples will be organized by the synthetic methodology employed, as opposed to by ancillary ligand.

Some complex zirconium halide clusters that contain hydride ligands have been synthesized and structurally characterized. They are formed by reaction of $^8\text{Bu}_3\text{SnH}$ with ZrCl$_4$ in the presence of phosphine ligands. These products are complex solids with molecular formulas such as Zr$_6$X$_{14}$H$_6$(PR$_3$)$_6$ or Zr$_5$X$_{18}$H$_5$(PPh$_4$)$_3$ (X = Cl, Br; R = Me, Et).$^{26-30}$

Phosphine-donors are also used in some of the earliest examples of non-Cp supported Zr hydrides. For example, reduction of ZrCl$_4$(dmpe)$_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane), using Na/Hg amalgam, in the presence of 1,3-cyclooctadiene or 1,3-cyclohexadiene yields the terminal hydride complexes ZrH($\eta^5$-cyclooctadienyl)(dmpe)$_2$ and ZrH($\eta^5$-cyclohexadienyl)(dmpe)$_2$, respectively.$^{31}$ Additionally, complex 1.31 that contains a tridentate phosphine ligand with a central phosphide-donor was employed in the synthesis of a bimetallic zirconium hydride complex 1.32 (Scheme 1.7).$^{32}$

![Scheme 1.7](image)

Scheme 1.7: Synthesis of a bimetallic zirconium monohydride complex (adapted from ref 32)
Simple monodentate and bidentate phosphines also react with Zr(BH₄)₄ and Hf(BH₄)₄ precursors. These reactions give rise to mixed hydride-tetrahydroborate bimetallic structures as shown in Scheme 1.8. The products obtained can be monometallic (1.35), bimetallic (1.33, 1.37) or trimetallic (1.34) complexes containing bridging hydrides, with the outcome of the reaction being stoichiometry dependent.³³,³⁴

Scheme 1.8: Synthesis of mixed hydride tetrahydroborate complexes, M = Zr or Hf (adapted from ref 32 and 33)
Additionally, PMe₃ has been used to generate hydride complexes from hafnium tetrahydroborate complexes supported by a PNP-type donor ligand (Scheme 1.9). Complex 1.38 reacts with PMe₃ to give bimetallic complex 1.39 that contains three bridging hydride ligands and three BH₄ moieties.³⁵ Interestingly, in solution this complex has two PNP ligand environments that are related by symmetry, which implies one of the BH₄-units is migrating from one hafnium center to the other. Addition of NEt₃ to the bimetallic complex 1.39 transforms another BH₄ unit to a bridging hydride resulting in the bimetallic hafnium tetrahydride complex 1.40.

Scheme 1.9: Bridging hydride species produced from tetrahydroborate complexes (adapted from ref 35)

In similar fashion, a zirconium bis(tetrahydroborate) complex supported by a 1,4-bis(trimethylsilyl)cyclooctatetraene (COT) ligand reacts with PMe₃ to produce an unusual
bimetallic complex, \((\text{COT})\text{Zr(µ-H)(µ-COT})\text{Zr(BH}_4\)), that contains a bridging COT-moiety that has been reduced by two electrons.\(^{36}\)

The homoleptic dimethylamido-complexes of zirconium and hafnium when treated with \(\text{Ph}_2\text{SiH}_2\) result in the formation of the linear trimetallic complex \(1.41\), wherein the zirconium centers are bridged by two dimethylamido fragments and one hydride.\(^{37}\) This reactivity pattern has been extended to a variety of silanes, as shown in Scheme 1.10.\(^{38}\)

\[
3 \text{M(NMe}_2\text{)}_4 + 2 \text{HSiR}_3 \rightarrow (\text{Me}_2\text{N})_3\text{M-} \text{H-M(M(NMe}_2\text{)}_3)
\]

\(\text{M} = \text{Zr}, \text{Hf} \quad \text{R}_3 = \text{H}_2\text{Ph}, \text{HPh}_2, \text{HMePh}, (\text{NMe}_2)\text{Ph}_2\)

**Scheme 1.10:** Trinuclear amido hydride zirconium and hafnium complexes (adapted from ref 38)

Heterobimetallic hydride complexes are known for porphyrinogen-supported zirconium complexes, and are sometimes referred to as LiH or KH carriers.\(^{39-41}\) Scheme 1.11 demonstrates an example of a bimetallic complex that ‘encapsulates’ LiH.\(^{42}\) The lithium atoms in \(1.43\) are ligated by \(\pi\)-interactions with the pyrrole rings in the porphyrinogen framework.
Scheme 1.11: Zirconium porphyrinogen lithium hydride complexes (adapted from ref 42)

There are examples of alkoxy and amido-based frameworks that support group IV hydrides. They are prepared by either hydrogenation of a metal-alkyl or by reaction of hydride reagents with metal chloride precursors. A remarkable zirconium alkylidene complex 1.44 (Figure 1.7) is synthesized by hydrogenation of the dibenzyl complex LZr(CH$_2$Ph)$_2$.\textsuperscript{43} While the related calixarene complexes 1.45 and 1.46 are synthesized from the corresponding metal halide using excess LiBHEt$_3$.\textsuperscript{44} Additionally, the complexes 1.47\textsuperscript{45} and 1.48\textsuperscript{46} were synthesized from a Zr-alkyl complex and H$_2$. 

\begin{figure}
\centering
\includegraphics[width=\textwidth]{scheme11}
\caption{Scheme 1.11: Zirconium porphyrinogen lithium hydride complexes (adapted from ref 42)}
\end{figure}
Figure 1.7: Examples of alkoxy and amido supported hydride complexes.

The reaction of H₂ with the side-on bound dinitrogen complexes 1.49 and 1.51 have been reported by the Fryzuk group (Scheme 1.12). The landmark discovery that productive bond-forming transformations between N₂ and H₂ at a metal center could be observed has had strong implications in the field of N₂ activation. The synthesis of 1.50, which contains a bridging hydride as well as the functionalized N₂-unit, was later followed up using a different amido-phosphine ligand (complex 1.52). The nature of the neutral donor (PMe₂Ph) in 1.51 was shown
to greatly affect the reactivity of the complex, which has prompted further alterations of the ancillary ligands in the Fryzuk group.

**Scheme 1.12**: Addition of H₂ to zirconium dinitrogen complexes (adapted from ref 47 and 48)

### 1.2 Phosphinoamide ligands

#### 1.2.1 Ligand design in the Fryzuk group

In the Fryzuk group ligand design has focused on the principle that combining ‘hard’ nitrogen donors in a chelate with ‘soft’ phosphorus donors would generate ligands suitable for coordination of a wide variety of metal centers from across the periodic table. The phosphinoamide ligand exemplifies this approach (1.53 in Figure 1.8) and complexes supported by this ligand system have shown remarkable reactivity (cf. Scheme 1.12). The cyclic motif evolved
via removal of one phosphorus donor to give an open tridentate NPN-type framework (1.54) in which the two amido-donors render this ligand suitable for coordination to early transition metals. Subsequent alterations of the NPN-motif involve changing the linker between the N and P donor atoms. A series of NPN-type ligands featuring a variety of N-P linkers have been investigated: silylmethylene (1.54), arene (1.55),\textsuperscript{48} thiophene (1.56),\textsuperscript{50} and cyclopentene (1.57).\textsuperscript{51} An alternative possibility for the N-P linker would be having no linker at all; two of these phosphinoamides on a metal center (1.58) would result in a donor set similar to that shown for P\textsubscript{2}N\textsubscript{2} (1.53).

**Figure 1.8:** ‘NPN’ ligand designs employed for the synthesis of early transition metal complexes.
All of the ligand sets 1.54 to 1.57 in Figure 1.8 have been examined for their ability to bind to Zr and activate molecular nitrogen.\textsuperscript{48,50-52} As will be mentioned in Chapter 3, efforts to activate dinitrogen using the linkerless phosphinoamide ligand set were unsuccessful; nevertheless, the attempted synthesis of metal hydrides revealed some interesting chemistry that will be discussed in Chapters 2 - 4.

1.2.2 Introduction to phosphinoamides

Ligand design is at the core of transition metal coordination chemistry. The ability to alter the ligand framework, which allows tuning of the steric and electronic environment at the metal center, is one of the basic tenets of ligand design. In the Fryzuk group this has taken the form of mixed donor ligands based on N and P-donors in a chelating array. Phosphorus-containing ligands are a common ligand type; traditional examples contain either P-C (phosphines) or P-O bonds (phosphites). However, there is increasing interest in developing new phosphorus ligands that contain P-N bonds. In particular phosphinoamides, which contain a direct phosphorus-nitrogen bond, have been actively pursued and this area has been recently reviewed.\textsuperscript{53} The assembly of P-N single bonds is generally accomplished by straightforward addition of an amine to a chlorophosphine in the presence of base (Scheme 1.13). Alternatively, alkali metal amido compounds can be added to the chlorophosphine to form the P-N bond and this route is typically used when the amine-substituent (R') is sterically demanding. The resulting phosphinoamines (1.59) (alternatively named aminophosphines) have been used as phosphine ligands for late transition metals.\textsuperscript{54}
Phosphinoamines also serve as precursors to phosphinoamide anions; deprotonation of \( \text{1.59} \) (when \( R = \text{Ph} \)) with alkyl lithium reagents generates lithium phosphinoamides (Scheme 1.14). The structure of the resulting lithium complex is dependent on the N-substituents of the phosphinoamide anion, as the examples below demonstrate.
Stoichiometry is important in these deprotonation reactions; when phosphinoamine 1.64 was treated with two equivalents of nBuLi an unusual mixed alkyl phosphinoamide lithium cluster 1.65 was obtained. Subsequent treatment of 1.65 with phenylsilane afforded a lithium hydride cluster that is ligated and solubilized by the phosphinoamide fragments 1.66 (Scheme 1.15).55

![Scheme 1.15](image)

**Scheme 1.15**: The synthesis of a phosphinoamide-containing lithium hydride complex (adapted from ref 55)

There are a few structural features that are noteworthy for the phosphinoamide anions (Figure 1.9). One is the short P-N bond, which is best described by a combination of phosphinoamide (A), and iminophosphide (B) resonance forms and the other feature is the potential for two geometric isomers: a cis or trans configuration. Computational modeling using *ab initio* methods has demonstrated that the iminophosphide resonance form is a relatively small contributor except when strongly electron-withdrawing fluoro groups on phosphorus.56 The
iminophosphide resonance form has been described as a $\pi \rightarrow \sigma^*$ interaction (negative hyperconjugation) from the N p-orbital to the P-R $\sigma^*$-orbital. In general, phosphinoamide anions are considered (and named for) resonance form A in Figure 1.9. The degree to which resonance form B contributes determines how long the P-N bond length will be, which has been shown using both experimental$^{57}$ and computational chemistry.$^{56}$ Typically the cis-conformer of phosphinoamide anions is observed; however, with sterically demanding substituents, such as in complex 1.5, the trans-conformer is obtained. For the parent H$_2$PNH anion, the cis isomer is predicted to be more stable by 0.5 kcal/mol and the rotational barrier between cis and trans isomers is predicted to be 8 kcal/mol.$^{56}$ Figure 1.1 shows the three bonding modes of the phosphinoamide ligands. Both $\kappa^1$-(N) and $\kappa^2$-(NP) bonding modes to a single metal center are accessible and a bridging ($\mu$) mode has also been observed. Examples of these bonding motifs follow in the next section.

![Diagram of phosphinoamide anions and bonding modes](image)

**Figure 1.9:** Resonance forms of the phosphinoamide anion (A and B), geometric isomers (cis and trans), and bonding modes for phosphinoamide anions.
1.2.3 Mononuclear transition metal phosphinoamide complexes

Rare earth metal ‘ate-complexes’ of the form \([\text{PhNPPPh}_2)_4M][\text{Li(THF)}_4]\) (1.67, \(M = Y, \ Yb, \ Lu\)) have been synthesized from the corresponding lithium phosphinoamide and \(\text{MCl}_3\) (Scheme 1.16). These complexes are 8-coordinate with each phosphinoamide fragment bound in a \(\kappa^2-(NP)\) fashion. Despite the complexes displaying \(C_i\) symmetry in the solid-state, the solution behavior was consistent with a highly symmetric species, with a doublet resonance (\(^2J_{PY} = 5.4 \text{ Hz}\)) observed in the \(^{31}\text{P}\{^1\text{H}\} \text{ NMR spectrum of 1.67 (M = Y)},\) implying \(\kappa^1-(N)\) bonding of all four phosphinoamides in solution.\(^{58}\)

Scheme 1.16: The synthesis of rare-earth metal phosphinoamide complexes (adapted from ref 58)

Phosphinoamide complexes of Ti and Zr have been prepared via a similar route as for the rare-earth metals, using lithium phosphinoamide ligands and \(\text{MCl}_4\) (\(M = \text{Ti, Zr}\)). A complex analogous to 1.67 of the form \((\text{PhNPPPh}_2)_4\text{Zr}\) has been synthesized and the solution structure assigned as octahedral, with two phosphinoamide ligands bound in an \(\kappa^1-(N)\) fashion and two phosphinoamide ligands bound in \(\kappa^2-(NP)\) fashion.\(^{59}\) When MAO (methylaluminoxane) was used as the activator with \((\text{PhNPPPh}_2)_4\text{Zr}\), it was found to be an active polymerization catalyst for the synthesis of high-molecular-weight polypropylene. Additionally, di(phosphinoamide)
dichlorotitanium complexes (1.68) have been synthesized\(^6\) (see Scheme 1.17) and zirconium analogues of 1.68 were initially reported although a later publication stated that the results could not be reproduced.\(^6\) Incorporation of phosphinoamide ligands in Cp* containing complexes could also be achieved, for example: complex 1.69, Cp*(RNPPPh\(_2\))TiCl\(_2\),\(^6\) and the linked Cp-phosphinoamide complexes 1.70.\(^6\) Complexes 1.68 – 1.70 all demonstrated low activity when tested as catalysts for olefin polymerization.

Scheme 1.17: The synthesis of a variety of group IV phosphinoamide complexes (adapted from ref 60, 62 and 63)
More recently, a hafnium diphosphinoamide complex has been synthesized from a diphosphinoamine and tetrabenzylhafnium (Scheme 1.18). The resulting complex 1.63 has been found to display interesting reactivity with CO2 when alkyl-group abstraction agents are used. Similar diphosphinoamine ligands (CH2NHPtBu2)2 and CH2(CH2NHPtBu2)2 have been coordinated to Ni and Pd. Subsequent deprotonation of the ligand sometimes occurs at nitrogen, to generate a phosphinoamide donor, and sometimes the carbon-backbone is deprotonated, giving a PCP-type ligand.

![Scheme 1.18: Synthesis of a diphosphinoamide hafnium dibenzyl complex (adapted from ref 64)](image)

1.2.4 Multimetallic phosphinoamide complexes

Phosphinoamide ligands have been employed for the synthesis of chromium complexes by the Gambarotta group. Both bimetallic (1.72) and tetrametallic (1.73) complexes can be obtained depending on the stoichiometry used (Scheme 1.19). These complexes were useful in the selective oligomerization of ethylene.
Bimetallic phosphinoamide complexes of Fe and Mn have also been synthesized. The structure of the resulting complexes has been shown to be highly dependent on the steric and electronic properties of the phosphinoamide ligand. Examples of three different bonding motifs in the iron complexes are shown in Scheme 1.20.
Scheme 1.20: The synthesis of iron phosphinoamide complexes (adapted from ref 68)

In the literature regarding reports of early transition metal complexes containing phosphinoamides, the reversible dissociation of the phosphine moieties is a key feature because it allows access to both $\kappa^1$-(N) and $\kappa^2$-(NP) bonding modes. The $\kappa^1$-(N) bonding mode renders the phosphines available to coordinate to late transition metals. Indeed, some of the aforementioned titanium complexes have been used to assemble Ti-Ru,\(^69\) and Ti-Pt heterobimetallic complexes.\(^70\) The synthetic route to these Ti-Pt complexes is shown below in Scheme 1.21. The reversible dissociation of the phosphorus donors in complex 1.68 allows it to be used as a bidentate chelating ligand for coordination to late transition metals. Additionally, analogous Zr-Pt heterobimetallic complexes 1.79 and 1.80 have been reported.\(^71\)
Scheme 1.21: Synthesis of Ti-Pt heterobimetallic complexes 1.77 and a Zr-Pt heterobimetallic complex 1.80 (adapted from ref 70 and 71)

Heterobimetallic complexes where the two metals are triply bridged by phosphinoamide ligands have been synthesized. These complexes are shown in Scheme 1.22 and display dative Cu-Zr\(^{61}\) and Co-Zr\(^{72}\) bonding interactions.
This very brief discussion on the synthesis of heterobimetallic complexes assembled using phosphinoamide ligands is not exhaustive. For further information on using phosphinoamide ligands for heterobimetallics the reader is encouraged to consult a recent review.\textsuperscript{73}

1.3 Scope of thesis

Alternatives to cyclopentadienyl-based ligands for early transition metal complexes are the focus of many ligand design strategies. In the Fryzuk group these ligand designs are based on N and P donors. Phosphinoamides were identified as interesting bidentate N,P-containing ligands because they are synthesized by straightforward methods and modular alterations are possible.
Phosphinoamide complexes of zirconium, scandium and yttrium are the focus of this thesis. In particular, determining if they are suitable frameworks to support metal hydride complexes.

Chapter 2 of this thesis describes the synthesis of phosphinoamide-containing scandium and yttrium organometallic complexes. Additionally, a ferrocene-linked diphosphinoamide system is introduced, which allows for the synthesis of a bimetallic scandium hydride complex.

Chapter 3 describes zirconium complexes supported by phosphinoamide ligands that are potential precursors to hydride complexes. The complexes described include possible intermediates for phosphine coupling reactions. The difficulties encountered using phosphinoamide ligands for this chemistry are discussed.

Chapter 4 describes the synthesis and characterization of ferrocene-linked diphosphinoamide zirconium complexes. Amido, chloro, alkyl and iminoacyl complexes, as well as the thermal reactivity of the alkyl and iminoacyl complexes are described. A kinetic study on the thermal rearrangement of an iminoacyl complex to an amidoalkene is reported.

Chapter 5 focuses on the electrochemical behavior of the ferrocene-linked diphosphinoamide complexes as observed using cyclic voltammetry. The resulting observations are rationalized based on examples from related complexes in the literature.

Chapter 6 describes other ligand systems investigated including the synthesis of a more sterically demanding ferrocene-linked diphosphinoamide ligand.
2 Phosphinoamide scandium and yttrium organometallic complexes

2.1 Introduction

The development of organometallic chemistry of the rare-earth elements has relied heavily on the use of cyclopentadienyl (Cp) based ligands.\textsuperscript{74-76} The early development of these metallocene rare-earth (Cp\textsubscript{2}LnX) complexes focused on catalytic alkene transformations, with an emphasis on polymerization.\textsuperscript{5,77,78} More recently, there has been an interest in developing non-cyclopentadienyl ligand environments.\textsuperscript{79} These alternative ligand sets are typically based on N and O donor atoms, which are well matched to the ‘hard’ metal centers. A few examples of such ligand motifs include amidinates, guanidinates, and \(\beta\)-diketiminates, which all feature chelating nitrogen donors. Additionally, mixed donor ligands incorporating ‘soft’ donors, such as phosphorus, have been employed for the synthesis of rare-earth metal complexes.\textsuperscript{80}

Of particular interest to our research group are ligand designs that contain both N and P donor atoms contained in a chelating array. Early work from the Fryzuk group using a PNP-type ligand (I in Figure 2.1) for yttrium and the lanthanides resulted in the successful synthesis of the organometallic complex (PNP)\textsubscript{2}YCH\textsubscript{2}Ph. However, not only was phosphine dissociation noted in the lanthanide derivatives, but thermolysis of the aforementioned yttrium complex resulted in metallation of the methylene group adjacent to phosphorus, with loss of toluene.\textsuperscript{81} Since this early report, subsequent ligand designs have met with more success, including an arene-linked PNP (II) scaffold used by the Hou group\textsuperscript{25,82} for the synthesis of scandium alkyl complexes and the Mindiola group\textsuperscript{83,84} for the generation of a scandium imido complex. Additionally both a
macrocyclic $P_2N_2$ (III)$^{85-87}$ and tridentate NPN (IV)$^{88}$ system have been developed in the Fryzuk group to support organoyttrium and organoscandium complexes respectively.

**Figure 2.1:** Several mixed donor ligand designs used for the synthesis of scandium and yttrium organometallic complexes.

In addition to these ligands, wherein the nitrogen and phosphorus atoms are linked by an organic group, there has also been interest in using P-N bonds to build ligand scaffolds.$^{89}$ Our interest in using P-N bound ligands is limited to systems where the ligand fragment is bound in a bidentate fashion to the metal center. Two classes of these compounds have been previously used in rare-earth metal chemistry: diphosphinoamides, $(R_2P)_2N-M$ and phosphinoamides, $(R_2P)RN-M$. To date both classes have only been shown to bind in a bidentate fashion, (cf. Figure 1.9) with one pendant phosphine in the case of diphosphinoamides.$^{53}$ This prompted us to attempt to prepare organometallic derivatives based on phosphinoamide ligands to study their potential for use as precursors for potentially reactive metal hydride complexes.
2.2 Phosphinoamide supported scandium and yttrium organometallics

2.2.1 Alkane-elimination route to scandium and yttrium complexes

Salt metathesis is generally the method of choice for the synthesis of rare-earth complexes. Since the metal trichloride starting materials are commercially available, they typically react with alkali-metal ligand precursors LM′ (L = monoanionic ligand, M′ = Li, Na, K). However, this strategy can be complicated by the propensity for the synthesis of ‘ate’ complexes, of the form Li₄M. Additionally, the LiCl byproduct can remain bound to the highly Lewis-acidic metal center when these approaches are used. In light of these difficulties, another method is to use elimination reactions, for example, using homoleptic starting materials such as Y[N(SiMe₃)₂]₃. Addition of amine ligand precursors to Y[N(SiMe₃)₂]₃ can effect a transamination reaction with elimination of HN(SiMe₃); however, due to the sterically demanding bis(trimethylsilyl)amido ligands this pathway is not always effective using bulky ligand precursors. In order to open the coordination sphere of these complexes, some less bulky triamido complexes such as Y[N(SiHMe₂)₂]₃(THF)₂ have also been employed. A related process is an alkane-elimination pathway to access scandium and yttrium organometallics directly from a trialkyl starting material, typically either M(CH₂Ar)₃(THF)₂ (Ar = Ph or xylyl) or M(CH₂SiMe₃)₃(THF)₂, where M is Sc or Y. The addition of amine ligand precursors to these starting materials will proceed via loss of toluene, mesitylene or tetramethylsilane, respectively, which are volatile and unreactive byproducts. If the substitution at the metal can be controlled, then this also results in direct access to organometallic complexes containing potentially reactive metal-carbon bonds. Due to its simplicity, the alkane-elimination method was chosen for the synthesis of phosphinoamide scandium and yttrium complexes.
2.2.2 Trisubstituted phosphinoamide scandium and yttrium complexes

The preparation of phosphinoamine 2.1 was performed by addition of ClP^iPr_2 to a solution of 3,5-dimethylaniline and triethylamine in dichloromethane. The product was extracted with pentane and cooling the filtrate gives large colourless crystals of 2.1. The characteristic signal in the ^1H NMR spectrum of 2.1 is the N-H resonance at δ 3.32, which displays a two-bond coupling to phosphorus (^2J_{HP}: 10.8 Hz). Resonances for the methine-protons at δ 1.48, and two distinct signals for the methyl-protons at δ 0.98 and 0.96 are assigned to the isopropyl groups on the phosphorus donor.

With phosphinoamine 2.1 in hand, the viability of an alkane-elimination pathway to phosphinoamide scandium and yttrium complexes was examined. Addition of three equivalents of 2.1 (ArNHP^iPr_2 where Ar = 3,5-dimethylphenyl) to M(CH_2SiMe_3)_3(THF)_2 (where M = Sc, Y) in hexanes produces complexes of the form (ArNP^iPr_2)_3M(THF), according to Scheme 2.1.

Scheme 2.1: Synthesis of seven-coordinate scandium and yttrium complexes.
The tri(phosphinoamide)yttrium complex 2.2 was isolated as single crystals by vapour diffusion of pentane into a concentrated diethyl ether solution. Figure 2.2 shows the solid state molecular structure of this highly distorted seven-coordinate molecule, where the metal-amido and metal-phosphine bond lengths are varied. The amido-donors are planar, with the sum of the angles about each amido donor between 358-360°. This planar geometry at each amido donor allows for potential π-donation into vacant yttrium orbitals. The N-P bonds lengths are approximately 1.67 Å, which is intermediate between a single and double bond, and is in the expected range for a phosphinoamide anion.53

Figure 2.2: ORTEP diagram of the solid-state molecular structure of 2.2. Thermal ellipsoids are drawn at 50% probability and hydrogen and ′Pr methyl atoms are omitted for clarity.
Table 2.1: Selected bond lengths and angles for complex 2.2

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</table>

The low-symmetry observed in the solid-state is not observed in solution: in C₆D₆, complex 2.2 has C₃ᵥ symmetry. This is evident from the ¹H NMR spectrum wherein equivalent aryl groups and isopropyl groups are observed. Additionally, the ³¹P{¹H} NMR spectrum of 2.2 displays a sharp doublet (¹Jᵢᵧ = 18.3 Hz) indicating equivalent phosphine environments. This coupling constant is larger than that observed for the related ‘ate-complex’ [(PhNPPP₂)₄𝑌][Li(THF)₄], for which a coupling constant of ²Jᵢᵧ = 5.4 Hz is reported. However, when the phosphine donor is contained in a chelating array, the reported ¹Jᵢᵧ coupling constants are typically within the range of 60 – 85 Hz. Notable exceptions are the ‘PNP’ ligated yttrium complexes obtained by the Hou group, which exhibit Jᵢᵧ coupling constants between 18 and 37 Hz. Upon cooling samples of 2.2 in toluene-d₆ no broadening of the resonances in either the ³¹P{¹H} or the ¹H NMR spectrum was observed. Based on these observations it is likely that the phosphine moieties undergo rapid intramolecular dissociation and reassociation on the NMR timescale, which would result in the observed high symmetry in
solution. The NMR spectra for scandium complex 2.3 are analogous to those obtained for complex 2.2, but without the presence of any $J_{HY}$ or $J_{HY}$ coupling, because yttrium is not present.

2.2.3 Mixed alkyl-phosphinoamide complexes of scandium and yttrium

Monitoring the course of reaction for the synthesis of 2.2, according to Scheme 2.1, several detectable intermediates are observed using $^{31}P\{^1H\}$ NMR spectroscopy. Additionally, the homoleptic yttrium alkyl complex reacts with fewer than three equivalents of 2.1 to yield a mixture of products. In these mixtures, complex 2.2 is present in addition to two other species (Scheme 2.2). Three separate NMR scale reactions were performed and analyzed by $^{31}P\{^1H\}$ and $^1H$ NMR spectroscopies: the addition of 1, 2 and 3 equivalents of Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ to 2.2 in C$_6$D$_6$. Based on the spectra (Figure 2.3), the two compounds present (in addition to 2.2) were tentatively assigned as the monoalkyl complex, (ArNP$i$Pr$_2$)$_2$Y(CH$_2$SiMe$_3$)(THF) 2.4, and the dialkyl complex, (ArNP$i$Pr$_2$)Y(CH$_2$SiMe$_3$)$_2$(THF) 2.5. These complexes have only been characterized in situ because they could not be separated by recrystallization. In Figure 2.3, it is apparent that upon addition of three equivalents of Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ to 2.2, that two new phosphorus containing products are formed, and 2.2 is almost fully consumed. The $^1H$ NMR analysis allows for comparison of the integrations of the resonances upfield of δ 0 (Y-CH$_2$), which have observable $^2J_{HY}$ coupling, and comparing them to the signals at δ 2.3 (Ar-CH$_3$); based on the integrations the two products can be assigned as 2.4 and 2.5 (additionally, a $^{13}C\{^1H\}$ NMR spectrum of these products is shown in Appendix A). When a ratio of 3:1 Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ to 2.2 is used, the complexes 2.4 and 2.5 are present in roughly a 1:1 ratio, albeit with a small amount of 2.2 still present in solution. It should be noted that there is a
significant amount of $\text{Y(CH}_2\text{SiMe}_3\text{)}_3(\text{THF})_2$ present, which is labeled in the $^1\text{H}$ NMR spectrum (YR$_3$).

![Diagram of molecular structures](image)

**Scheme 2.2:** Mixtures arising from the attempted synthesis of yttrium organometallics.

The composition of these solutions does not change over a period of hours when monitored using NMR spectroscopy nor is there any detectable change upon cooling as low as $-45$ °C (in toluene-$d_8$). Solutions of these mixtures decompose slowly over several days standing at room temperature, or within minutes of heating the samples to 40°C. Decomposition results in the formation of tetramethylsilane, which was detected using $^1\text{H}$ NMR spectroscopy, accompanied by formation of a precipitate. It is noteworthy that attempts to generate the mixed alkyl-phosphinoamide yttrium complexes in coordinating solvents such as THF were unsuccessful using either of the aforementioned methods. These findings are consistent with the
three phosphinoamide yttrium complexes 2.2, 2.4 and 2.5 being in equilibrium, although we were unable to confirm this using variable temperature NMR spectroscopy.

\[
\begin{align*}
2.2 &= (\text{ArNPPr}_{2})_{3}Y(\text{THF}) \\
2.4 &= (\text{ArNPPr}_{2})_{2}YR(\text{THF}) \\
2.5 &= (\text{ArNPPr})_{2}YR(\text{THF}) \\
YR_{3} &= YR_{3}(\text{THF})_{2} \\
(R &= \text{CH}_{2}\text{SiMe}_{3})
\end{align*}
\]

Figure 2.3: NMR analysis of mixtures of \(\text{Y(CH}_{2}\text{SiMe}_{3})_{3}(\text{THF})_{2}\) to 2.2 (x:y) in C\(_{6}\)D\(_{6}\), (A) \(^{31}\text{P}\{^{1}\text{H}\}\) spectra: 162 MHz, and (B) \(^{1}\text{H}\) spectrum: 400 MHz.
While mixed alkyl-phosphinoamide yttrium complexes could not be isolated, the analogous reactions with scandium are more straightforward. Monoalkyl compound (ArNPPr2)2Sc(CH2SiMe3)(THF) 2.6 was synthesized by addition of two equivalents of 2.1 to Sc(CH2SiMe3)3(THF)2 at room temperature when the reaction is allowed to proceed for 24 hours (Scheme 2.3). The only detectable intermediate during the course of reaction is tri(phosphinoamide) complex 2.3 and using two equivalents of (ArNPPr2)3Sc(THF) with Sc(CH2SiMe3)3(THF)2 yields complex 2.6, and this reaction is not limited to non-coordinating solvents. Single crystals of 2.6 suitable for X-ray crystallography were obtained from a concentrated hexanes solution stored at -35 °C for three days.

Scheme 2.3: Synthesis of a disubstituted phosphinoamide scandium alkyl complex.
The solid-state molecular structure (Figure 2.4) contains a scandium-bound THF molecule in a position *cis* to the alkyl group. Although the phosphinoamide fragments are inequivalent in the solid-state, the $^{31}$P\{\textsuperscript{1}H\} NMR spectrum displays a singlet indicating that both phosphine environments are equivalent on the NMR timescale in solution. Cooling samples of \textbf{2.6} in THF-$d_8$ to -90°C results in decoalescence of the methine-resonances in the $^1$H NMR spectrum, and also broadening of the single resonance in the $^{31}$P\{\textsuperscript{1}H\} NMR spectrum. While the solution spectroscopic data does not perfectly match the solid-state structure, it is consistent with phosphine dissociation that is fast on the NMR time scale at temperatures above -80°C. When compared to recent literature values, the Sc-N,$^{94,95}$ Sc-C$^{96}$ and Sc-P$^{83,97}$ bond lengths of 2.099(2), 2.7115(9), and 2.243(3) Å are as expected.

\textbf{Figure 2.4:} ORTEP representations of the solid-state molecular structure of \textbf{2.6}. Thermal ellipsoids are drawn at 50% probability and hydrogen and $^3$Pr methyl atoms are omitted for clarity.
Table 2.2: Selected bond lengths and angles for complex 2.6

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The marked difference in the synthesis of monoalkyl complexes 2.4 and 2.6 must be rationalized based on the size difference between Y(III) and Sc(III). Ultimately the smaller size of scandium allows for greater control of phosphinoamide substitution at the metal center.

The scandium monoalkyl complex 2.6 is stable for days in solution at room temperature. This is in contrast to the mixtures of yttrium alkyl complexes 2.4 and 2.5, which were susceptible to thermal decomposition over hours at room temperature or by mild heating at 40°C. However, toluene solutions of 2.6 begin to decompose at 90°C and over a period of 18 hours production of a significant amount of 2.3 was noted, along with the formation of some precipitate. Additionally, placing solutions of 2.6 under an atmosphere of 4 atm of H₂ gas in toluene for 48 hours gives the same result as thermolysis – partial conversion of 2.6 to 2.3 is observed, accompanied by precipitate formation. These results demonstrate that redistribution of the phosphinoamide fragments is problematic in these mixed alkyl-phosphinoamide complexes. This type of behavior has been previously observed in rare-earth complexes; one such example from the literature involves a lutetium alkyl complex. Ligand redistribution is observed when complex
L₂Lu(THF)CH₂SiMe₃ (where L = κ²-(PN)-Ph₂P(o-C₆H₄NCH₂Ph)) is left in solution at room temperature, it converts slowly to L₃Lu over a period of 6 days.⁹⁸

2.3 Ferrocene-linked phosphinoamides as supporting ligands for scandium

2.3.1 Ferrocene as a diamine linker in ligand design

In order to overcome the ligand redistribution problem, diamine building blocks were sought to link the two phosphinoamide fragments. This would result in a potentially tetradentate mixed-donor array. Using fc(NH₂)₂, where fc = 1,1'-diaminoferrocene, as a building block was intriguing because it has been used previously in diamido ligand sets for coordination to scandium.⁹⁹-¹⁰¹ These ligands are formed from fc(NH₂)₂ and chlorosilane to generate ligand precursors of the form fc(NHSiMe₂Bu)₂ (I in Figure 2.5).⁹³ In addition, fc(NH₂)₂ can be used in Buchwald-Hartwig coupling with arylbromides to generate ligand precursors of the form fc(NHAr)₂ (II in Figure 2.5)¹⁰,¹⁰²-¹⁰⁵

![Figure 2.5: Examples of fc(NH₂)₂ based bidentate ligand designs.](image-url)
The Diaconescu group have advocated using \( \text{fc(NH}_2\text{)}_2 \) in ligand design, citing desirable features such as: enforced \( cис \)-amido geometry, thereby sterically blocking one side of the metal center; the flexible geometry at iron can allow for electronic changes at the metal center; a weak-interaction is possible between iron and the metal; and the ferrocene backbone is redox active.\(^9\)

Our interest in using ferrocene to link the two nitrogen donors was based on the distance between the two nitrogen atoms. In order to best orient the phosphines to coordinate to the metal center in a tetradeutate array, we hypothesized that an appropriately large spacing of the amido donors would be beneficial. Additionally, the ability of the ferrocene unit to bend would allow some flexibility in the nitrogen-nitrogen distance. To this end, there are numerous examples of bridging groups as small as one atom connecting the two Cp rings of ferrocene.\(^1\) The steric protection offered by the ferrocene unit over simple organic diamines was deemed to be desirable.

While the redox-active nature of the ferrocene moiety has been studied in some of the related ligand designs, this was not a major factor in introducing ferrocene to our systems. However, our cyclic voltammetry studies have uncovered some interesting behavior, which will be discussed in Chapter 5.

### 2.3.2 Synthesis of a ferrocenyl diphosphinoamine

Treatment of \( 1,1\text{'}-\text{diaminoferrocene} \) with two equivalents of \( \text{ClP}^\text{Pr}_2 \) in the presence of \( \text{NEt}_3 \) gave di(phosphinoamine) 2.7 in 73 % yield (Scheme 2.4). Complex 2.7 in \( \text{C}_6\text{D}_6 \) displays high symmetry as is evident from the \( ^1\text{H} \) NMR spectrum: there are two resonances for the Cp ring protons and the N-H resonance exhibits \( ^2J_{\text{HP}} \) coupling of 8.8 Hz. The isopropyl groups are
all equivalent; thus, only one methine resonance is observed at δ 1.45 in the $^1$H NMR spectrum, however, there are two distinct signals for the methyl groups at δ 1.03 and 1.01.

![Scheme 2.4: Synthesis of a ferrocene-linked di(phosphinoamine)](image)

**Scheme 2.4:** Synthesis of a ferrocene-linked di(phosphinoamine)

### 2.3.3 Synthesis of a ferrocenyl phosphinoamide scandium alkyl complex

The scandium alkyl complex **2.8** is synthesized by alkane-elimination following the same protocol as for **2.6**. Due to the room temperature $^1$H NMR spectrum of **2.8** in C₆D₆ exhibiting very broad signals, a variable temperature study was performed in toluene-$d_8$ (Figure 2.6). At -75 °C the $^1$H NMR spectrum is consistent with a $C_5$ symmetric species in solution. At this temperature, four relatively sharp Cp resonances are observed, and there are two distinct isopropyl environments, which appear as four inequivalent methyl groups. At temperatures above -35 °C, the coalescence of the ferrocene and isopropyl methyl resonances occurs. In contrast to the broad room temperature $^1$H NMR spectrum, the $^{31}$P{$^1$H} NMR spectrum of **2.8** shows a sharp singlet in toluene-$d_8$. This behavior is consistent with reversible dissociation of THF in non-coordinating solvent.
Figure 2.6: 400 MHz variable temperature $^1$H NMR spectra of 2.8 recorded in toluene-$d_8$ (#), THF (*) and TMS (^
) are identified in the bottom spectrum.

When NMR samples of 2.8 are prepared in THF-$d_8$ a higher symmetry species is observed in the $^1$H NMR spectrum with only two resonances for the ferrocene backbone, whereas addition of one equivalent of THF to a C$_6$D$_6$ NMR sample led only to further broadening of the ferrocene and isopropyl resonances. These findings suggest that in THF solution the scandium center has two THF molecules bound to the metal in positions $trans$ to one another, while in C$_6$D$_6$ reversible dissociation of one bound THF molecule is observed (Scheme 2.5).
Scheme 2.5: Proposed equilibrium for 2.8, where in C_{6}D_{6} the left equilibrium was observed, and in THF the equilibrium favors the structure on the far right.

In order to shed light on the room temperature behavior of complex 2.8, the THF donor was exchanged for another neutral oxygen-based donor. Complex 2.8 was treated with triphenylphosphine oxide in toluene, subsequent removal of the volatiles furnished fc(NP^iPr_2)Sc(CH_2SiMe_3)(OPPh_3) 2.9, see Scheme 2.6. The room temperature $^1$H NMR spectrum for 2.9 has sharp resonances and the spectrum is consistent with a complex of C_{s} symmetry, like that observed at -75 °C for 2.8. The room temperature behavior of 2.9 confirms that it is likely the reversible dissociation of THF that results in the fluxional behavior seen in scandium alkyl complex 2.8.

Scheme 2.6: Synthesis of scandium alkyl complexes 2.8 and 2.9.
The low temperature $^1$H NMR data for complex 2.8 is as expected when compared to the geometry observed in the solid-state molecular structure (shown in Figure 2.7). In the solid state, 2.8 contains a bound THF molecule, and the scandium-oxygen bond length of 2.1918(11) Å is no longer than that found in complex 2.6, 2.197(2) Å.

**Figure 2.7**: ORTEP diagrams (drawn with 50 % ellipsoids) for comparison of the core geometries around scandium in complexes 2.6 and 2.8, all hydrogen atoms and some carbon atoms are omitted for clarity.
Table 2.3: Comparison of bond lengths and angles at scandium in 2.6 and 2.8.

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<tr>
<td>O1-Sc1-C29/C23</td>
<td>88.3(1)</td>
<td>100.83(5)</td>
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<tr>
<td>Sc1---Fe1</td>
<td></td>
<td>3.95</td>
</tr>
<tr>
<td>P2N2(plane)---Sc1</td>
<td></td>
<td>1.0454(4)</td>
</tr>
</tbody>
</table>

A comparison of complexes 2.6 and 2.8 shows the geometric changes imparted by linking the two phosphinoamide fragments; the two structures are shown in Figure 2.7 and selected bond lengths and angles are summarized in Table 2.2. The most obvious change is the enforced *cis* orientation of the two amido-donors in complex 2.8. The Sc-N distances of 2.0627(13) and 2.0624(13) Å in 2.8 are slightly shorter than those in 2.6, 2.099(2) and 2.100(2) Å. In contrast, we observed much longer Sc-P distances of 2.9201(5) and 2.9582(5) Å in 2.8 compared to 2.7115(9) and 2.6965(9) Å in 2.6. In fact, the scandium-phosphorus bond lengths are greater than the sum of the covalent radii (2.78 Å), indicative of a very weak phosphorus-scandium bond. This seems to result in a more open-coordination sphere, which is evident from O-Sc-C bond angles that increase from roughly 88° in 2.6 to 100° in 2.8. Also noteworthy in the solid-state structure of 2.8, is that the scandium-iron distance of 3.95 Å is much longer than the
sum of the covalent radii for those elements (3.02 Å); and the scandium center sits approximately 1 Å above the plane defined by the N₂P₂ donor set.

2.3.4 Synthesis of a discandium dihydride complex

Having accomplished the synthesis of a scandium alkyl complex with a more rigid ferrocene-based ligand set, the reactivity of the alkyl complex with H₂ was examined. Complex 2.8 reacts slowly under 4 atm of H₂ in hexanes to generate scandium hydride 2.10 as shown in Scheme 2.7. The formation of 2.10 takes 2 weeks under 4 atm of H₂ and is performed without stirring to yield a yellow, crystalline product in 79 % yield. Interestingly, performing the reaction with stirring has a negative effect on the outcome of the reaction: a dark brown powder is obtained that when characterized by elemental analysis is not consistent with 2.10. It is unlikely that decoordination of THF is required (as shown in Scheme 2.6) for 2.8 to react with H₂ because complex 2.6 reacts with H₂ gas to give 2.2. As well, the presence of coordinated THF in bimetallic product 2.10 implies that the loss of THF from 2.8 is not required for reaction with H₂. Hydrogenation of 2.9 gave only a complex mixture of phosphorus-containing products, as did exposure of THF solutions of 2.8 to 4 atm of H₂. This implies that the six-coordinate complex 2.8, the central structure in Scheme 2.6, is most likely the species to react dihydrogen. It may also be that precipitation from solution prevents 2.10 from undergoing subsequent undesirable reactions.
Scheme 2.7: Synthesis of discandium dihydride complex 2.10

The solid-state molecular structure of 2.10 is shown in Figure 2.8. An unexpected structural feature of 2.10 is that one amidophosphine fragment per ferrocene unit bridges the two metal centres, in addition to the bridging hydrides. This results in a Sc-Sc distance of 3.2026(8) Å, that is shorter than other structurally characterized scandium hydride complexes for which this Sc-Sc distance is observed to be between 3.30 and 3.33 Å for bimetallic complexes; however, the Sc-Sc separation in 2.10 is comparable to a hydride bridged tetrametallic complex. The Sc-P bond length for the bridging unit is 2.9097(7) Å, which is similar to the Sc-P bond lengths of 2.9201(5) and 2.9582(5) Å in complex 2.8. The nonbridging phosphinoamide arm is not coordinated to scandium, and these pendant phosphine arms are 3.0782(7) Å from the metal center. Interestingly, the N₂P₂Sc₂ core atoms in the solid-state structure of 2.10 form an inorganic, planar, six-membered ring.
Figure 2.8: ORTEP representations of the solid-state molecular structure of 2.10. Thermal ellipsoids are drawn at 50% probability 'Pr methyl atoms and hydrogen atoms are omitted for clarity, except the hydride ligands, which were located in the Fourier difference map and refined isotropically.

Table 2.4: Selected bond lengths and angles for complex 2.10

<table>
<thead>
<tr>
<th>Parameter</th>
<th>(Å/°)</th>
<th>Parameter</th>
<th>(Å/°)</th>
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<tr>
<td>N1-Sc1</td>
<td>2.0977(18)</td>
<td>Sc1---Fe1</td>
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<td>N2-Sc1</td>
<td>2.1185(19)</td>
<td>Sc1-H27</td>
<td>1.93(2)</td>
</tr>
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<td>P1---Sc1</td>
<td>3.0782(7)</td>
<td>N1-Sc1-N2</td>
<td>98.43(7)</td>
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<tr>
<td>P2-Sc1 i</td>
<td>2.9097(7)</td>
<td>N1-Sc1-H27</td>
<td>109.5(7)</td>
</tr>
<tr>
<td>Sc1-O1</td>
<td>2.2417(15)</td>
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<td>87.0(7)</td>
</tr>
<tr>
<td>Sc1---Sc1 i</td>
<td>3.2026(8)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The extremely low solubility of complex 2.10 proved problematic for carrying out solution phase characterization. Attempts to obtain suitable NMR spectra of 2.10 in THF-\textit{d}_8, pyridine-\textit{d}_5 or CD$_2$Cl$_2$ all failed. In an effort to show that the molecular structure of 2.10 was representative of the bulk sample powder X-ray diffraction data was obtained. A plot of the simulated powder pattern from the single crystal X-ray diffraction data was compared to that measured for powder samples. The data from these measurements are included in Appendix B and show very good agreement between the two powder patterns. Additionally, the elemental analysis for 2.10 is in good agreement with the composition obtained from the single crystal X-ray structure.

Complex 2.10 was also characterized using solid-state $^{31}$P{\textit{1}H} NMR spectroscopy, employing cross-polarization (CP) $^{1}$H-decoupling and magic angle spinning (MAS) to obtain suitable spectra.$^{111}$ The expected spectrum for 2.10 should contain only two inequivalent nuclei in the solid-state, due to two of the four phosphorus nuclei in the unit cell being generated by inversion symmetry. Indeed, in the solid-state only inversion symmetry ensures magnetically equivalent nuclei at all possible orientations.$^{112}$ The spectra taken with various spinning rates are shown in Figure 2.9. At a fast spinning rate the spinning side bands, which result from anisotropy,$^{112}$ are almost completely removed and the isotropic resonances can be identified at $\delta$ 39.2 and 53.6. Using variable recovery-delay times we have estimated the T$_1$ values to be between 10 and 12 s, employing 60 s delay times we can reliably integrate the resonances as 1:1, which is consistent with the solid-state molecular structure.
Figure 2.9: $^{31}$P CP-MAS NMR spectra (162 MHz) of 2.10 recorded at room temperature at various spinning rates.
All attempts to solubilize 2.10 using polar solvents failed: using THF, pyridine or CH₂Cl₂ results in no dissolution. By extension, the insolubility of 2.10 has been problematic for reactivity studies, for example, reaction of 2.10 with CO in a THF results in no evidence of reaction. When a suspension of 2.10 in fluorobenzene was treated with excess 1-hexene a mixture of phosphorus-containing products was evident by NMR spectroscopy and no polymer formation was observed. Ultimately, attempted small molecule reactivity studies of 2.10 were abandoned due to problems of insolubility.

2.4 Conclusion

An alkane-elimination pathway to phosphinoamide complexes of scandium and yttrium was employed to synthesize complexes of the form (ArNPᵢPr₂)₃M(THF). While mixed alkyl-phosphinoamide yttrium complexes were observed in solution they could not be isolated from the reaction mixtures. In contrast, an alkyl-diphosphinoamide scandium complex was isolated and structurally characterized. Reaction of the alkyl-diphosphinoamide scandium complex with H₂ resulted in the formation of (ArNPᵢPr₂)₃Sc(THF), demonstrating that redistribution of the phosphinoamide ligands was occurring. This discovery led to the development of a dianionic and tetradentate ligand set based on 1,1′-diaminoferrocene. The new ferrocene-linked diphosphinoamide scandium alkyl complex demonstrated fluxional behavior, which has been attributed to a labile THF molecule. Hydrogenation of the ferrocenyl diphosphinoamide scandium alkyl complex resulted in the isolation of a discandium dihydride complex. The solid-state molecular structure revealed that in the bimetallic complex the scandium centers are bridged not only by the hydride ligands but also by two of the phosphinoamide fragments. The low solubility of the discandium dihydride complex prompted NMR spectroscopic analysis in the
solid state using magic angle spinning. The solid state NMR data is consistent with the
discandium dihydride structure observed by X-ray crystallography. Unfortunately insolubility of
this interesting discandium complex hindered attempts to examine its reactivity toward small
molecules. However, the potential for the ferrocene-linked phosphinoamide ligand to act as
either a tetradeutate chelating ligand or as a bridging ligand has been observed.
3 Tri(phosphinoamide) complexes of zirconium

3.1 Introduction

Early applications of zirconium hydrides have focused on stoichiometric transformations such as the hydrozirconation of alkenes and alkynes. Indeed, methodology such as hydrozirconation has received widespread attention\textsuperscript{\ref{113}} and a number of subsequent transformations are known that introduce a variety of functional groups to the organic fragment. Additionally, zirconium hydrides have been shown to be intermediates in catalytic transformations. One example is the dehydrocoupling of main-group element hydrides to generate element-element bonds and H\textsubscript{2}. Zirconium complexes in particular have proven to be effective catalysts for the dehydrocoupling of phosphines, which is an attractive approach for P-P bond formation because the byproduct is hydrogen gas. The general strategy for early transition metal catalyzed dehydrocoupling is shown in Scheme 3.1.\textsuperscript{\ref{114}}

\begin{center}
\begin{tikzpicture}
    \node (lp) at (0,0) {\text{Ln}M\text{--}H};
    \node (l1) at (-2,-1) {\text{Ln}M\text{--}PR\textsubscript{2}};
    \node (l2) at (2,-1) {\text{Ln}M\text{--}PR\textsubscript{2}};
    \node (r1) at (-2,1) {R\textsubscript{2}P\text{--}PR\textsubscript{2}};
    \node (r2) at (2,1) {HPR\textsubscript{2}};
    \node (r3) at (0,-2) {HPR\textsubscript{2}};
    \node (r4) at (0,2) {H\textsubscript{2}};
    \draw [-stealth] (lp) to (l1);
    \draw [-stealth] (l1) to (l2);
    \draw [-stealth] (l2) to (lp);
    \draw [-stealth] (l1) to (r1);
    \draw [-stealth] (l2) to (r2);
    \draw [-stealth] (r1) to (lp);
    \draw [-stealth] (r2) to (lp);
    \draw [-stealth] (lp) to (r3);
    \draw [-stealth] (l2) to (r4);
    \draw [-stealth] (lp) to (r4);
\end{tikzpicture}
\end{center}

\textbf{Scheme 3.1}: General strategy for dehydrocoupling primary phosphines with early transition metal catalysts (adapted from ref 114)

There are currently two types of zirconium complexes with a demonstrated ability to catalytically dehydrocouple phosphines. The Stephan group has designed zirconium metallocene precatalysts, of the form Cp\textsuperscript{*}\textsubscript{2}ZrH\textsubscript{3}M (M = Li, K), that have been successfully employed.\textsuperscript{\ref{115,116}}
Using this catalyst system with primary phosphines, RPH₂ (R = Ph, Cy, 2,4,6-trimethylphenyl), a five membered phosphorus cycle (RP)₅ was the major product. The proposed mechanism by which this catalyst operates is by initial activation of both P-H bonds in a single phenylphosphine molecule to form a zirconium phosphinidene intermediate. Subsequent addition of one and two equivalents of phosphine generates three and four membered metallacycle intermediates respectively and these intermediates were observed using NMR spectroscopy. One part of the mechanism that is poorly understood is the formation of the (RP)₅ product. Two possible explanations are: initial reductive elimination of (RP)₃ (which is known to thermally isomerize to (RP)₅), or via additional insertions of primary phosphine. The proposed intermediates for the catalytic transformation are shown in Scheme 3.2.

![Scheme 3.2: Proposed intermediates in the catalytic oligomerization of primary phosphines using Cp*₂ZrH₃M (M = Li, K) (adapted from ref 116)
The second zirconium catalyst system for phosphine dehydrocoupling was developed by the Waterman group. In this system, primary phosphines, RPH₂ (R = Ph, 'Bu), were selectively dehydrocoupled at 90 °C to give rise to products of the form (RHP-PHR). In addition, CyPH₂ was dehydrocoupled but gave a mixture of (CyPH)₂ and (CyPH)₄. Scheme 3.3 depicts the proposed mechanism using the Waterman catalyst system, which proceeds via σ-bond metathesis steps. The key step is opening of the strained four-membered metallacycle to activate the P-H bond of the phosphine, to form the metal phosphide complex (see below). The subsequent steps involve σ-bond metathesis at the Zr-P bond to generate a zirconium hydride complex. A cyclometallation step releases the dihydrogen byproduct, and regenerates the four-membered metallacycle.

Scheme 3.3: A proposed mechanism for phosphine dehydrocoupling (adapted from ref 117).
The aforementioned systems serve only to highlight the role of zirconium catalysis in the field of phosphine dehydrocoupling. This is a growing research area and catalysts based on Ti\(^{116,118}\) and late transition metals\(^{119}\) are emerging, along with main group reagents for stoichiometric dehydrocoupling.\(^{120,121}\) Interesting applications for phosphine dehydrocoupling include the synthesis of a P\(_{16}\)Ph\(_8\) macrocycle via catalytic dehydrocoupling of 1,2-(PH\(_2\))\(_2\)Ph.\(^{122}\) These reports serve to demonstrate that zirconium phosphide complexes are interesting synthetic targets because they may serve as precursors to zirconium hydrides.

The zirconium complex of the form \((\text{ArNP}^\text{Pr}_2)_3\text{ZrCl}\) (Ar = 3,5-dimethylphenyl) was synthesized and used as a precursor for the synthesis of organometallic complexes. Additionally, a tetrahydroborate and phenylphosphide zirconium complex were synthesized and examined as precursors to a zirconium hydride complex.

### 3.2 Synthesis of phosphinoamide zirconium complexes

The generation of phosphinoamide lithium complexes has been well studied due to interest in the fundamental nature of the bonding of phosphinoamides. Using phosphinoamine 2.1 \((\text{ArNHP}^\text{Pr}_2)\) and \(^9\text{BuLi}\) in diethyl ether the dinuclear lithium complex 3.1 was synthesized, which has one diethyl ether molecule bound to each lithium atom. Colourless single crystals of the dinuclear lithium complex were obtained by cooling a concentrated hexanes solution of 3.1 to -35 °C. The solid-state molecular structure (Figure 3.1) reveals that the two lithium atoms are bridged by the amide-nitrogen atoms, and are also coordinated by one diethyl ether molecule. The phosphorus atoms are not coordinated to the lithium atoms: the Li-P distance is 2.9096(9) Å. This is different from the related complex \([(\text{PhNPPh}_2\text{Li(OEt}_2)]\)\(_2\) which contains lithium atoms coordinated by both P and N donors from the phosphinoamide ligand.\(^{123}\) The P-N bond length in
3.1 is 1.6937(12) Å, which is very similar to the P-N length of 1.672(2) Å reported for the closely related derivative, [(PhNPPh$_2$Li(OEt$_2$)]. Other examples include complexes of the form [RNPPh$_2$Li(Et$_2$O)$_x$]$_y$ (R = $^t$Pr, CH$_2$Bu, C$_6$H$_2$-2,4,6-$^t$Bu), which have all been studied crystallographically, and contain N-P bond lengths in the range of 1.660(2) - 1.730(2) Å. The large range in N-P bond length is due to substituent effects, as was discussed in Section 1.1.

**Figure 3.1:** ORTEP diagram of the solid-state molecular structure of 3.1. Thermal ellipsoids are drawn at 50 % probability; hydrogen atoms and isopropyl methyls are omitted for clarity, and half the molecule is generated by symmetry.
Table 3.1: Selected bond lengths and angles for 3.1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>(Å)</th>
<th>Parameter</th>
<th>(Å / °)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1-P1</td>
<td>1.6937(12)</td>
<td>P1---Li1</td>
<td>2.9096(9)</td>
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<tr>
<td>N1-Li1</td>
<td>2.038(2)</td>
<td>Li1---Li2</td>
<td>2.510(5)</td>
</tr>
<tr>
<td>N1-Li2</td>
<td>2.046(2)</td>
<td>N1-Li2-N1</td>
<td>103.88(16)</td>
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<td>O1-Li1</td>
<td>1.957(4)</td>
<td>Li1-N1-Li2</td>
<td>75.84(11)</td>
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<tr>
<td>O2-Li2</td>
<td>1.941(4)</td>
<td>O1-Li1-Li2</td>
<td>180.0</td>
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</table>

In solution, complex 3.1 has a structure consistent with that observed in the solid state. A single resonance is observed at δ 55.3 in the $^{31}$P{¹H} NMR spectrum for complex 3.1 in C₆D₆. In addition, the resonances in the ¹H NMR spectrum are consistent with a single phosphinoamide environment, and the resonances attributed to the bound diethyl ether molecule are sharp implying the ether donors remain bound to Li in solution on the NMR time scale.

Upon reaction of 3.1 with ZrCl₄(THF)₂ in THF, the tri(phosphinoamide)zirconium complex (ArNPᵢPr₂)₃ZrCl, 3.2, was obtained as the sole product (Scheme 3.4). The outcome of this reaction is independent of the solvent used, and is also independent of the stoichiometry employed. For example, using a ratio of less than 1.5 (3.1 : ZrCl₄(THF)₂) still results in complex 3.2, even when 3.1 is added slowly to (toluene or THF) solutions at -78°C. These findings are not unusual and have been noted previously in reactions of lithium phosphinoamides with ZrCl₄(THF)₂.⁶¹
**Scheme 3.4:** The synthesis of lithium dinuclear complex 3.1, and the tri(phosphinoamide) zirconium complex 3.2.

The solid-state molecular structure of complex 3.2 was determined and is shown in Figure 3.2. There is a high degree of variability in the orientation of the phosphinoamide fragments, which are reminiscent of those observed for the yttrium complex 2.2. Indeed, structure 3.2 is analogous to 2.2 but with a substitution of yttrium for zirconium, and a THF molecule for a chloride ligand. The Zr-N bond lengths of 2.1032(19), 2.149(2) and 2.150(2) Å are as expected for zirconium phosphinoamide complexes and the Zr-P bond lengths of 2.6834(7) to 2.6874(7) Å are not unusual. The $^1$H and $^{31}$P-$^1$H NMR spectra are consistent with a complex of $C_3v$ symmetry due to reversible phosphine decoordination that results in
equivalent phosphinoamide ligands. The phosphine behavior observed in complex 3.2 has also been observed for yttrium and scandium complexes 2.2 and 2.3.

![Figure 3.2: ORTEP diagram of the solid-state molecular structure of 3.2. Ellipsoids are drawn at 50 % probability; hydrogen atoms and isopropyl methyls are omitted for clarity.](image)

**Table 3.2**: Selected bond lengths and angles for complex 3.2

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<td>2.1032(19)</td>
<td>N1-Zr1-N2</td>
<td>111.45(8)</td>
</tr>
<tr>
<td>Zr1-N2</td>
<td>2.149(2)</td>
<td>N1-Zr1-N3</td>
<td>104.37(8)</td>
</tr>
<tr>
<td>Zr1-N3</td>
<td>2.150(2)</td>
<td>N2-Zr1-N3</td>
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<td>Zr1-P1</td>
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</tr>
<tr>
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<td>P2-Zr1-P3</td>
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<td>2.4716(7)</td>
<td>Cl1-Zr1-P1</td>
<td>95.97(2)</td>
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</table>
The synthetic goal for this project was to obtain diphosphinoamide zirconium complexes, and one possible methodology for accomplishing this involved transamination. This approach has been used by the Thomas group to generate di(phosphinoamide)zirconium dimethylamido complexes. When complexes of the form (iPrNPPh2)2Zr(NMe2)2 were synthesized, from Zr(NMe2)4 and two equivalents of iPrNHPPh2, they were subsequently used as bidentate phosphine ligands for platinum.

Using Zr(NMe2)4 and two equivalents of phosphinoamine 2.1 (ArNH'Pr2) yields complex 3.3 (ArNP'Pr2)2Zr(NMe2)2 (Scheme 3.5). Subsequent exchange of the dimethylamido groups for chloride ligands was attempted using TMSCl. At room temperature, complex 3.3 does not react with 8 equivalents of TMSCl in toluene or THF solution. However, gentle heating to 60 °C in either solvent results in the generation of a complex mixture containing no fewer than 8 phosphorus resonances in the 31P{1H} NMR spectrum of the crude reaction mixture.

**Scheme 3.5**: Synthesis of 3.3 and the subsequent attempted synthesis of (ArNP'Pr2)2ZrCl2.

In order to test whether or not the phosphinoamide moieties are also being exchanged for chloride ligands the reaction of lithium salt 3.1 with TMSCl was performed and the resulting colourless oil was characterized by NMR spectroscopy. The 1H NMR spectrum for 3.4 in C6D6
contains a resonance at $\delta$ 0.31, which appears as a singlet corresponding to the silyl-methyl protons. The $^{31}\text{P} \{^1\text{H}\}$ NMR spectrum for 3.4 in C$_6$D$_6$ contains a singlet at $\delta$ 63.8. When reaction mixtures of complex 3.3 and (2, 4 or 8 equivalents) TMSCl are analyzed by $^{31}\text{P} \{^1\text{H}\}$ NMR spectroscopy a resonance at $\delta$ 63.8 is observed. Therefore, it can be concluded that the phosphinoamide fragments are competitively being exchanged along with the dimethylamido ligands upon reaction of 3.3 with TMSCl.

This problematic reaction of the phosphinoamide moieties with TMSCl, in conjunction with the ligand redistribution problems encountered in Chapter 2, highlight the difficulties associated with controlling ligand substitution using these phosphinoamide fragments as ancillary ligands.

3.3 Synthesis of organometallic tri(phosphinoamide) zirconium complexes

Attempts to control substitution of the phosphinoamide ligands on zirconium were ultimately unsuccessful. However, the trisubstituted complex 3.2 has a remaining chloride ligand that could be functionalized. To this end, ethyl Grignard and benzylpotassium were employed to generate monoalkyl zirconium derivatives via salt-metathesis (Scheme 3.6).

Scheme 3.6: Synthesis of organometallic tri(phosphinoamide) zirconium complexes.
Complexes 3.5 and 3.6 are synthesized as the sole phosphorus-containing products of the reactions. Solutions of 3.5 and 3.6 in C\textsubscript{6}D\textsubscript{6} have \textsuperscript{1}H NMR spectra that are consistent with complexes of C\textsubscript{3v} symmetry and the phosphinoamide ligand resonances are similar to those observed for complex 3.2. Notably, the \textsuperscript{1}H NMR resonances for the \(\alpha\)-protons on the ethyl and benzyl groups have \(^3J\text{HP}\) coupling constants of 2.8 Hz and 4.8 Hz, respectively. A complete \textsuperscript{1}H NMR spectrum for 3.6 is shown in Figure 3.3.

![NMR spectrum](image)

**Figure 3.3:** \textsuperscript{1}H NMR spectrum (400 MHz) of complex 3.6 in C\textsubscript{6}D\textsubscript{6}

Single crystals of the benzyl complex (3.6) were obtained from cooling a concentrated hexanes solution to -35 °C for 2 weeks. The solid-state molecular structure is shown in Figure 3.4, and all the phosphinoamides moieties are distinct. However, there is not as much variation in
the metal-amido lengths within the molecule as compared to complex 3.2. The benzyl group is bound in a simple $\eta^1$-fashion to the zirconium center, which is apparent from the Zr1-C43-C44 angle of 126.62(14)$^\circ$; benzyl groups that are designated as $\eta^2$-bound typically have angles Zr-C-C bond angles smaller than 96$^\circ$.\textsuperscript{124}

Figure 3.4: ORTEP diagram of the solid-state molecular structure of 3.6. Ellipsoids are drawn at 50 % probability; hydrogen atoms and isopropyl methyls are omitted for clarity.
Table 3.3: Selected bond lengths and angles for 3.6

<table>
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<th>(°)</th>
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<td>105.89(6)</td>
</tr>
<tr>
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<td>105.04(6)</td>
</tr>
<tr>
<td>Zr1-N3</td>
<td>2.1588(17)</td>
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<td>125.49(6)</td>
</tr>
<tr>
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<td>95.15(5)</td>
</tr>
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<td>89.96(5)</td>
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<tr>
<td>Zr1-C43</td>
<td>2.308(2)</td>
<td>Zr1-C43-C44</td>
<td>126.62(14)</td>
</tr>
</tbody>
</table>

The zirconium alkyl complexes, 3.5 and 3.6, are thermally stable. Heating toluene solutions at 110 °C for three days resulted in no observable decomposition. This thermal stability was somewhat surprising in the case of complex 3.5, due to the presence of β-hydrogens on the ethyl-substituent, which raised the possibility of an elimination pathway to potentially result in a zirconium hydride via loss of ethylene. However, this is likely prevented due to steric congestions around the metal center.

3.4 Attempted hydrogenolysis of zirconium alkyls

The hydrogenolysis of zirconium alkyl complexes is a reaction of fundamental importance, due to the interest in the resulting zirconium hydride species. To this end, solutions of the organometallic derivatives 3.5 and 3.6, were stirred under 4 atm of H₂. While 3.6 does not react with H₂ under these conditions, complex 3.5 undergoes extremely slow conversion to a new complex (see Scheme 3.7); this reaction was approximately 10 % complete after 6 weeks. This conversion was estimated both by $^{31}$P{¹H} NMR spectroscopy by integration of a new singlet at...
δ 7.1, and integration of a new resonance in the $^1$H NMR spectrum that appears at δ 8.75 as a quartet with a coupling constant of $^2J_{HP} = 18.9$ Hz. While the spectroscopic analysis of the reaction mixture is consistent with a terminal hydride zirconium complex, we were unable to isolate the product from the reaction mixture or obtain any solid-state characterization.

**Scheme 3.7**: Reaction of complex 3.5 with H$_2$ to generate a terminal hydride complex.

Despite the sluggish nature of the reaction of complex 3.5 with H$_2$, it demonstrated that a phosphinoamide zirconium hydride complex may be accessible. This motivated further investigation into alternate methods of synthesizing zirconium hydride complexes.

### 3.5 Alternative approaches to hydride complexes

The generation of early transition metal hydride complexes can be accomplished by many different methodologies. While addition of H$_2$ to a metal-alkyl complex (cf. section 3.4) is one of the simplest approaches, there are other functional groups that can be transformed into metal hydrides. For example, tetrahydroborate and tetrahydroaluminate metalloocene complexes have been synthesized and upon reaction with a strong Lewis base, the BH$_3$ or AlH$_3$ unit can sometimes be removed to generate the desired metal hydride complex.
To this end, tetrahydroborate and tetrahydroaluminate tri(phosphinoamide) zirconium complexes were sought. While reaction of complex 3.2 with LiAlH₄ gave a mixture of products, using an excess of NaBH₄ gave very slow conversion to a single product (Scheme 3.8).

Scheme 3.8: Synthesis of zirconium tetrahydroborate complex 3.7.

The $^{31}$P{¹H} NMR spectrum of complex 3.7 in C₆D₆ contains a single resonance at δ 5.7, which is slightly shifted upfield from 3.2, at δ 7.2. The $^{11}$B{¹H} NMR spectrum of 3.7 displays a resonance at δ -20.4, and the ¹H NMR spectrum is consistent with a complex of C₃ᵥ symmetry. In the ¹H NMR spectrum, resonances for the BH₄ protons appear as four broad signals centered at 1.80; this is due to the quadrupolar $^{11}$B nucleus, which has a spin of 3/2.
Single crystals of tetrahydroborate complex 3.7 were obtained by cooling a concentrated hexanes solution to -35 °C, and the solid-state molecular structure is shown in Figure 3.5. Complex 3.7 contains a BH₄⁺ ligand that is coordinated in η³-fashion to the zirconium center. While other bonding modes (η¹ and η²) are known, the η³ bonding mode is the most common for the early transition metals.¹²⁵ The Zr-B distance of 2.431(2) Å is slightly longer than typical η³-BH₄⁻ ligands on zirconium, which are reported to be between 2.32 and 2.40 Å.³⁶,¹²⁶,¹²⁷ The Zr-H distances observed in complex 3.7 (2.22(2) - 2.28(2) Å) are not unusual for tetrahydroborate complexes.

![Figure 3.5](image-url)  
**Figure 3.5:** ORTEP diagram of the solid-state molecular structure of 3.7. Thermal ellipsoids are drawn at 50 % probability; isopropyl methyls and hydrogen atoms are omitted for clarity with the exception of the tetrahydroborate hydrogens, which were located in the Fourier difference map and were refined isotropically.
Table 3.4: Selected bond lengths and angles for 3.7

<table>
<thead>
<tr>
<th>Parameter</th>
<th>(Å)</th>
<th>Parameter</th>
<th>(Å / °)</th>
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<td>Zr1-H100</td>
<td>2.24(2)</td>
</tr>
<tr>
<td>Zr1-N2</td>
<td>2.1611(14)</td>
<td>Zr1-H101</td>
<td>2.28(2)</td>
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<tr>
<td>Zr1-N3</td>
<td>2.1666(15)</td>
<td>Zr1-H102</td>
<td>2.22(2)</td>
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<tr>
<td>Zr1-P1</td>
<td>2.7213(5)</td>
<td>N1-Zr1-B1</td>
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<td>Zr1-P2</td>
<td>2.6781(5)</td>
<td>N2-Zr1-B1</td>
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<td>Zr1---B1</td>
<td>2.431(2)</td>
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For zirconium and hafnium tetrahydroborate complexes, the addition of donors such as PMe₃ has been shown to result in formation of Me₃PBH₃, and the associated metal hydride complex.³³⁻³⁵ Unfortunately, when NEt₃, PMe₃ or pyridine was added to toluene solutions of complex 3.7 no reaction was observed.

3.6 Synthesis of a zirconium phosphide complex

The primary phosphide complex, 3.8, can be synthesized using 3.2, and PhPHLi, which is generated in situ (Scheme 3.9). Single crystals of 3.8 were obtained and the solid-state structure is shown in Figure 3.6. The zirconium-phosphorus distance of 2.6830(6) Å for the phosphide is equal, within experimental error, to other zirconium-phosphorus distances (2.66 – 2.71 Å) in the molecular structure of 3.8. However, a comparison to other structurally characterized zirconium phosphide complexes reveals this Zr-P bond length to be relatively long. For example, the Zr-P bond distance found for Cp₂ZrCl(PH(C₆H₂-2,4,6-‘Bu₃))¹²₈ is 2.543(3) Å and for Cp₂ZrCl(P(SiMe₃)₂)¹²⁹ is 2.547(6) Å. A longer Zr-P distance of 2.629 Å has been reported for a
terminal phosphide in $\text{Cp}_2\text{ZrCH}_3[\text{P(SiMe}_3\text{)}_2]^{130}$ and bridging phosphide-units have bond distances in the range of 2.6161(8) - 2.722(5) Å. $^{32,131,132}$

**Scheme 3.9: Synthesis of a zirconium phosphide complex**

In the solid-state structure, complex 3.8 has contains a phosphide fragment in which the phosphorus atom has pyramidal geometry. The sum of the bonding angles at P4 is 315°, whereas for a planar geometry the sum of angles would be 360°. In contrast, zirconium phosphide complexes have been reported with planar geometry at phosphorus. For example, chelating tridentate ligands containing a central phosphide-ligand which is planar,$^{32,132}$ and is consistent with $\pi$-donation from the phosphide-unit to the zirconium center.

Additionally, the three phosphinoamide fragments in the solid-state structure of 3.8 are arranged in a pattern similar to that observed in complexes 3.2, 3.6, and 3.7. The Zr-N and Zr-P bond lengths and angles are unremarkable as compared to these aforementioned complexes.
Figure 3.6: ORTEP diagram of the solid-state molecular structure of 3.8. Thermal ellipsoids are drawn at 50% probability; isopropyl methyls and hydrogen atoms are omitted for clarity with the exception of H100, which was located in the Fourier difference map and was refined isotropically.

Table 3.5: Selected bond lengths and angles for 3.8

<table>
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<th>Parameter</th>
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<th>(Å / °)</th>
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<td>2.0977(16)</td>
<td>P4-H100</td>
<td>1.29(2)</td>
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<td>Zr1-N3</td>
<td>2.1676(16)</td>
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<td>113.56(7)</td>
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<td>Zr1-P4-H100</td>
<td>102.9(10)</td>
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<td>Zr1-P3</td>
<td>2.6564(5)</td>
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</tbody>
</table>
Interestingly, the solid-state structure of 3.8 contains two phenyl groups arranged in a π-π stacking geometry. The arene groups attached to atoms N1 and N2 in Figure 3.5 display this interaction. The centroid-centroid distance of the two rings is 3.654 Å, and the ipso carbons are only 3.386 Å apart. The carbon-carbon separations increase going from the ortho position toward the para position and Table 3.6 presents a summary of these distances. While the π-π stacking interactions are potentially useful for crystal design in supramolecular systems,133 the appearance of such an interaction in 3.8, but not the related complexes 3.2, 3.6 or 3.7 is merely a point of curiosity, secondary to the synthetic applications being investigated.

Table 3.6: Carbon-carbon distances of two π-stacked arene rings in complex 3.8

<table>
<thead>
<tr>
<th>Carbon Pair</th>
<th>Distance (Å)</th>
<th>Carbon Pair</th>
<th>Distance (Å)</th>
</tr>
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<tbody>
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<td>Meta</td>
<td>3.724</td>
</tr>
<tr>
<td>Ortho</td>
<td>3.596</td>
<td>Meta</td>
<td>3.861</td>
</tr>
<tr>
<td>Ortho</td>
<td>3.446</td>
<td>Para</td>
<td>3.938</td>
</tr>
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</table>

The solution behavior of complex 3.8 has been examined using NMR spectroscopy. The $^{31}$P{$^1$H} NMR spectrum of 3.8 in C$_6$D$_6$ displays two resonances, a doublet at δ 2.4 corresponding to the three equivalent phosphinoamide fragments and a quartet at δ -38.8 ($^2$J$_{PP}$ = 27.9 Hz). Additionally, in the $^1$H NMR spectrum the resonance corresponding to the P-H moiety on the phosphide-group at δ 4.66 appears as a doublet of quartets, with a $^1$J$_{HP}$ coupling constant of 214 Hz and a $^3$J$_{HP}$ coupling constant of 9.2 Hz: these spectra are shown in Figure 3.7.
Figure 3.7: $^{31}$P-$^1$H NMR spectrum (161 MHz) of 3.8 (A) and $^1$H NMR spectrum (400 MHz) of 3.8 (B), both in C$_6$D$_6$. 
The reactivity of complex 3.8 was investigated with a view towards generating a zirconium hydride complex. Complex 3.8 was found to be unreactive towards PhPH$_2$ in toluene solution, even at temperatures of 120 °C. Additionally, complex 3.9 was found to be unreactive toward PhSiH$_3$; this reaction was attempted due to the finding by the Waterman group that heterodehydrocoupling can also be accomplished with zirconium-based catalysts.$^{134}$

3.7 Conclusion

The synthesis of [(ArNP$i$Pr$_2$)Li(OEt$_2$)$_2$]$_2$ was accomplished via simple deprotonation of the phosphinoamine using $^n$BuLi. This lithium phosphinoamide proved to be a good starting material for the synthesis of (ArNP$i$Pr$_2$)$_2$ZrCl, but the disubstituted derivative [(ArNP$i$Pr$_2$)$_2$ZrCl$_2$] could not be synthesized via the lithium phosphinoamide or from reaction of (ArNP$i$Pr$_2$)$_2$Zr(NMe$_2$)$_2$ with TMSCl. Complex (ArNP$i$Pr$_2$)$_2$ZrCl was shown to be an excellent precursor for (ArNP$i$Pr$_2$)$_2$ZrBH$_4$, (ArNP$i$Pr$_2$)$_2$ZrPHPh and organometallic zirconium complexes. The organometallic complexes of the form (ArNP$i$Pr$_2$)$_2$ZrR (R = Et, CH$_2$Ph) were found to be highly stable and relatively unreactive towards H$_2$, with the ethyl-derivative converting very slowly to generate traces of (ArNP$i$Pr$_2$)$_2$ZrH. (ArNP$i$Pr$_2$)$_2$ZrBH$_4$ could not be induced to react with Lewis bases such as NEt$_3$ or PMe$_3$ to yield (ArNP$i$Pr$_2$)$_2$ZrH, and (ArNP$i$Pr$_2$)$_2$ZrPHPh was similarly unreactive toward primary phosphines and silanes.

The work described in this chapter demonstrates that it is difficult to control the substitution of phosphinoamides on zirconium, which parallels the difficulties encountered controlling the substitution pattern at scandium and yttrium in Chapter 2. The use of the ferrocene-linked diphosphinoamide ligand 2.7 on zirconium is explored in Chapter 4.
4 Ferrocene-linked phosphinoamide complexes of zirconium

4.1 Introduction

Zirconium organometallic complexes have found numerous uses, the most prominent of which are olefin polymerization\textsuperscript{135,136} and the hydrozirconation reaction.\textsuperscript{113} Additionally, migratory insertion processes such as CO and most appropriately isocyanide insertions have garnered interest. One reason is that migratory insertion of these substrates into the zirconium-carbon bond results in carbon-carbon bond formation. While one of the most widely used substrates for migratory insertion is carbon monoxide,\textsuperscript{137} which when inserted into a zirconium-carbon bond generates an acyl complex. The resulting metal acyl complexes are of interest but they are also highly reactive intermediates, and in some cases the insertion is reversible.\textsuperscript{138} In contrast isocyanides (CNR), which are isoelectronic to CO, can insert into metal-carbon bonds in a similar fashion to generate iminoacyl complexes, which are generally stable. The insertion of isocyanides into a zirconium alkyl bond occurs \textit{via} coordination of the isocyanide to the metal center, followed by migration of the alkyl group to the metal-bound carbon. In zirconocenes, it has been demonstrated that the initial isocyanide coordination occurs adjacent to both alkyl groups; in other words, the alkyl groups remain \textit{cis} to one another.\textsuperscript{139} Following coordination, the migration of the alkyl group forms the kinetically favored ‘N-outside’ complex, or proximal (the R groups remain adjacent), which undergoes low temperature rearrangement to the more thermodynamically favorable ‘N-inside’ complex, or distal (the R groups are separated), as shown in Scheme 4.1.\textsuperscript{140}
Iminoacyl complexes are of interest due to the possibility of several subsequent transformations, which are illustrated in Scheme 4.2: (a) iminoacyl ‘coupling’ to form an enediamido moeity\textsuperscript{141,142} (b) a 1,2-hydrogen shift reaction to give an imidoalkene functionality, or (c) a second alkyl group migration to generate a zirconaziridine\textsuperscript{143} In some cases, pathway (c) has also been shown to result in complete breaking of the N-C triple bond resulting in a zirconium imido complex, with concomitant production of an alkene byproduct\textsuperscript{144-146}.
Scheme 4.2: Various outcomes of isocyanide insertion reactions with zirconium dialkyl complexes (adapted from ref 146).

The insertion of isocyanides into zirconium-carbon bonds is also of interest from the perspective of ligand design. One example involves using linked and unlinked guanidinate ligands: 'PrNC(NH'Pr)N'Pr, and ['PrNC(NH'Pr)NCH₂]₂. Following insertion of one arylisocyanide and thermolysis, the zirconium dibenzyl complex featuring the two unlinked ligands yields a zirconium imido (pathway c).₁⁴⁵ In contrast, using the linked guanidinate system, a zirconium amidoalkene complex is produced (pathway b).₁⁴⁷ The difference in reactivity has been ascribed to the more open coordination sphere in the linked system, which results in trans-arrangement of the benzyl groups in the parent zirconium dibenzyl complex. Other studies
employing zirconium guanidinate complexes have also proposed that steric bulk has an effect on the outcome of isocyanide insertion chemistry.\textsuperscript{146}

Many types of ancillary ligands, such as aryloxides,\textsuperscript{141,142,148} calixarenes,\textsuperscript{139,148-150} amidates,\textsuperscript{151} amidinates,\textsuperscript{152} cyclopentadienes,\textsuperscript{140,153-156} and tridentate diamido-carbene\textsuperscript{157} have been employed to study zirconium iminoacyl complexes. The effect of the ancillary ligand on the outcome of these reactions remains difficult to predict.

The possibility of generating a zirconium imido complex from isocyanide insertion prompted us to examine this chemistry \textit{in lieu} of CO insertion. Herein, the synthesis of a series of organometallic zirconium complexes of the form fc(NP\textsuperscript{t}Pr\textsubscript{2})\textsubscript{2}ZrR\textsubscript{2} (fc = 1,1'-ferrocenyl, R = CH\textsubscript{3}, CH\textsubscript{2}Ph, CH\textsubscript{2}tBu, tBu) and the corresponding iminoacyl complexes are synthesized by insertion of one equivalent of (2,6-dimethylphenyl)isocyanide. The resulting iminoacyl complexes are thermally stable, with the exception of the benzyliminoacyl complex, which rearranges \textit{via} a 1,2-hydrogen shift to give an alkene-amido complex.

\textbf{4.2 Synthetic route to ferrocenyl diphosphinoamide zirconium complexes}

A potential strategy for the synthesis of zirconium amido complexes is \textit{via} transamination. In particular, the commercially available Zr(NMe\textsubscript{2})\textsubscript{4} offers an attractive entry point, as the resulting dimethylamine byproduct is volatile, and therefore easily removed. Furthermore it is known that addition of two equivalents of \textsuperscript{t}PrNHPPh\textsubscript{2} to Zr(NMe\textsubscript{2})\textsubscript{4} results in diphosphinoamide complex (\textsuperscript{t}PrNPPh\textsubscript{2})Zr(NMe\textsubscript{2})\textsubscript{2}.\textsuperscript{71} Although, subsequent exchange of the dimethylamido groups for chlorides in these diphosphinoamide complexes was not possible, as was reported in Chapter 3.
Addition of an equimolar amount of \( \text{fc(NP}^\text{iPr}_2\text{)}_2\text{H}_2 \) \( 2.7 \) (\( \text{fc} = 1,1'-\text{ferrocenyl} \)) to a hexanes solution of \( \text{Zr(NMe}_2)_4 \) resulted in smooth conversion to \( \text{fc(NP}^\text{iPr}_2\text{Zr(NMe}_2)_2 \) \( 4.1 \) according to Scheme 4.3. A single resonance is observed in the \( ^{31}\text{P}\{^1\text{H}\} \) NMR spectrum at \( \delta \) 29.4.

Additionally, the \( ^1\text{H} \) NMR spectrum displays two distinct \( \text{Cp} \)-resonances at \( \delta \) 4.09 and 3.90, and a single resonance for the dimethylamido protons at \( \delta \) 3.27, which is consistent with a structure of \( C_{2v} \) symmetry.

**Scheme 4.3**: Synthesis of diphosphinoamide zirconium dimethyl amido complex \( 4.1 \)

Single crystals suitable for X-ray diffraction were obtained by cooling a concentrated hexanes solution of \( 4.1 \) to -35 °C. The solid-state molecular structure is shown in Figure 4.1; it should be noted that the zirconium center sits approximately 1 Å out of the plane defined by the PNNP donor atoms of the diphosphinoamide ligand. Additionally, the Fe to Zr distance is approximately 4.27 Å and Zr sits 0.364(2) Å out of the plane defined by Fe1, N1 and N2. The \( C_s \) symmetry of the molecule in the solid-state renders the two dimethylamido substituents inequivalent and the Zr-N bond lengths observed for the dimethylamido substituents are 2.0349(18) and 2.0930(17) Å, while the Zr-N bonds of the phosphinoamides are slightly longer: 2.1616(17) and 2.1299(17) Å. The Zr-P bonds are 2.8005(6) and 2.7405(6) Å, and these values along with those found for the Zr-N bond lengths are comparable to those reported by the
Thomas group for ($\text{PrNPPh}_2$)Zr(NMe$_2$)$_2$. Although complex 4.1 is $C_s$ symmetric in the solid-state, as previously mentioned the complex has $C_{2v}$ symmetry in solution. This suggests the metal center is moving in and out of the PNNP plane on the NMR timescale.

![Figure 4.1](image)

**Figure 4.1:** ORTEP solid-state molecular structure of complex 4.1; thermal ellipsoids are drawn at 50% probability; all hydrogen atoms and isopropyl methyl groups are omitted for clarity.

**Table 4.1:** Selected bond lengths and angles for complex 4.1

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<td>Zr1-P1</td>
<td>2.8005(6)</td>
</tr>
<tr>
<td>Zr1-N2</td>
<td>2.1299(17)</td>
<td>Zr1-P2</td>
<td>2.7405(6)</td>
</tr>
<tr>
<td>Zr1-N3</td>
<td>2.0349(18)</td>
<td>N1-Zr1-N2</td>
<td>84.66(6)</td>
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<tr>
<td>Zr1-N4</td>
<td>2.0930(17)</td>
<td>N3-Zr1-N4</td>
<td>103.67(7)</td>
</tr>
</tbody>
</table>

Treatment of complex 4.1 with excess trimethylsilylchloride (TMSCl) in toluene at 60 °C gives chloride-bridged dimer complex 4.2 (Scheme 4.4). The $^{31}$P-$^1$H NMR spectrum of 4.2
displays a single resonance at $\delta$ 19.2, which is shifted upfield from the dimethylamido complex 4.1. The dimethylamido resonance at $\delta$ 3.27 is absent in the $^1H$ NMR spectrum of 4.2, and the remaining peaks are consistent with a complex of high symmetry with two resonances for the Cp-protons, at $\delta$ 4.21 and 3.79. Dissolution of complex 4.2 in THF and subsequent drying \textit{in vacuo} resulted in the formation of a new complex containing one bound THF molecule. Complex 4.3 appears as a singlet in the $^{31}P\{^1H\}$ NMR spectrum at $\delta$ 20.5. The $^1H$ NMR spectrum of complex 4.3 again displays two resonances at $\delta$ 4.50 and 3.93, which are assigned to the Cp-protons. Additionally, the coordinated THF gives rise to two resonances in the $^1H$ NMR spectrum at $\delta$ 4.10 and 1.42.

\textbf{Scheme 4.4}: Synthetic route to phosphinoamide zirconium dichloride complexes.
Single crystals for X-ray diffraction were obtained by slow diffusion of pentane to a concentrated benzene solution of 4.2, and by cooling a concentrated hexanes solution of 4.3 to -35 °C. The solid-state molecular structure of 4.2 (Figure 4.2) demonstrates that the phosphinoamide fragments remain bound in a κ²-(NP) fashion to a single zirconium center. In 4.2 the two zirconium centers are bridged by two chloride ligands, and the two fc(NP^2Pr)_2 ligands are eclipsed. The distance between the zirconium centers is approximately 3.5 Å and the distance between the Fe and Zr atoms is approximately 4.0 Å. A structure of the related compound, [fc(NSiMe_3)_2ZrCl_2], has been reported by the Arnold group\textsuperscript{158} wherein the distance between Fe and Zr atoms is 3.22 Å, and between the two Zr atoms is 4.13 Å. The differences in the Fe to Zr distances can be rationalized by examination of the geometry at zirconium: the N1-Zr1-N2 angle in 4.2 is 86.64(8)°, while in [fc(NSiMe_3)_2ZrCl_2] the corresponding N-Zr-N angle is 136.7(1)°. The Zr-N bond lengths of 2.069(2) and 2.075(2) Å in 4.2 are comparable to those reported for [fc(NSiMe_3)_2ZrCl_2] (2.046(4) Å), and the Zr-Cl bond lengths are within experimental error. Complex 4.3 has C_{2v} symmetry in the solid-state, and as can be seen from Table 4.2 the bond lengths and angles for the orientation of the phosphinoamide ligand on zirconium are not notably different. The Zr-Cl bond distances in 4.3 of 2.4845(5) Å are shorter than those in the chloride bridge of 4.2, which were 2.5477(6) and 2.6962(6) Å, as is expected for terminal and bridging Zr-Cl bonds. The Fe to Zr distance is approximately 4.19 Å in both 4.2 and 4.3. The Zr center sits in the PNNP plane in both solid-state structures, but the Zr center sits out of the Fe1, N1 and N2 plane by 0.142(2) Å in 4.2, and 0.2139(3) Å in 4.3.
Figure 4.2: ORTEP solid-state molecular structures for complexes 4.2 and 4.3; thermal ellipsoids are drawn at 50 % probability; all hydrogen atoms and isopropyl methyl groups are omitted for clarity. One half of each molecule is generated by symmetry.
Table 4.2: Selected bond lengths and angles for complexes 4.2 and 4.3

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The overall synthesis of complex 4.3 proceeds in high yield over three steps to generate the desired zirconium dichloride starting material. The zirconium dichloride complex 4.3 serves as an excellent precursor for the synthesis of organometallic complexes, as attested by previous work in the Fryzuk group.\(^{159,160}\)

4.3 Synthesis of organometallic zirconium complexes

4.3.1 Synthesis and characterization of primary alkyl zirconium complexes

The synthetic route for the preparation of a series of zirconium organometallic complexes using alkyllithium or alkylpotassium reagents and complex 4.3 is shown in Scheme 4.5. The complexes 4.4 – 4.6 are all of \(C_2\)\(v\) symmetry in solution, with only 2 resonances observed for the Cp-protons of the ferrocene backbone in the \(^1\)H NMR spectra. The protons on the \(\alpha\)-carbon of the alkyl groups display coupling to two equivalent \(^{31}\)P nuclei in the \(^1\)H NMR spectra of all three complexes (Table 4.3).
Scheme 4.5: Synthesis of organometallic zirconium complexes (4.4 – 4.6).

Table 4.3: Selected resonances from NMR spectra of 4.4, 4.5 and 4.6 in C₆D₆.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^{31}$P{¹H}: (δ)</th>
<th>$^{1}$H: Zr-CH₃ (δ)</th>
<th>$^{3}$J_HP (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4</td>
<td>23.0 (s)</td>
<td>0.75 (t)</td>
<td>4.2</td>
</tr>
<tr>
<td>4.5</td>
<td>15.7 (s)</td>
<td>1.91 (t)</td>
<td>6.0</td>
</tr>
<tr>
<td>4.6</td>
<td>18.7 (s)</td>
<td>0.88 (t)</td>
<td>7.0</td>
</tr>
</tbody>
</table>

Complexes 4.5 and 4.6 have been studied in the solid-state by single crystal X-ray diffraction, and the molecular structures are depicted in Figure 4.3. Complex 4.5 contains two benzyl groups, one of which is bound η¹ while the other is η². This is in contrast to the related complex [fc(NSiMe₃)₂]Zr(CH₂Ph)₂, which contains two η¹-bound benzyl substituents.¹⁰³ The η²-interaction in 4.5 is apparent from the acute Zr1-C30-C31 angle of 88.52(12) Å and the Zr-C31 distance of 2.720(2) Å. The ligand geometry at zirconium is not unusual when compared to complexes 4.1 – 4.3. The variable coordination modes of benzyl groups will be further discussed in the next section. The bond lengths and angles at zirconium are not notably affected (except for the Zr-C-C angles) by changing the Zr substituents from benzyl to neopentyl, as is shown in
Table 4.4. The Zr to Fe distances are long at 4.22 (4.5) and 4.23 Å (4.6) and the Zr center sits out of the Fe1, N1 and N2 plane by 0.144(2) and 0.232(2) Å, respectively.

Figure 4.3: ORTEP solid-state molecular structures for complexes 4.5 and 4.6; thermal ellipsoids are drawn at 50 % probability; all hydrogen atoms and isopropyl methyl groups are omitted for clarity. For clarity one benzene molecule is omitted from the asymmetric unit for 4.5.

Table 4.4: Selected bond lengths and angles for complexes 4.5 and 4.6

<table>
<thead>
<tr>
<th>Parameter</th>
<th>4.5 (Å)</th>
<th>4.6 (Å)</th>
<th>Parameter</th>
<th>4.5 (Å / °)</th>
<th>4.6 (Å / °)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr1-N1</td>
<td>2.1024(17)</td>
<td>2.121(2)</td>
<td>Zr1-(C30 or C28)</td>
<td>2.327(2)</td>
<td>2.265(3)</td>
</tr>
<tr>
<td>Zr1-N2</td>
<td>2.0745(17)</td>
<td>2.112(2)</td>
<td>Zr1-C31</td>
<td>2.720(2)</td>
<td></td>
</tr>
<tr>
<td>Zr1-P1</td>
<td>2.7576(8)</td>
<td>2.7853(8)</td>
<td>C23-Zr1-(C30 or C28)</td>
<td>117.40(8)</td>
<td>111.81(10)</td>
</tr>
<tr>
<td>Zr1-P2</td>
<td>2.7208(8)</td>
<td>2.7811(8)</td>
<td>Zr1-C30-C31</td>
<td>88.52(12)</td>
<td></td>
</tr>
<tr>
<td>Zr1-C23</td>
<td>2.277(2)</td>
<td>2.327(3)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.3.2 Benzyl bonding modes in zirconium complexes

Zirconium benzyl ligands have been found to display a variety of bonding modes, ranging from simple $\eta^1$-coordination via the methylene carbon to $\eta^2$ and $\eta^3$-modes where the ipso-phenyl and ortho-phenyl carbons are also involved in bonding (Scheme 4.6). The numerous examples of $\eta^2$-benzyl coordination in the literature have allowed for identification of some spectroscopic features that indicate such a bonding mode in solution.\(^{124}\) Upfield $^1$H NMR resonances for the ortho-phenyl protons is observed, as well as $^1J_{CH}$ coupling constants that are small in magnitude are observed for the methylenic carbon in the $^{13}$C NMR spectrum when a benzyl group is bound in an $\eta^2$-fashion. In the solid state, the criteria for assigning the bonding mode is based solely on Zr-C bond distances. In particular, any arene-carbons deemed to be bound to zirconium should be within 0.5 Å of the Zr-methylene bond distance; this typically results in a Zr-C-C bond angle of less than 96°.\(^{124}\)

Scheme 4.6: Depiction of the geometric parameters for classifying $\eta^1$ and $\eta^2$-bonding in zirconium benzyl groups (adapted from ref 124).

In the case of complex 4.5, analysis by NMR spectroscopy reveals $^1$H NMR shifts, and a C-H coupling constant (123 Hz) from the $^{13}$C NMR experiment that are consistent with $\eta^1$-benzyl coordination. Cooling solutions of 4.5 in toluene-$d_8$ does not result in any noticeable
broadening of resonances, or in the appearance of any upfield shifts for the resonances in the aromatic region of the $^1$H NMR spectrum.

A recent publication\textsuperscript{124} has indicated that there is inherent flexibility of the benzyl ligand when bound to zirconium; in tetrabenzyl zirconium the calculated energetic difference when changing Zr-C-C angle between 85° and 120° is less than 1.5 kcal/mol. Based on this evidence it is entirely possible that the η\textsuperscript{2}-coordination mode is non-existent in solution, but present only in the solid-state. The aforementioned article compiles all of the structurally characterized zirconium benzyl complexes and their various bonding modes.\textsuperscript{124}

4.3.3 Attempted hydrogenolysis of dialkyl zirconium complexes

The primary alkyl complexes 4.4 – 4.6 were all thermally stable; heating toluene solutions to 110 °C for 3 days resulted in no change observable by NMR spectroscopy. Diethyl ether solutions of complexes 4.4 and 4.5 were stirred under 4 atm of H\textsubscript{2} for 1 week without any signs of reaction. However, under the same conditions solutions of complex 4.6 form a precipitate over the course of several days. Conversion to this insoluble product was low based on the mass obtained and the solids were sparingly soluble in THF, but insoluble in all other common solvents. NMR analysis of the precipitate was inconclusive and all attempts to obtain crystalline material for X-ray diffraction were unsuccessful.

4.3.4 Synthesis of a zirconium complex containing β-hydrogens

The organometallic complexes 4.4 – 4.6 did not contain β-hydrogens and these complexes were found to be quite thermally robust. It was hypothesized that hydride complexes could be formed by β-hydride elimination as has been observed for a variety of substituted
zirconocene complexes.\textsuperscript{161} Therefore tert-butyl complexes were identified as synthetic targets in order to maximize the number of $\beta$-hydrogens in the organometallic complexes.

The addition of one equivalent of $t^3$BuLi to 4.3 at low temperature resulted in an intractable mixture of products, addition of two equivalents of $t^3$BuLi to 4.3 gives the thermally sensitive dialkyl zirconium complex, fc(NP$i^3$Pr$_2$)Zr($t^3$Bu)$_2$ ($t^3$Bu = CMe$_3$) 4.7 (Scheme 4.7). The $^{31}$P\{\textsuperscript{1}H\} NMR spectrum of 4.7 in C$_6$D$_6$ contains a single resonance at $\delta$ 22.7, which is not unusual when compared to complexes 4.4 - 4.6 (cf. Table 4.3). The $^1$H NMR spectrum of 4.7 in C$_6$D$_6$ is consistent with a complex of $C_{2v}$ symmetry, and the resonance attributed to the $t^3$Bu-protons is a singlet $\delta$ 1.65.

\begin{center}
\textbf{Scheme 4.7:} The synthesis of di-\textit{tert}-butyl complex 4.7 and transformation to 4.8
\end{center}
Crystalline 4.7 was obtained from a concentrated hexanes solution stored at -35 °C for one week. The solid-state structure (shown in Figure 4.4) confirms that two intact tert-butyl groups have been incorporated but surprisingly, the phosphine arms of the diphosphinoamide ligand have decoordinated from the zirconium center. This is likely due to the steric effect of having two large tert-butyl substituents bound to the metal center. Interestingly, in the solid-state the zirconium center adopts a distorted tetrahedral geometry with two amido donors and two tert-butyl groups. This results in a N-Zr-N angle of 129° and a geometric change at ferrocene, with a centroid-Fe-centroid angle of 186° (cf. 175° in 4.5, 4.6). This geometric change at ferrocene results in a Fe to Zr distance of 3.47 Å (cf. 4.22 Å in 4.5, 4.6), and the Zr sits out of the Fe1, N1 and N2 plane by 0.190(3) Å. Early transition metal tert-butyl complexes are often only stable at low temperatures; however, some rare examples are stable enough to be studied crystallographically, including several titanium, one zirconium complex, one tantalum complex, and several group 3 complexes.
Figure 4.4: ORTEP solid-state molecular structures for complex 4.7; thermal ellipsoids are drawn at 50% probability; all hydrogen atoms and isopropyl methyl groups are omitted for clarity. Only one half of the molecule forms the asymmetric unit, with the other half generated by symmetry.

Table 4.5: Selected bond lengths and angles for complex 4.7

<table>
<thead>
<tr>
<th>Parameter</th>
<th>(Å)</th>
<th>Parameter</th>
<th>(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr1-N1</td>
<td>2.0838(14)</td>
<td>C12-Zr1-C12\textsuperscript{i}</td>
<td>107.07(12)</td>
</tr>
<tr>
<td>Zr1-C12</td>
<td>2.254(2)</td>
<td>N1-Zr1-N2</td>
<td>129.18(8)</td>
</tr>
</tbody>
</table>

While the solid-state structure of 4.7 has phosphines that are dissociated from the metal center, the \(^{31}\text{P}\{\text{H}\}\) NMR chemical shift of \(\delta 22.7\) implies that in solution the ligand has the same binding mode as for complexes 4.4 - 4.6. It is likely that the ligand undergoes isomerization from \(\kappa^4\)-(PNNP) to \(\kappa^2\)-(NN) bonding on the NMR timescale in solution.
Over a period of hours at room temperature 4.7 can be observed to convert to a single product, 4.8. Using $^1$H NMR spectroscopy, the production of iso-butane is indicated by the presence of a doublet at $\delta$ 0.85, with a coupling constant of $^3J_{\text{HH}} = 6.6$ Hz. The new complex 4.8 has $C_s$ symmetry in solution: the $^1$H NMR spectrum displays 4 resonances for the Cp-protons at $\delta$ 4.37 and 4.25, and two overlapping resonances at $\delta$ 3.90. The $^1$H NMR resonances for the coordinated iso-butylene fragment are a singlet at $\delta$ 1.47 for the two methyl-groups, and a broad signal at $\delta$ 1.35 for the methylene group. A related complex Cp$_2$Zr($\eta^2$-CH$_2$CMe$_2$) has been reported, and the NMR spectroscopic analysis agrees well with 4.8.

4.4 Isocyanide insertion reactivity with dialkyl zirconium complexes

4.4.1 Synthesis of iminoacyl complexes

In all cases the addition of one equivalent of (2,6-dimethylphenyl)isocyanide to dialkylzirconium complexes (4.5, 4.6, 4.7 and 4.8) forms the alkyl(iminoacyl)zirconium products, according to Scheme 4.8.

**Scheme 4.8**: Synthesis of iminoacyl alkyl zirconium complexes
The $^{13}$C{$^{1}$H} NMR spectra for these complexes show diagnostic downfield signals in the region of $\delta$ 240 – 255 corresponding to the iminoacyl quaternary carbon, see Table 4.6. The iminoacyl moiety also has a distinct band in the FT-IR spectrum for the C=N stretch; these values are tabulated with the $^{13}$C-NMR data in Table 4.6. Additionally, the $^1$H NMR spectra of the alkyl(iminoacyl)zirconium complexes contain 4 distinct resonances for the ferrocenyl protons, which is indicative of $C_s$ symmetry. The $\alpha$-protons on the alkyl fragment in complexes 4.9 - 4.11 are also shifted considerably downfield from the starting dialkyl complexes 4.5 - 4.7 as shown in Table 4.6.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^1$H: Zr−N=C−CH$_x$ (δ)</th>
<th>$^{13}$C{$^{1}$H}: Zr−C=N (δ)</th>
<th>FT-IR: C=N (ν / cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.9</td>
<td>2.28 (s)</td>
<td>242.8 (s)</td>
<td>1448</td>
</tr>
<tr>
<td>4.10</td>
<td>3.75 (s)</td>
<td>246.4 (s)</td>
<td>1486</td>
</tr>
<tr>
<td>4.11</td>
<td>2.60 (s)</td>
<td>252.5 (s)</td>
<td>1434</td>
</tr>
<tr>
<td>4.12</td>
<td>-</td>
<td>255.2 (s)</td>
<td>1436</td>
</tr>
</tbody>
</table>
Figure 4.5: ORTEP solid-state molecular structures for complexes 4.10 and 4.12; thermal ellipsoids are drawn at 50 % probability; all hydrogen atoms and isopropyl methyl groups are omitted for clarity. Only one of three molecules in the asymmetric unit is shown for complex 4.10.
The solid-state molecular structures of 4.10 and 4.12 have been determined using X-ray crystallography and are shown in Figure 4.5. Both of the resulting iminoacyl functional groups, containing benzyl\(^{151,170-175}\) and tert-butyl\(^{176}\) substituents, have been previously reported in zirconium complexes. The bond lengths and angles in complexes 4.10 and 4.12 are unremarkable, with C=N bond lengths of 1.284(4) and 1.286(4) Å, and Zr-C bond lengths of 2.258(3) and 2.230(3) Å, when compared to other structurally characterized Zr-iminoacyl complexes. The Fe to Zr distance in 4.12 is approximately 3.47 Å, which is much shorter than that in 4.10 (4.22 Å) but the Zr centers both sit only marginally out of the Fe1, N1 and N2 plane at 0.053(2) and 0.058(3) Å, respectively.

### 4.4.2 Isomerization from iminoacyl to an amido-alkene complex

The alkyl(iminoacyl)zirconium complexes 4.9 – 4.12 were all heated to 110 °C in toluene-\(d_8\). The complex with no hydrogens adjacent to the iminoacyl moiety, 4.12, undergoes no transformation under these conditions. Complexes 4.9 and 4.11 undergo thermal
decomposition only upon prolonged heating (several days) at 110 °C to give a complex mixture of products, as ascertained using NMR spectroscopy. In contrast, complex 4.10 undergoes thermal rearrangement to generate an alkyl(imidoalkene)zirconium complex, 4.13. Solutions of 4.13 give rise to a $^1$H NMR spectrum with two downfield doublet resonances, at δ 8.3 and 4.8, with $^3J_{HH}$ coupling of 13.5 Hz, consistent with a trans-alkene group.\footnote{177}

Scheme 4.9: Two possible mechanisms for the transformation of 4.10 to 4.13.

It has been reported that the transformation of a zirconium iminoacyl complex into a zirconium amidoalkene complex follows first order kinetics, but the mechanistic details remain unknown.\footnote{177} There are two probable pathways that such a transformation could follow: one is a 1,2-hydrogen shift, which would occur due to the carbene-character in the iminoacyl moiety, and the second involves a $\beta$-elimination step to generate a metal hydride and a coordinated
cumulene, with subsequent insertion to generate the amidoalkene. One kinetic study has demonstrated that the relative rates are not dependent on the metal or ancillary ligand.\textsuperscript{177} Indeed, in zirconocene or hafnocene complexes it was found that iminoacyl groups with a substituted pyridine adjacent the methylene group on the iminoacyl fragment allowed for facile isomerization to the amido-alkene complex, while phenyl-substituted complexes result in no isomerization.\textsuperscript{177} A kinetic study on the formation of 4.13 was undertaken in order to obtain the activation parameters of the transition state.

Monitoring 20 mM toluene-\textit{d}_8 solutions of complex 4.10 by \textsuperscript{1}H NMR spectroscopy indicates that the transformation follows first-order kinetics. Furthermore, the rate of reaction was monitored at various temperatures and the temperature-dependent rate constants were obtained. A representative plot for the decay of 4.10 can be found in Appendix C, as well as the first-order rate constants obtained, and a brief discussion of error propagation. Thermodynamic data for the transition state of the rate-determining step can be obtained using the Eyring equation. The Eyring plot is shown in Figure 4.6, and the resulting values are: $\Delta H^\ddagger = 26.7 \pm 2.1$ (kcal / mol) and $\Delta S^\ddagger = -5.7 \pm 0.7$ (cal / K mol). In addition to the thermodynamic data, a deuterium isotope effect was measured. Using 4.10-\textit{d}_{14}, which has both benzyl groups fully deuterated, the rate of the corresponding decomposition has been measured and the isotopic rate dependence is $k_{H/D} = 4.6 \pm 0.3$. This value is consistent with a primary isotope effect for the migrating proton in the benzylic position of the iminoacyl complex. The activation parameters obtained from the temperature-dependent rate constants cannot be used to distinguish between the two proposed mechanisms for this transformation, since both would be expected to have a primary isotope effect in the rate-limiting step. However, the observation that complex 4.12 does not undergo $\beta$-elimination, even at elevated temperatures, implies that the 1,2-hydrogen shift
mechanism is more likely. It also appears that the nature of the group attached to the methylene carbon is important for the transformation, because the 1,2-hydrogen shift reaction is not observed for complexes 4.9 or 4.11.

![Graph showing the Eyring plot for the thermal rearrangement of 4.10 to 4.13.](image)

**Figure 4.6:** The Eyring plot for the thermal rearrangement of 4.10 to 4.13.

### 4.5 Conclusions

A ferrocenylidiphosphinoamide ligand has been coordinated to zirconium using transamination to form a bis(dimethylamido)zirconium complex. A chloride-bridged dinuclear complex was formed by the reaction of trimethylsilyl chloride with the zirconium diamido complex in toluene via the elimination of trimethylsilyl(dimethylamide). This resulting chloride-bridged complex could be cleaved using THF as a coordinating solvent to generate a monomeric species. These zirconium dichloride complexes were useful precursors to a variety of zirconium
dialkyl derivatives, which were subsequently reacted with an arylisocyanide. The resulting iminoacyl alkyl complexes were characterized and examined for further reactivity through thermolysis. In particular, the zirconium benzyliminoacyl complex undergoes a 1,2-hydrogen shift reaction to generate an alkene-amido complex. Kinetic studies indicate the transformation occurs via a highly ordered transition state, and the deuterium labeling studies are consistent with a 1,2-hydrogen-shift mechanism. The reluctance of the tert-butyliminoacyl complex to undergo β-hydride elimination even upon prolonged heating provides further evidence to support this mechanism.

From the perspective of ligand design, the ferrocenyl-based phosphinoamide ligand was found to bind zirconium as a tetradentate ligand and when sterically demanding substituents are bound to the metal it can adopt a bidentate coordination mode, although in solution it undergoes isomerization from the κ²-(NN) to the κ⁴-(PNNP) bonding mode.
5 Electrochemistry of ferrocenyl diphosphinoamide complexes

5.1 Introduction

The introduction of ferrocene-based ligands in transition metal complexes raises the possibility of exploiting the stability of ferrocene when the Fe center is in either the +2 or +3 oxidation state. Indeed, several research groups employing ferrocene-based chelating ligands have been studying the effect of oxidation of the ferrocene to generate a ferrocenium backbone. For example, using a phosfen (1,10-di(2-tert-butyl-6-diphenylphosphinimino-phenoxy)ferrocene) ligand system in yttrium and indium alkoxide complexes, the corresponding cationic complexes could be obtained by one electron oxidation of the ferrocene backbone (Scheme 5.1), leaving the yttrium and indium in their +3 oxidation but incurring a positive charge on the whole complex. In this study, different lactide polymerization rates were observed when using the neutral versus the cationic complexes. Interestingly, the rate enhancement was found to be dependent on the metal: for yttrium the neutral complex was the faster catalyst while with indium, the cationic complex resulted in more rapid polymerization.
Another example of ferrocene redox behavior is the demonstration that uranium allows for electronic interaction between two ferrocene fragments. The synthesis of \([\text{fc(NSiMe}_2^t\text{Bu})_2]_2\text{U}\) (fc = 1,1’-ferrocenyl) and its characterization by cyclic voltammetry revealed that the two ferrocenyl units are oxidized in a stepwise manner.\(^{179}\) This is in contrast to the related complex \([\text{fc(NSiMe}_2^t\text{Bu})_2]_2\text{Zr}\) where no electronic communication is observed through the zirconium center.

While the two examples above highlight why the redox behavior of new ferrocene-containing ligands should be examined, it is not an exhaustive review of this area. Such a literature review is beyond the scope of this thesis, but the area of redox-active ligands remains of current interest.\(^{180-184}\)

### 5.2 Introduction to cyclic voltammetry

Cyclic voltammetry (CV) is an electroanalytical technique used to observe the reduction or oxidation behaviour of an analyte of interest. The redox potentials can then be used to identify
chemical redox reagents suitable to effect a electrochemical transformation on a bulk scale. One advantage of CV is the ability to rapidly observe the redox activity over a wide range of potentials. The technique consists of scanning the potential of a working electrode (typically Pt), which is controlled versus a reference electrode (often Ag). The potential scan is linear, has a triangular waveform, shown in Figure 5.1, and is sometimes called the excitation signal. The minimum and maximum potentials are sometimes called the switching potentials, and the slope of the excitation signal is the scan rate. Both the switching potentials and the scan rate can be easily varied on modern instruments.

![Figure 5.1: A plot of potential vs time in a cyclic voltammetry experiment with switching potentials at -0.2 and 0.7 V (adapted from ref 186).](image)

The current between the working electrode and counter electrode (glassy carbon) is monitored and is known as the response signal. The recorded response signal is referred to as a voltammogram. Figure 5.2 shows a typical cyclic voltammogram for ferrocene and some key parameters are identified. As the potential is increased in the positive direction (identified by
the horizontal arrow) there is no change in current recorded until point A, when the potential is high enough to begin oxidizing the electrolyte. The current continues to become more negative as the rate of oxidation increases until point B, the anodic peak potential, when analyte concentration is depleted. Once the concentration of analyte is depleted the diffusion-controlled oxidation continues, meaning that analyte must now diffuse across the depleted layer to reach the electrode. The switching potential is then reached at C and upon sweeping to point D, the oxidized analyte can now be reduced and the cathodic peak E is observed, for similar reasons as for the anodic peak.

Figure 5.2: Typical electrochemically reversible cyclic voltammogram (of ferrocene)
The observations in Figure 5.2 can be used to interpret electrochemically reversible redox events using cyclic voltammetry. However, chemical reactions are sometimes induced by the reduction or oxidation events and must be considered. In the case where the chemical reaction is occurring faster than the redox event, the return peak will be of smaller magnitude or completely absent, which is called electrochemical irreversibility.\(^{188}\)

5.3 **Redox behavior in ferrocene-linked diphosphinoamide complexes**

5.3.1 **Redox behavior of fc(NP\(^{t}\)Pr\(_2\))\(_2\)H\(_2\)**

As a starting point for the examination of the redox activity of the ferrocene-linked diphosphinoamide ligand, the cyclic voltammogram of fc(NP\(^{t}\)Pr\(_2\))H\(_2\) (2.7) was recorded (Figure 5.3). A reversible oxidation consistent with a ferrocene to ferrocenium couple is observed at a potential where \(E_{1/2} = -0.71\) V. Notably, the oxidation of 2.7 occurs at lower potentials than the oxidation of fc(NH\(_2\))\(_2\) (-0.60 V).\(^{189}\) A similar trend was observed in two related systems with both fc(NHSiMe\(_3\))\(_2\) (-0.63 V)\(^{103}\) and fc(N=P(o-PhOH))\(_2\) being oxidized at -0.63 V.\(^{190}\) The ferrocene-unit is more electron-rich when P\(^{t}\)Pr\(_2\) substituents are attached at both nitrogens, as in 2.7, and this substitution has a more marked effect than SiMe\(_3\) groups. Other comparable ferrocene derivatives include fc(NMe\(_2\))\(_2\) (-0.63 V)\(^{191}\) and fc(NHPh)\(_2\) (-0.46 V).\(^{104}\)
Figure 5.3: Cyclic voltammogram of 2.7 (5 mM) using a scan rate of 100 mV/s in 0.1 M solution of "Bu₄N(PF₆) in THF under argon, referenced to Fc(+/-0) at 0 V.

5.3.2 Redox behavior of fc(NPᵢPr₂)₂Sc(CH₂SiMe₃)(THF)

The redox behavior of fc(NPᵢPr₂)₂Sc(CH₂SiMe₃)(THF) (2.8) was also examined using cyclic voltammetry. From the voltammogram shown in Figure 5.4, two oxidation events and one reduction event can be observed. Another oxidation event of lesser magnitude (marked x) is also observed and correlates to complex 2.7, which is presumably generated from reaction of 2.8 with adventitious water in the electrochemical cell. Traces of 2.7 are present in small quantities in subsequent voltammograms and are always identified in the same way (marked x).
Figure 5.4: Cyclic voltammogram of 2.8 (5 mM) using a scan rate of 100 mV/s in 0.1 M solution of "Bu₄N(BPh₄) in THF under argon, referenced to Fc(+/0) at 0 V.

A quasi-reversible reduction event can be observed at approximately -3.30 V, presumably a reduction of the scandium center to the +2 oxidation state. An irreversible oxidation is evident at approximately -0.46 V, which is followed closely by a quasi-reversible oxidation at -0.28 V. Despite altering the switching potential to -0.40 V in order to isolate the irreversible oxidation event, the event remained irreversible at all rates scanned. Also, obtaining the voltammogram by scanning from negative to positive potentials gives a result identical to the one obtained running a scan in the opposite direction. To examine whether these oxidation events are ligand-based, further electrochemical studies were performed on zirconium complexes supported by the
ferrocene-linked diphosphinoamide ligand.

5.3.3 Redox behavior of fc(NPPr₂)₂ZrX₂ (X = NMe₂, CH₂Ph)

Complex fc(NPPr₂)₂Zr(NMe₂)₂ (4.1) displays very similar redox behavior to that observed for 2.8. A quasi-reversible reduction event at approximately -3.33 V can be observed in the cyclic voltammogram of 4.1, shown in Figure 5.5. This event is likely a reduction of the zirconium center down to either the +3 or +2 oxidation state. The two oxidations are irreversible events located at -0.27 and 0.14 V. This provides some indirect evidence that the oxidation events are ligand-based.

![Cyclic voltammogram of 4.1](image)

Figure 5.5: Cyclic voltammogram of 4.1 (5 mM) using a scan rate of 100 mV/s in 0.1 M solution of "Bu₄N(BPh₄) in THF under argon, referenced to Fc(+/0) at 0 V.
Interestingly, a reversible ferrocene-ferrocenium couple can be observed by cyclic voltammetry at -0.42 V for the related Zr complex fc(NPh)₂Zr(NMe₂)₂NHMe₂. This is in contrast to the voltammogram recorded for 4.1, possibly due the electron-rich nature of the amido-donors in the phosphinoamide moieties when compared to other previously reported examples. This notion is supported by the oxidation potential observed for 2.7 (cf Section 5.3.1) and raises the possibility of oxidation occurring first at the phosphinoamide, followed by ferrocene-based processes. Additionally, complexes 4.1 and 2.8 were both modeled using DFT calculations and diagrams of their highest occupied molecular orbital (HOMO) (located in Appendix D) are mostly ferrocene-based but have strong contributions from the phosphinoamide N-atoms.

To examine the role of the other substituents on zirconium, fc(NPr₂)₂Zr(CH₂Ph)₂ (4.6) was also examined by cyclic voltammetry (Figure 5.6). The voltammogram has two overlapping, irreversible reduction events at approximately -3.33 V which likely correspond to the reduction of Zr(IV) to Zr(III) and then Zr(II). The irreversible nature of the event likely indicates a subsequent chemical reaction of the Zr(II) species. The oxidation events are both irreversible, occurring at approximately -0.24 V and 0.02 V, which are at similar potentials to those observed for complex 4.1. The irreversible nature of the oxidation at 0.0 V may be due to a Zr-C bond breaking process akin to that reported for the reaction of Cp₂Zr(CH₂Ph)₂ with [Cp₂Fe][BPh₄] salts. This reaction results in the breaking of the Zr-C bond to give cationic complexes of the form [Cp₂ZrCH₂Ph(THF)][BPh₄] via loss of half an equivalent of PhCH₂CH₂Ph. Similar reactivity may result from generation of a ferrocenium-backbone in a zirconium dialkyl complex such as 4.6 and cannot be ruled out.
Figure 5.6: Cyclic voltammogram of 4.6 (5 mM) using a scan rate of 100 mV/s in 0.1 M solution of "Bu₄N(BPh₄) in THF under argon, referenced to Fc(+/0) at 0 V.

5.3.4 Synthesis and redox behavior of fc(NP'iPr₂)Li₂

A lithiated complex of the ferrocene-linked diphosphinoamide ligand was synthesized in order to have a complex without other potential redox activity, as was observed in disubstituted zirconium complexes 4.1 and 4.6. Addition of two equivalents of "BuLi to 2.7 in diethyl ether resulted in the formation of complex 5.1. The structure of the new complex is most likely as formulated, in Scheme 5.2, based on the previously reported fc(NSiMe₃)Li₂(NC₅H₅). Additional, the NMR spectra of 5.1 are consistent with a complex with C₂ᵥ symmetry.
Scheme 5.2: Synthesis of dilithium complex 5.1.

The cyclic voltammogram of complex 5.1 is shown in Figure 5.7 and exhibits two irreversible oxidation events at largely negative potentials (-1.69 and -1.11 V). There is also a quasi-reversible event at -0.27 V that may correspond to a ferrocene-based redox couple. The shift in irreversible oxidation potential to more negative values in 5.1 would be consistent with oxidation the phosphinoamide. In the zirconium complexes 4.1 and 4.6 π-donation from the amido to the empty zirconium d-orbitals should render the oxidation more difficult compared to the lithium phosphinoamide 5.1.
Figure 5.7: Cyclic voltammogram of 5.1 (5 mM) using a scan rate of 100 mV/s in 0.1 M solution of "Bu₄N(BPh₄) in THF under argon, referenced to Fc(+/0) at 0 V.

5.3.5 Attempted synthetic strategies

The diphosphinoamine 2.7 was oxidized using [Cp₂Fe][BPh₄] or [Cp₂Fe][PF₆] in THF at room temperature to generate deep green solutions of the presumed paramagnetic products [fc(NPᵢPr₂)₂H₂][BPh₄] or [fc(NPᵢPr₂)₂H₂][PF₆]. These complexes were used in situ and were allowed to react with either Zr(NMe₂)₄, Zr(CH₂Ph)₄ or Sc(CH₂SiMe₃)₃(THF)₂; in each case, only mixtures of diamagnetic products were observed by NMR spectroscopy. Additionally, attempts to chemically oxidize complex 2.8 and 4.1 using one or two equivalents of [Cp₂Fe][BPh₄] or [Cp₂Fe][PF₆] in THF also gave products that were insoluble in common organic solvents. In contrast, the addition of 3 equivalents of [Cp₂Fe][BPh₄] to 4.1 in THF gave a paramagnetic off-white product with ferrocene as the only diamagnetic byproduct. All attempts to obtain single crystals for X-ray diffraction studies were unsuccessful.
The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the diamagnetic mixtures contain resonances that are in the expected region for phosphinoamide complexes and no resonances that could be attributed to $[^i\text{Pr}_2\text{P}]^-$ or $[^i\text{Pr}_2\text{P}-[^i\text{Pr}_2\text{P}]$ products were observed. While N-P bond breaking processes cannot be completely discounted, there is no direct evidence for such processes when bulk oxidation of the phosphinoamide complexes was performed.

5.4 Conclusions

The reversible oxidation of ferrocene-linked diphosphinoamine was observed, using cyclic voltammetry, to occur at lower potential than other reported diaminoferrocene derivatives. Several complexes containing the ferrocene-linked diphosphinoamide ligand displayed unusual redox activity, which was examined using cyclic voltammetry. While other reported ferrocene-containing metal complexes display reversible redox reactions based at ferrocene, this behavior is not observed in complexes containing the ferrocene-linked diphosphinoamide ligand reported in this thesis. The electron-rich amido ligands in the diphosphinoamide framework were identified as likely competitive redox sites. However, attempts to determine whether or not the N-P bond is cleaved during oxidation, by using chemical oxidants, were unsuccessful.
6 Diversions and future directions

6.1 Diversions with porphyrin-supported tantalum complexes

The work described in this thesis has been focused on the synthesis of transition metal hydrides. In particular, the ability of some transition metal hydrides to activate small molecules, such as N\textsubscript{2}\textsuperscript{194} is of interest. Using a P\textsubscript{2}N\textsubscript{2} macrocycle, a ditantalum tetrahydride complex ((P\textsubscript{2}N\textsubscript{2})Ta\textsubscript{2}(\mu-H)\textsubscript{4}) which contains a highly reducing metal-metal bond was synthesized from (P\textsubscript{2}N\textsubscript{2})TaMe\textsubscript{3} and H\textsubscript{2}\textsuperscript{195}. Similarly, the corresponding ditantalum tetrahydride complex supported by an NPN ligand has been synthesized, and remarkably was shown to spontaneously activate N\textsubscript{2} via reductive elimination of H\textsubscript{2}\textsuperscript{196,197}. Meanwhile, it has been demonstrated that hydrogenation of a dialkyl zirconium complex supported by octaethylporphyrin (OEP) results in reductive elimination to generate a complex of the form (OEP)ZrCH\textsubscript{2}SiMe\textsubscript{3}\textsuperscript{198}. OEP is a macrocyclic dianionic ligand with similar properties to P\textsubscript{2}N\textsubscript{2}, where large early transition metals sit above the plane of the donor atoms (Figure 6.1). Therefore tantalum OEP complexes were examined with in anticipation that similar chemistry to the tantalum P\textsubscript{2}N\textsubscript{2} system would be observed. To this end, reaction of the previously reported complex\textsuperscript{199} (OEP)TaMe\textsubscript{3} with H\textsubscript{2} was performed, but gave a mixture of products. There was no remaining (OEP)TaMe\textsubscript{3} in the reaction mixture, nor was there any (OEP)H\textsubscript{2} detected by \textsuperscript{1}H NMR spectroscopy.
Given the lack of success via hydrogenation as described above, a more direct route to tantalum dinitrogen complexes was examined by using a preformed tantalum dinitrogen starting material. The reaction of (OEP)K₂ with ((THF)₂Cl₃Ta)₂(μ-N₂) was examined; however, only (OEP)K₂ starting material could be isolated from the reaction mixture. It should be noted that ((THF)₂Cl₃Ta)₂(μ-N₂) contains an end-on bridging N₂ unit that is derived not from molecular N₂, but from reaction of the alkylidene complex Cl₃TaCHᵗBu(THF)₂ with 1,2-dibenzylidenehydrazine (PhCH=N=N=CHPh).²⁰⁰

6.2 Future work on tantalum porphyrin complexes

Further work toward the synthesis of tantalum porphyrin complexes should focus on the synthesis of alkylidene complexes. Scheme 6.1 provides two possible synthetic routes starting either from Cl₃TaCHᵗBu(THF)₂,²⁰¹ or from (OEP)TaCl₃.¹⁹⁹ Both of these synthetic methodologies would give access to a bridging dinitrogen ditantalum complex if successful.
Additionally, chemical reduction of (OEP)TaCl₃ would also be an interesting reaction because the reduced species may be stable as was the case in (OEP)ZrCH₂SiMe₃.¹⁹⁸

![Scheme 6.1: Proposed routes to porphyrin-supported tantalum N₂-complexes](image)

### 6.3 Diversions synthesizing phosphine-bridged amidate ligands

Another project undertaken was to join two amidate ligands with a phosphine-donor, this was performed via an ortho-lithiation strategy, as shown in Scheme 6.2. The phosphine-linked diamide ligand (6.1) was synthesized, and characterized using NMR spectroscopy. The $^{31}$P{$^{1}$H} NMR spectrum of 6.1 in C₆D₆ contains a singlet resonance at δ -32.3, and the $^{1}$H NMR spectrum is shown in Figure 6.2.
Scheme 6.2: Synthesis of a phosphine-bridged diamide ligand and subsequent coordination to zirconium.

Figure 6.2: 400 MHz $^1$H NMR spectrum of 6.1 in C$_6$D$_6$.

The proposed zirconium complex outlined in Scheme 6.3 was not examined. This is because during these investigations it was reported that reduction of tantalum amidate complexes results in oxygen extrusion to give oxo-containing tantalum iminoacyl complexes.$^{202}$ Since the
overall goal of developing this ligand was to examine its ability to support dinitrogen activation via reduction, the project was halted.

### 6.4 Alteration of the ferrocenyl diphosphinoamide ligand system

One aspect of the ligand design strategy using phosphinoamides in this thesis was systematic alteration of the ligand environment. The complexes supported by the ferrocenyl-linked diphosphinoamide ligand had relatively open coordination spheres near the metal center. In an attempt to add steric protection to the zirconium, a derivative with di-tert-butyl groups on phosphorus was synthesized (Scheme 6.3).

![Scheme 6.3: Synthesis of a more sterically demanding ferrocenyl diphosphinoamine](Image)

This approach of adding more bulky substituents at phosphorus is not likely to provide more steric protection because of the demonstrated ability of the ligand to bind in a $\kappa^2$-(NN) fashion as opposed to $\kappa^4$-(PNNP) fashion, for an example see complex 4.7. The addition of more sterically demanding phosphorus substituents will likely promote $\kappa^2$-(NN) binding, which renders the phosphorus donors redundant on the ancillary ligand.
One possibility would be using smaller transition metals, such as tantalum, to achieve better steric protection. Indeed, the coordination environment generated by the ferrocene-linked phosphinoamide ligand is well suited to a metal bearing three additional substituents (such as in complex 4.3). Potentially, the reaction of the lithiated precursor 5.1 with Cl₂TaMe₃ would give a tantalum complex with three methyl groups in a meridional conformation (Scheme 6.4). Indeed, this may be an excellent starting material for the synthesis of tantalum hydride complexes. As mentioned at the beginning of this chapter, tantalum hydride complexes are attractive targets due to their demonstrated reactivity toward small molecules.

Scheme 6.4: Proposed synthesis of a tantalum diphosphinoamide complex.

In addition to tantalum, titanium would be an interesting metal for use in the ferrocenyl diphosphinoamide framework. Titanium is smaller than zirconium and also the Ti(III) oxidation state is readily available, which may also shed some light on some of the redox processes, observed using cyclic voltammetry, in the zirconium diphosphinoamide complexes.
6.4.1 Overview

The chemistry of scandium, yttrium and zirconium with simple phosphinoamides demonstrated the difficulty of controlling the number of ligands bound to the metal center. The development of the ferrocenyl-linked diphosphinoamide system improved the stability of the ligand scaffold when bound to the metal center because it can bind in a tetradentate fashion. Interestingly, when the solid-state structure of a discandium dihydride complex was obtained the ligand was observed to span both metal centers with one bridging phosphinoamide arm while the other arm adopted a monodentate coordination mode. Additionally, during the course of studies in synthesizing zirconium alkyls the solid-state structure of one complex revealed that the ferrocene-linked framework had undergone phosphine dissociation to act as a bidentate ligand. This flexibility in the ligand framework allows it to adopt variable coordination modes depending on the steric environment at the metal center. The future development of multidentate phosphinoamide scaffolds should render the ligand framework more rigid to improve upon the current design.
7 Experimental

7.1 General procedures

7.1.1 Laboratory equipment and procedures

Unless otherwise noted all experiments were carried out using oven-dried glassware cooled under vacuum, and all compounds were handled under an atmosphere of dry N$_2$ in a glovebox (Innovative Technology) equipped with a freezer (-35°C), or using standard Schlenk technique.

7.1.2 Solvents

Hexanes, Et$_2$O, toluene and THF were purchased anhydrous from Aldrich, were passed over alumina under a nitrogen atmosphere and were collected over activated 4 Å molecular sieves under vacuum. Pentane was degassed by sparging with N$_2$ and was dried by distillation from potassium benzophenone-ketyl. CH$_2$Cl$_2$ was degassed by sparging with N$_2$ and was dried by distillation from calcium hydride. C$_6$D$_6$, THF-$d_8$ and toluene-$d_8$ were distilled from sodium benzophenone-ketyl, and were degassed via 3 freeze-pump-thaw cycles.

7.1.3 Materials

ZrCl$_4$(THF)$_2$, Zr(NMe$_2$)$_4$, PhPH$_2$, PhPCl$_2$, ClP$^t$Pr$_2$, ClP$^t$Bu$_2$, were all purchased from commercial sources and used as received. M(CH$_2$SiMe$_3$)$_3$(THF)$_2$ where M = Sc or Y were prepared according to published procedures.$^{203}$ Complex fc(NH$_2$)$_2$ was synthesized according to literature procedure$^{189}$ and was purified by washing with anhydrous Et$_2$O. Alkylation reagents
MeLi, "BuLi, tBuLi, EtMgCl and PhCH₂MgCl were purchased as solutions and were used as received. Ph₃PO and NaBH₄ were purchased and dried in vacuo prior to use. KCH₂Ph and tBuCH₂Li were synthesized according to literature procedures. KEt₃BH was purchased as THF solution and was obtained as a solid by drying in vacuo. NEt₃ and 3,5-dimethylaniline were dried by distillation from CaH₂ and degassed by sparging with N₂. PMe₃ and TMSCl were purchased from commercial sources and were distilled prior to use. LiN(SiMe₃)₂ was purchased and purified by sublimation. (OEP)TaMe₃, K₂(OEP) and ((THF)₂Cl₃Ta)₂(µ-N₂) were all synthesized according to the literature procedure. N-phenylpivalamide was synthesized from the corresponding commercially obtained trimethylacyl chloride and aniline and was dried in vacuo prior to use. Ferrocene was purchased and purified by Soxhlet extraction using hexanes, the solvent was removed by filtration and the solids were dried in vacuo. nBu₄NPF₆ and nBu₄NBPh₄ were purchased from commercial sources and were dried under vacuum (1 x 10⁻⁵ Torr) for 24 hours in a schlenk flask heated to 100 °C.

7.1.4 Instrumentation and methods of analysis

¹H, ¹³C, ³¹P, ⁷Li and ¹¹B NMR spectra were recorded on a Bruker Avance 300, 400 MHz or 600 MHz spectrometer. ¹H and ¹³C NMR chemical shifts were referenced to residual solvents signals from the deuterated solvents. ³¹P NMR chemical shifts were referenced to external samples of phosphoric acid (85 % in aqueous solution) at δ = 0 ppm. ¹¹B NMR chemical shifts were referenced to external samples of BF₃OEt₂ (neat) at δ = 0 ppm. ⁷Li NMR chemical shifts were referenced to external samples of LiCl (1 M in D₂O) at δ = 0 ppm.
FT-IR spectra were recorded on a Perkin Elmer Frontier Spectrometer with attenuated total reflectance. Samples (typically crystalline) were coated in nujol to prevent oxidation, and nujol backgrounds were subtracted from the FT-IR spectra.

Elemental analyses (EA) determinations were performed using a Carlo Erba Elemental Analyzer 1108, and were performed in the Department of Chemistry at the University of British Columbia by Mr. David Wong or Mr. Derek Smith.

Single crystal X-ray data was collected on a Bruker X8 Apex II diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) integrated using the Bruker SAINT software package. Suitable single crystals were selected, coated in Fomblin oil and mounted on a glass fiber. All absorption corrections were performed using the multi-scan technique (SADABS). Structures were solved by direct methods and refined using all reflections with the SHELX-97 program package. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms (unless specified) were placed in calculated positions and assigned to an isotropic displacement parameter, other specified hydrogen atoms were located in the difference map and were refined isotropically. Structures were solved and refined using the WinGX (version 1.80.05) software package. Crystallographic tables containing unit cell and refinement information are located in Appendix E.

Powder X-ray diffraction experiments were performed on a Bruker Apex II diffractometer with Cu Kα radiation (λ = 1.54184 Å) using an area detector. Powder samples were packed in a borosilicate glass capillary (0.7 mm diameter, from Charles Supper Company) under nitrogen and then flame sealed. Two measurements were taken on the sample, centering the X-ray beam on two different positions of the capillary to ensure reproducibility.

Cyclic voltammetry was performed using a CH instruments potentiostat connected to
electrodes located in a glovebox connected by BNC junctions. The working (platinum button, 2 mm diameter) and counter (glassy carbon, 3 mm diameter) electrodes were polished with 0.3, 0.1 and 0.05 µm powder polish (alumina slurry) sequentially, sonicated for 10 minutes in deionized water, and rinsed with acetone before being brought into an argon filled glovebox. The reference electrode (99.9% silver wire, 0.25 mm diameter) was exposed to the flame of a butane torch and wiped with a fine polish pad in order to remove the residual organic matter before being brought into the glove box with the other electrodes. All the electrodes were fitted with a b14 septum with a 5/16” opening cut by a cork borer for easy attachment to a 25 mL round bottom flask. The analyte, either "Bu₄NPF₆ (387 mg, 1 mmol) or "Bu₄NBPh₄ (562 mg, 1 mmol), was dissolved in 10 mL of dry THF (0.1 mol L⁻¹) that had been sparged with argon and transferred to a 25 mL 3-necked round bottom flask with b14 female joints. The electrodes were connected to the appropriate leads from the potentiostat and inserted into the necks of the flask with the counter electrode installed in the central position. Once the solution had settled, a cyclic voltammogram (100 mV/s, -2.8 to 1.5 V, negative scan starting at 0 V) was collected to act as the baseline for the experiment. Upon successful completion of the baseline the analyte (0.05 mmol, 0.005 mol L⁻¹) was dissolved in the electrolyte/THF solution and added to the flask and further CV experiments were conducted. Between each run, the flask was agitated to aid with diffusion and if a decrease in signal intensity was observed, the electrodes were wiped with a KimWipe. After completion of the set of experiments, a single crystal of ferrocene (Cp₂Fe) was added to the solution and a cyclic voltammogram (100 mV/s, -2.8 to 1.5 V, negative scan starting at 0 V) was collected for reference.

In order to examine the nature of the HOMO and LUMO, complexes 2.8 and 4.1 were modeled using quantum chemical calculations, specifically density functional theory. All
calculations described herein were performed using the Gaussian suite of programs\textsuperscript{211,212} and run on the Orcinus cluster maintained by WestGrid, a division of ComputeCanada. Based on previous success in the modeling of early transition metal complexes, density functional theory (DFT) was chosen as the modelling method.\textsuperscript{213} All geometries have been optimized using the B3LYP hybrid functional\textsuperscript{214-217} due to its ability to accurately predict crucial molecular properties such as bond lengths and vibrational frequencies.\textsuperscript{218} The double zeta 6-31G Pople basis set was modified to include polarization functions for C, H, O, N, P, Fe, and Sc to better describe interactions with the metal centres. The zirconium centre was modeled using the Los Alamos LANL2DZ basis set with an effective core potential.\textsuperscript{219,220} Geometric optimization of local minima was confirmed using vibrational analysis with only positive frequencies observed. These calculations are performed under the default conditions in the Gaussian program (298.15 K, 1 atm). All ball-and-stick models of calculated structures presented herein have been produced using GaussView5.\textsuperscript{221} Molecular orbital surfaces are generated from natural bond orbital (NBO) analysis,\textsuperscript{222} plotted at an isovalue of 0.02.

7.2 Synthesis of compounds

7.2.1 Complexes pertaining to Chapter 2

\textbf{ArNHP\textsuperscript{3}Pr\textsubscript{2} (2.1)}

This synthesis is a modified version of a published procedure for the synthesis of other phosphinoamines.\textsuperscript{223,224} Triethylamine (33.5 mL, 0.24 mol) and 3,5-dimethylaniline (15.0 mL, 0.12 mol) were added \textit{via} syringe to 250 mL CH\textsubscript{2}Cl\textsubscript{2} in a 500 mL Schlenk flask equipped with a stir bar. At room temperature ClP\textsuperscript{3}Pr\textsubscript{2} (19.1 mL, 0.12 mol) was added dropwise by syringe over the course of 30 minutes. The reaction mixture was stirred at room temperature for 19 hours, and
the volatiles were removed *in vacuo*. The residues were extracted with 3 x 75 mL of hexanes and filtered through a 1-inch plug of Celite. The hexanes were removed *in vacuo* and the solids were crystallized from 50 mL pentane at -35 °C. The large colourless crystals were collected on a glass frit and were dried *in vacuo*. (Yield: 23.1 g, 81 %). 31P{1H} NMR (δ in ppm, C6D6, 293 K, 162 MHz): 47.1 (s); 1H NMR (δ in ppm, C6D6, 293 K, 400 MHz): 6.67 (s, 2H, o-Ar), 6.39 (s, 1H, p-Ar), 3.32 (d, 1H, 2JHP: 10.8 Hz, N-H), 2.16 (s, 6H, Ar-CH3), 1.48 (d of septets, 2H, 2JHP: 2.4 Hz, 3JHH: 7.0 Hz, P-CH), 0.98 (dd, 6H, 3JHP: 16.2 Hz, 3JHH: 7.0 Hz, CH3-iPr), 0.96 (dd, 6H, 3JHP: 10.4 Hz, 3JHH: 7.0 Hz, CH3-iPr); 13C{1H} NMR (δ in ppm, C6D6, 293 K, 100.6 MHz): 149.4 (d, 2JCP: 21.5 Hz, N-Cipso), 138.6 (s, Cmeta), 120.9 (s, Cpara), 114.4 (d, 3JCP: 11.6 Hz, Cortho), 27.1 (d, 1JCP: 12.9 Hz, P-CH), 21.6 (s, CH3-Ar), 19.1 (d, 2JCP: 20.6 Hz, CH3-iPr), 17.3 (d, 2JCP: 8.2 Hz, CH3-iPr). For C14H24N1P1: EA (%: calc.): C, 70.85; H, 10.19; N, 5.90. EA (%: found): C, 70.71; H, 9.88; N, 5.90.

**ArNP2Pr3Y(THF) (2.2)**

In a 50 mL Schlenk flask equipped with a stir bar Y(CH2SiMe3)3(THF)2 (197 mg, 0.40 mmol) was dissolved in 2 mL hexanes. At room temperature a solution of ArNHP2Pr2 (284 mg, 1.20 mmol) in 2 mL hexanes was added dropwise. The solution was stirred for 3 hours at which point a white precipitate was collected on a glass frit, was washed with 2 x 2 mL hexanes, and was dried *in vacuo*. (Yield: 319 mg, 92 %). X-ray quality crystals were obtained by slow diffusion of pentane into a concentrated Et2O solution of the yttrium complex.

31P{1H} NMR (δ in ppm, C6D6, 293 K, 162 MHz): 29.6 (d, JPY: 18.3 Hz); 1H NMR (δ in ppm, C6D6, 293 K, 400 MHz): 6.98 (s, 6H, o-Ar), 6.52 (s, 3H, p-Ar), 6.01 (br, 4H, THF), 2.58 (d of septets, 6H, 2JHP: 2.0 Hz, 3JHH: 7.2 Hz, P-CH), 2.32 (s, 18H, Ar-CH3), 1.35 (br, 4H, THF), 1.19 (dd, 18H, 2JHP: 15.0 Hz, 3JHH: 7.2 Hz, CH3-iPr) 1.15 (dd, 18H, 3JHP: 12.2 Hz, 3JHH: 7.2Hz, CH3-
\(^1\)Pr; \(^{13}\)C\(^{1}H\) NMR (\(\delta\) in ppm, \(\text{C}_6\text{D}_6\), 100.6 MHz): 154.5 (d, \(^2J_{\text{CP}}\): 11.7 Hz, N-\(\text{C}_{\text{ipso}}\), 137.4 (s, \(\text{C}_{\text{meta}}\), 121.3 (d, \(^3J_{\text{CP}}\): 8.7 Hz \(\text{C}_{\text{ortho}}\), 120.9 (s, \(\text{C}_{\text{para}}\), 72.3 (s, THF), 28.0 (d, \(^1J_{\text{CP}}\): 10.6 Hz, P-CH), 25.7 (s, THF), 21.9 (s, \(\text{CH}_3\)-Ar), 20.8 (d, \(^2J_{\text{CP}}\): 16.9 Hz, \(\text{CH}_3\)-iPr), 20.6 (d, \(^2J_{\text{CP}}\): 8.2 Hz, \(\text{CH}_3\)-iPr). \(\text{C}_{46}\text{H}_{77}\text{N}_3\text{O}_1\text{P}_3\text{Sc}_1\) EA (\%, calc.): C, 63.51; H, 8.92; N, 4.83. EA (\%, found): C, 63.80; H, 9.14; N, 4.61.

\((\text{ArNP}^i\text{Pr}_2)_3\text{Sc(THF)}\) (2.3)

In a 50 mL Schlenk flask, equipped with a stir bar, \(\text{Sc(CH}_2\text{SiMe}_3)_3\text{(THF)}_2\) (451mg, 1.0 mmol) was dissolved in 3 mL hexanes. At room temperature a solution of \(\text{ArNHP}^i\text{Pr}_2\) (712 mg, 3.0 mmol) in 5 mL hexanes was added dropwise. The solution was stirred for 24 hours at which point an off-white precipitate was collected on a glass frit, was washed with 2 x 2 mL hexanes, and was dried \textit{in vacuo}. (Yield: 498 mg, 60%).

\(^{31}\)P\(^{1}H\) NMR (\(\delta\) in ppm, \(\text{C}_6\text{D}_6\), 293 K, 162 MHz): 34.4 (s); \(^1\)H NMR (\(\delta\) in ppm, \(\text{C}_6\text{D}_6\), 293 K, 400 MHz): 6.90 (s, 6H, o-Ar), 6.50 (s, 3H, p-Ar), 3.74 (br, 4H, THF), 2.63 (d of septets, 6H, \(^2J_{\text{HP}}\): 2.8 Hz, \(^3J_{\text{HH}}\): 7.2 Hz, P-CH), 2.25 (s, 18H, Ar-CH\(_3\)), 1.41 (br, 4H, THF), 1.28 (dd, 18H, \(^2J_{\text{HP}}\): 18.4 Hz, \(^3J_{\text{HH}}\): 7.2 Hz, \(\text{CH}_3\)-iPr); \(^{13}\)C\(^{1}H\) NMR (\(\delta\) in ppm, \(\text{C}_6\text{D}_6\), 100.6 MHz): 152.7 (d, \(^2J_{\text{CP}}\): 12.2 Hz, N-\(\text{C}_{\text{ipso}}\), 137.9 (s, \(\text{C}_{\text{meta}}\), 121.4 (s, \(\text{C}_{\text{para}}\), 120.4 (d, \(^3J_{\text{CP}}\): 8.8 Hz, \(\text{C}_{\text{ortho}}\), 69.2 (s, THF), 28.1 (d, \(^1J_{\text{CP}}\): 7.2 Hz, P-CH), 25.7 (s, THF), 21.7 (s, Ar-CH\(_3\)), 20.7 (br m, \(\text{CH}_3\)-iPr). \(\text{C}_{46}\text{H}_{77}\text{N}_3\text{O}_1\text{P}_3\text{Sc}_1\) EA (\%, calc.): C, 66.89; H, 9.40; N, 5.09. EA (\%, found): C, 66.59; H, 9.41; N, 5.68.

\((\text{ArNP}^i\text{Pr}_2)_2\text{Y(CH}_2\text{SiMe}_3\text{(THF)}\) (2.4) and \((\text{ArNP}^i\text{Pr}_2)_2\text{Y(CH}_2\text{SiMe}_3\text{(THF)}\) (2.5)

To a 0.6 mL \(\text{C}_6\text{D}_6\) (or toluene-\(d_8\)) solution of 2.2 (9 mg, 0.01 mmol) was added solid \(\text{Y(CH}_2\text{SiMe}_3)_3\text{(THF)}_2\) (5, 10 or 15 mg; 0.01, 0.02 or 0.03 mmol). The solutions were transferred to an NMR tube and were analyzed by NMR spectroscopy.
(ArNPr)2Sc(CH2SiMe3)(THF) (2.6)

**Method A**: To a mixture of solid 2.1 (949 mg, 4.0 mmol) and Sc(CH2SiMe3)3(THF)2 (902 mg, 2.0 mmol) was added 10 mL toluene at room temperature. The mixture was stirred for 24 hours at which point the volatiles were removed *in vacuo*; the residues were recrystallized twice from 5 mL hexanes at -35 °C to give colourless crystals (some suitable for X-ray analysis) of 2.4 (Yield: 910 mg, 67 %).

**Method B**: To a mixture of solid 2.2 (33 mg, 0.04 mmol) and Sc(CH2SiMe3)3(THF)2 (9 mg, 0.02 mmol) was added 2 mL of THF at room temperature. After stirring for 5 hours the volatiles were removed *in vacuo*. Conversion to 2.4 was quantitative as ascertained by NMR spectroscopy.

31P{1H} NMR (δ in ppm, C6D6, 293 K, 162 MHz): 26.6 (s); 1H NMR (δ in ppm, C6D6, 293 K, 400 MHz): 6.87 (s, 4H, o-Ar), 6.50 (s, 2H, p-Ar), 4.01 (br, 4H, THF), 2.59 (d of septets, 4H, 2JHP: 3.2 Hz, 3JHH: 7.0 Hz, P-CH), 2.29 (s, 12H, Ar-CH3), 1.24 (br, 4H, THF), 1.19 (br ov, 24H, CH3-Pr), 0.43 (s, 9H, CH3-Si), 0.09 (s, 2H, Sc-CH2-Si); 13C{1H} NMR (δ in ppm, C6D6, 100.6 MHz): 152.7 (d, 2JCP: 10.0 Hz, N-Cipso), 137.7 (s, Cmeta), 121.7 (s, Cpara), 120.1 and 120.0 (ov d, 3JCP: 4.6 Hz, Cpara), 72.9 (s, THF), 37.7 (br and weak, Sc-CH2), 28.0 (d, 1JCP: 10.6 Hz, P-CH), 25.4 (s, THF), 21.8 (s, CH3-Ar), 20.8 (br, CH3-Pr), 4.8 (s, CH3-Si). For C36H65N2O1P2Sc1Si1 EA (% calc.): C, 63.88; H, 9.68; N, 4.14. EA (% found): C, 63.83; H, 9.70; N, 4.18.

fc(NHPiPr2)2 (2.7)

fc(NH2)2 (4.000g, 18.5 mmol) was suspended in (250 mL) Et2O in a Schlenk flask. First triethylamine (20.6 mL, 148.1 mmol) and then ClPiPr2 (5.9 mL, 37.0 mmol) were added via syringe at room temperature. After stirring at room temperature for 18 hours the volatiles were removed *in vacuo*. The residues were extracted with 100 mL pentane and filtered through Celite.
The filtrate was cooled to -35°C overnight to give 6.080 g of orange crystalline solid (73% yield).

\(^{31}\text{P}\{^1\text{H}\}\) NMR (δ in ppm, C\(_6\)D\(_6\), 293 K, 162 MHz): 57.8 (s); \(^1\text{H}\) NMR (δ in ppm, C\(_6\)D\(_6\), 293 K, 400 MHz); 4.14 (t, 4H, \(^3\text{J}_{\text{HH}}\): 1.9 Hz, Cp-\(H\)), 3.92 (t, 4H, \(^3\text{J}_{\text{HH}}\): 1.9 Hz, Cp-\(H\)), 2.42 (d, 2H, \(^2\text{J}_{\text{HP}}\): 8.8 Hz, N\(H\)), 1.45 (septet of d, 4H, \(^2\text{J}_{\text{HP}}\): 1.6 Hz, \(P\)-\(C\)H), 1.03 (dd, 12H, \(^3\text{J}_{\text{HH}}\): 7.2 Hz, \(C\)H\(_3\)-iPr), 1.01 (dd, 12H, \(^3\text{J}_{\text{HH}}\): 7.2 Hz, \(C\)H\(_3\)-iPr);

\(^{13}\text{C}\{^1\text{H}\}\) NMR (δ in ppm, C\(_6\)D\(_6\), 100.6 MHz): 109.9 (d, \(^2\text{J}_{\text{CP}}\): 21.3 Hz, (Cp)C-N), 64.6 (s, (Cp)C), 60.6 (d, \(^3\text{J}_{\text{CP}}\): 7.9 Hz, (Cp)C-CN), 27.0 (d, \(^1\text{J}_{\text{CP}}\): 13.3 Hz, P-CH), 19.3 (d, \(^2\text{J}_{\text{CP}}\): 20.6 Hz, \(CH\)_3-iPr), 17.6 (d, \(^2\text{J}_{\text{CP}}\): 8.5 Hz, \(CH\)_3-iPr).

For C\(_{22}\)H\(_{38}\)N\(_2\)P\(_2\)Fe\(_1\)EA (%, calc.): C, 58.94; H, 8.54; N, 6.25. EA (%, found): C, 59.21; H, 8.57; N, 6.52.

\(\text{fc(NP}^2\text{Pr}_2)\text{Sc(CH}_2\text{SiMe}_3)\text{(THF)}\) (2.8)

To a Schlenk flask containing solid 2.7 (1.000 g, 2.23 mmol) and Sc(CH\(_2\)SiMe\(_3\))\(_3\) (THF)\(_2\) (1.002 g, 2.23 mmol) was added hexanes (40 mL) at room temperature. After stirring for 3 hours all volatiles were removed \textit{in vacuo} to give 1.455 g of yellow solid (yield: 96%). The product was crystallized from hexanes at -35°C, and X-ray quality crystals were obtained in this manner.

\(^{31}\text{P}\{^1\text{H}\}\) NMR (δ in ppm, C\(_6\)D\(_6\), 293 K, 162 MHz): 48.1 (s); \(^1\text{H}\) NMR (δ in ppm, C\(_6\)D\(_6\), 293 K, 400 MHz); 4.42 (br), 4.28 (br), 4.02 (br), 3.91 (br), 2.07 (br), 1.93 (br), 1.38 (THF), 1.23 (br), 1.14 (br), 1.01 (br), 0.45 (s, Si-CH\(_3\)), 0.32 (s, Sc-CH\(_2\)) ; \(^{13}\text{C}\{^1\text{H}\}\) NMR (δ in ppm, C\(_6\)D\(_6\), 100.6 MHz): 106.3 (d, \(^2\text{J}_{\text{CP}}\): 13.6 Hz, (Cp)C-N), 73.5 (br, THF), 67.9 (br, Cp), 66.7 (br, Cp), 65.6 (br, Cp), 64.6 (br, Cp), 28.4 (br), 25.2 (s, Sc-CH\(_3\)), 24.7 (br), 19.7 (br). \(^{31}\text{P}\{^1\text{H}\}\) NMR (δ in ppm, THF-\text{d}_8, 293 K, 162 MHz): 47.4 (s); \(^1\text{H}\) NMR (δ in ppm, THF-\text{d}_8, 293 K, 400 MHz); 3.95 (tr, 4H, \(^3\text{J}_{\text{HH}}\): 1.6 Hz, Cp-\(H\)), 3.83 (tr, 4H, \(^3\text{J}_{\text{HH}}\): 1.6 Hz, Cp-\(H\)), 3.57 (m, 4H, THF), 3.54 (THF), 1.86 (septet of d, \(^2\text{J}_{\text{HP}}\): 2.8 Hz, \(^3\text{J}_{\text{HH}}\): 7.2 Hz, 4H, P-\(CH\)), 1.72 (m, 4H, THF), 0.97 (ov dd, \(^2\text{J}_{\text{HP}}\): 5.2 Hz,
$^3J_{HH}$: 6.6 Hz, CH$_3$-Pr) 0.95 (ov dd, $^2J_{HP}$: 6.8 Hz, $^3J_{HH}$: 6.6 Hz, CH$_3$-Pr) -0.03 (s, Si-CH$_3$), -0.12 (s, Sc-CH$_2$); $^{13}$C{${}^1$H} NMR (δ in ppm, THF-$d_8$, 100.6 MHz): 106.2 (d, $^2J_{CP}$: 13.2 Hz, C-N), 73.0 (s, THF), 66.3 (s, (Cp)C), 64.4 (s, (Cp)C), 25.9 (d, $^1J_{CP}$: 18.4 Hz, P-CH), 31.1 (s, THF), 19.3 (d, $^2J_{CP}$: 11.2 Hz, CH$_3$-Pr), 18.5 (d, $^2J_{CP}$: 15.1 Hz, CH$_3$-Pr), 3.3 (s, Si-CH$_3$), not observed: Sc-CH$_2$.

For C$_{32}$H$_{61}$N$_2$O$_1$P$_2$Fe$_1$Sc$_1$Si$_1$ EA (%; calc.): C, 56.47; H, 9.03; N, 4.12. EA (%; found): C, 56.18; H, 8.84; N, 4.26.

**fc(NPPr$_2$)$_2$Sc(CH$_2$SiMe$_3$)(OPPh$_3$) (2.9)**

A Schlenk flask was charged with solid 2.8 (204 mg, 0.30 mmol) and Ph$_3$PO (83 mg, 0.30 mmol) and 5 mL of toluene was added at room temperature. The solution was allowed to stir for 1 hour at room temperature and the volatiles were removed *in vacuo*. The solids were washed onto a glass frit with 5 mL hexanes and were dried *in vacuo* to give 155 mg of yellow powder (yield: 58 %).

$^{31}$P{${}^1$H} NMR (δ in ppm, C$_6$D$_6$, 293 K, 162 MHz): 52.4 (s, 2P, Sc-P), 40.4 (s, 1P, Sc-O=P); $^1$H NMR (δ in ppm, C$_6$D$_6$, 293 K, 400 MHz): 7.97 (ov m, 6H, Ph-H); 7.10 (br m, 9H, Ph-H); 4.51 (s, 2H, Cp-H); 4.07 (s, 2H, Cp-H); 4.03 (s, 2H, Cp-H); 3.94 (s, 2H, Cp-H); 2.03 (m, 4H, P-CH$_2$);

1.31 (ov dd, 6H, $^2J_{HP}$: 11.6 Hz, $^3J_{HH}$: 7.2 Hz, CH$_3$-Pr); 1.28 (ov dd, 6H, $^2J_{HP}$: 12.2 Hz, $^3J_{HH}$: 7.2 Hz, CH$_3$-Pr); 1.00 (dd, 6H, $^2J_{HP}$: 12.8 Hz, $^3J_{HH}$: 6.8 Hz, CH$_3$-Pr); 0.86 (dd, 6H, $^2J_{HP}$: 14.0 Hz, $^3J_{HH}$: 7.2 Hz, CH$_3$-Pr); $^{13}$C{${}^1$H} NMR (δ in ppm, C$_6$D$_6$, 100.6 MHz): 133.9 (t, $^1J_{CP}$: 3.5 Hz, Ph); 133.8 (t, $^1J_{CP}$: 3.5 Hz, Ph); 133.5 (d, $^1J_{CP}$: 2.6 Hz, Ph); 128.9 (d, $^1J_{CP}$: 13.2 Hz, Ph); 105.6 (d, $^2J_{CP}$: 13.7 Hz, C-N); 68.0 (s, (Cp)C); 66.5 (s, (Cp)C); 66.1 (s, (Cp)C); 64.1 (s, (Cp)C); 28.3 (d, $^2J_{CP}$: 21.2 Hz, P-CH), 25.1 (d, $^2J_{CP}$: 21.2 Hz, P-CH), 20.7 (ov d, $^3J_{CP}$: 13.6 Hz, CH$_3$-Pr), 20.6 (ov d, $^3J_{CP}$: 11.2 Hz, CH$_3$-Pr), 20.1 (d, $^3J_{CP}$: 11.5 Hz, CH$_3$-Pr), 19.0 (d, $^3J_{CP}$: 20.4 Hz, CH$_3$-Pr), 4.7 (s,
Si-CH₃), not observed: Sc-CH₂. For C₄₆H₆₈N₂O₁P₃Fe₁Sc₁Si₁ EA (%, calc.): C, 62.30; H, 7.73; N, 3.16. EA (%; found): C, 61.12; H, 7.21; N, 3.45; repeated analyses were low in carbon.

\[\text{[fc(NP}^\text{iPr}^\text{2})\text{Sc(THF)H]}_2 (2.10)\]

A 100 mL hexanes solution of 2.8 (1.100 g, 1.616 mmol) was transferred to a 1 L thick walled Teflon-sealed flask and was freeze-pump-thaw degassed (3 cycles). While the flask remained frozen (at -196 °C, using N₂(g)), hydrogen gas (1 atm) was added, after passing over activated molecular sieves, and the flask was sealed. The solution was warmed to room temperature behind a blast shield and was left undisturbed for 16 days; a yellow crystalline product is produced, with some crystals suitable for X-ray diffraction studies. The solids were collected on a glass frit and were dried in vacuo. Yield: 745 mg, 1.253 mmol (78 %). Due to low solubility suitable NMR spectra in solution could not be obtained. For C₅₆H₁₀₂N₄O₂P₄Fe₂Sc₂ EA (%; calc.): C, 56.57; H, 8.65; N, 4.71. EA (%; found): C, 55.76; H, 8.24; N, 5.14.

7.2.2 Complexes pertaining to Chapter 3

\[\text{[(ArNP}^\text{iPr}^\text{2})\text{Li(OT}_{\text{et}}\text{)}]_2 (3.1)\]

To a solution of ArNHP^iPr₂ (18.8 mmol, 4.47 g) in 50 mL of diethyl ether was added a 1.6 M solution of “BuLi in hexanes (20.7 mmol, 13 mL) dropwise via syringe at room temperature. After stirring the solution for 15 hours at room temperature, the volatiles were removed in vacuo. The white solids were washed with 5 mL pentane on a glass frit, and were dried in vacuo, yield: 3.50 g (59 %). Crystals suitable for X-ray diffraction were obtained from a dilute hexanes solution at -35 °C. \(^{31}\text{P}\{^1\text{H}\}\) NMR (δ in ppm, C₆D₆, 293 K, 162 MHz): 55.3 (s); \(^7\text{Li}\) NMR (δ in ppm, C₆D₆, 293 K, 155.4 MHz): 1.00 (br); \(^1\text{H}\) NMR (δ in ppm, C₆D₆, 293 K, 300 MHz): 6.92 (s, 2H, o-Ar), 6.71 (s, 1H, p-Ar), 3.05 (quartet, 4H, \(^3\text{J}_{\text{HH}}\) : 6.9 Hz, Et₂O), 2.57 (septet, 2H, \(^3\text{J}_{\text{HH}}\) : 6.9 Hz, 2H), 2.17 (m, 2H).
Hz, P-CH), 2.32 (s, 6H, Ar-CH₃), 1.30 (dd, 6H, ³Jₜₚₚ : 16.2 Hz, ³Jₜₜ : 10.0 Hz, CH₃-iPr), 1.25 (dd, 6H, ³Jₜₚ : 10.4 Hz, ³Jₜₜ : 11.5 Hz, CH₃-iPr), 0.88 (t, 6H, ³Jₜₜ : 6.9 Hz, Et₂O); ¹³C{¹H} NMR (δ in ppm, C₆D₆, 293 K, 100.6 MHz): 157.8 (N-Cipso), 138.6 (s, Cmeta), 119.9 (d, ³JCP : 11.6 Hz, Cortho), 118.7 (s, Cpara), 64.9 (s, Et₂O) 28.0 (d, ¹JCP : 19.6 Hz, P-CH), 22.0 (s, Ar-CH₃), 21.4 (d, ²JCP : 22.6 Hz, H₃C-iPr), 21.1 (d, ²JCP : 11.3 Hz, H₃C-iPr), 14.2 (s, Et₂O). For C₁₈H₃₃N₁O₁P₁Li₁
EA (%, calc.): C, 68.12; H, 10.48; N, 4.41. EA (%, found): C, 68.00; H, 10.61; N, 4.80.

(ArNP²Pr₂)₃ZrCl (3.2)

Phosphinoamine 2.1 (3.56 g, 15.0 mmol) was dissolved in 200 mL Et₂O in a Schlenk flask. A solution of "BuLi (9.4 mL of a 1.6 M in hexanes, 15.0 mmol) was added dropwise via syringe. After stirring for 1 hour, the solution was transferred dropwise via cannula to another flask containing an 80 mL Et₂O suspension of ZrCl₄(THF)₂ (1.89 g, 5.0 mmol). The reaction mixture was allowed to stir for 3 hours at which point the volatiles were removed in vacuo. The residues were extracted with 40 mL toluene and filtered through Celite, and the filtrate was dried in vacuo. The resulting solids were washed with 2 x 5 mL hexanes onto a glass frit and were dried in vacuo, to yield 3.75 g of white powder (90%).

³¹P{¹H} NMR (δ in ppm, C₆D₆, 293 K, 162 MHz): 7.2 (s); ¹H NMR (δ in ppm, C₆D₆, 293 K, 600 MHz): 6.94 (s, 6H, o-Ar), 6.46 (s, 3H, p-Ar), 2.52 (d of septet, 6H, ³Jₜₜ : 6.6 Hz, ³Jₜₚ : 1.8 Hz, P-CH), 2.22 (s, 12H, Ar-CH₃), 1.21 (dd, 6H, ³Jₜₚ : 16.8 Hz, ³Jₜₜ : 7.2 Hz, CH₃-iPr), 1.14 (dd, 6H, ³Jₜₚ : 16.2 Hz, ³Jₜₜ : 7.2 Hz, CH₃-iPr); ¹³C{¹H} NMR (δ in ppm, C₆D₆, 293 K, 150.9 MHz): 152.0 (d, ²JCP : 8.5 Hz, Cipso-Ar), 137.5 (s, C-Ar), 123.5 (s, C-Ar), 121.7 (d, ³JCP : 5.1 Hz, Cortho-Ar), 27.8 (d, ¹JCP : 2.6 Hz, P-CH), 21.7 (s, Ar-CH₃), 20.9 (d, ²JCP : 9.5 Hz, CH₃-iPr), 19.8 (d, ²JCP : 9.4 Hz, CH₃-iPr). For C₄₂H₆₉Cl₁N₁P₃Zr₁ EA (%, calc.): C, 60.37; H, 8.32; N, 5.03. EA (%, found): C, 60.06; H, 8.62; N, 5.08.
(ArNP′Pr₂)₂Zr(NMe₂)₂ (3.3)

Phosphinoamine 2.1 (237 mg, 1.0 mmol), and Zr(NMe₂)₄ (134 mg, 0.50 mmol) were weighed to a Schlenk flask, and 5 mL hexanes were added at room temperature. The reaction mixture was allowed to stir for 18 hours at which point the volatiles were removed in vacuo to give colourless oil in quantitative yield.

³¹P{¹H} NMR (δ in ppm, C₆D₆, 293 K, 162 MHz): 15.8 (s); ¹H NMR (δ in ppm, C₆D₆, 293 K, 400 MHz): 6.92 (s, 4H, o-Ar), 6.54 (s, 2H, p-Ar), 3.35 (s, 12H, N-C₃H₃), 2.53 (d of septet, 4H, ³JHH: 6.8 Hz, ³JHP: 2.8 Hz, P-CH), 2.28 (s, 12H, Ar-CH₃), 1.15 (dd, 6H, ³JHP: 17.2 Hz, ³JHH: 7.2 Hz, CH₃-Pr), 1.08 (dd, 6H, ³JHP: 14.4 Hz, ³JHH: 6.8 Hz, CH₃-Pr), 13C{¹H} NMR (δ in ppm, C₆D₆, 293 K, 100.6 MHz): 152.1 (d, ²JC: 8.8 Hz, Cipso-Ar), 138.0 (s, Ar), 122.5 (s, Ar), 120.6 (d, ³JC: 7.0 Hz, Cortho-Ar), 46.5 (t, ³JC: 18.4 Hz, N-CH₃), 27.0 (d, ¹JC: 7.1 Hz, P-CH), 21.9 (s, Ar-CH₃), 20.3 (d, ²JC: 16.0 Hz, CH₃-Pr), 19.8 (d, ²JC: 7.2 Hz, CH₃-Pr). Solid samples suitable for elemental analysis could not be obtained.

(ArNP′Pr₂)SiMe₃ (3.4)

Complex 3.1 (130 mg, 0.20 mmol) was dissolved in 5 mL of pentane in a Schlenk flask. At room temperature TMSCl (0.5 mL, 0.4 mmol) was added via syringe. After stirring the reaction mixture for 30 minutes the volatiles were removed in vacuo. The residues were redissolved in 5 mL pentane and were filtered through Celite, removal of the pentane in vacuo gave 130 mg of a colourless, viscous oil.

³¹P{¹H} NMR (δ in ppm, C₆D₆, 293 K, 162 MHz): 63.8 (s); ¹H NMR (δ in ppm, C₆D₆, 293 K, 400 MHz): 6.76 (s, 2H, o-Ar), 6.63 (s, 1H, p-Ar), 2.13 (s, 6H, Ar-CH₃), 1.92 (septet of d, 2H, ³JHH: 7.2 Hz, ³JHP: 0.8 Hz, P-CH), 1.12 (dd, 3H, ³JHP: 12.8 Hz, ³JHH: 7.2 Hz, CH₃-Pr), 0.98 (dd, 3H, ³JHP: 13.6 Hz, ³JHH: 6.8 Hz, CH₃-Pr), 0.31 (s, 9H, SiCH₃); ¹³C{¹H} NMR (δ in ppm, C₆D₆,
293 K, 100.6 MHz): 146.7 (d, $^{2}J_{CP}$: 8.7 Hz, C$_{ipso}$-Ar), 138.0 (s, C-Ar), 127.4 (s, C-Ar), 126.5 (s, C$_{ortho}$-Ar), 26.1 (d, $^{1}J_{CP}$: 20.1 Hz, P-CH), 21.5 (s, Ar-CH$_{3}$), 20.1 (d, $^{2}J_{CP}$: 14.9 Hz, CH$_{3}$-i-Pr), 18.8 (d, $^{2}J_{CP}$: 18.2 Hz, CH$_{3}$-i-Pr), 2.1 (s, Si-C$_{H3}$), 2.0 (s, Si-CH$_{3}$). Solid samples suitable for elemental analysis could not be obtained.

(ArNP$^{i}$Pr$_{2}$)$_{2}$ZrCH$_{2}$CH$_{3}$ (3.5)

Complex 3.2 (910 mg, 1.09 mmol) was dissolved in 20 mL Et$_{2}$O in a Schlenk flask and the solution was cooled to 0 ºC. A solution of EtMgCl (0.7 mL of 2.0 M THF solution, 1.40 mmol) was added via syringe dropwise. Upon completion of the addition, the solution was warmed to room temperature and was allowed to stir for 2 hours, at which point the volatiles were removed in vacuo. The residues were extracted with 10 mL of pentane, and the solution was filtered through Celite. Cooling the filtrate to -35 ºC overnight gave white precipitate, which was collected on a glass frit and dried in vacuo, yield: 611 mg (68%).

$^{31}$P{$^{1}$H} NMR (δ in ppm, C$_{6}$D$_{6}$, 293 K, 162 MHz): 6.6 (s); $^{1}$H NMR (δ in ppm, C$_{6}$D$_{6}$, 293 K, 400 MHz): 6.88 (s, 6H, o-Ar), 6.47 (s, 3H, p-Ar), 2.50 (d of sept, 6H, $^{3}$J$_{HH}$: 7.2 Hz, $^{3}$J$_{HP}$: 3.2 Hz, P-CH), 2.23 (ov s, 18H, Ar-CH$_{3}$), 2.23 (ov t, 3H, $^{3}$J$_{HH}$: 7.2 Hz, Zr-CH$_{2}$-CH$_{3}$), 1.42 (qq, 2H, $^{3}$J$_{HH}$: 7.2 Hz, Zr-CH$_{2}$-CH$_{3}$), 1.19 (ov dd, 18H, $^{3}$J$_{HP}$: 14.4 Hz, $^{3}$J$_{HH}$: 7.2 Hz, CH$_{3}$-i-Pr), 1.16 (ov dd, 18H, $^{3}$J$_{HP}$: 14.4 Hz, $^{3}$J$_{HH}$: 7.2 Hz, CH$_{3}$-i-Pr). $^{13}$C{$^{1}$H} NMR (δ in ppm, C$_{6}$D$_{6}$, 293 K, 75.5 MHz): 152.5 (d, $^{2}$J$_{CP}$: 7.8 Hz, C$_{ipso}$-Ar), 137.4 (s, C$_{meta}$-Ar), 123.0 (s, C$_{para}$-Ar), 121.7 (d, $^{2}$J$_{CP}$: 5.7 Hz, C$_{ortho}$-Ar), 45.1 (s, Zr-CH$_{2}$), 28.1 (d, $^{1}$J$_{CP}$: 6.7 Hz, P-CH), 21.6 (s, Ar-CH$_{3}$), 20.9 (d, $^{2}$J$_{CP}$: 10.7 Hz, CH$_{3}$-i-Pr), 20.1 (d, $^{2}$J$_{CP}$: 11.5 Hz, CH$_{3}$-i-Pr), 1.5 (s, Zr-CH$_{2}$CH$_{3}$). For C$_{44}$H$_{74}$N$_{3}$P$_{2}$Zr$_{1}$ EA (%, calc.): C, 63.73; H, 8.99; N, 5.07. EA (%, found): C, 63.24; H, 9.54; N, 5.64.
(ArNP\(^3\)Pr\(^2\))\(_3\)ZrCH\(_2\)Ph (3.6)

Complex 3.2 (167 mg, 0.20 mmol) and benzylpotassium (26 mg, 0.20 mmol) were weighed to a Schlenk flask, and 5 mL of toluene were added at room temperature. The suspension was stirred for 20 hours and the volatiles were removed in vacuo. The residues were extracted with 5 mL of pentane and the solution was filtered through Celite. Removal of the volatiles in vacuo gave 161 mg of the desired product as a colourless solid, yield: 90 %.

\(^{31}\)P\({\{^1}\text{H}\}}\) NMR (δ in ppm, C\(_6\)D\(_6\), 293 K, 121.5 MHz): 4.3 (s); \(^1\)H NMR (δ in ppm, C\(_6\)D\(_6\), 293 K, 300 MHz): 7.55 (d, 2H, \(^3\)J\(_{HH}\): 7.2 Hz, o-Ph), 7.25 (t, 2H, \(^3\)J\(_{HH}\): 7.6 Hz, m-Ph), 6.89 (t, 1H, \(^3\)J\(_{HH}\): 7.6 Hz, p-Ph), 6.83 (s, 6H, o-Ar), 6.49 (s, 6H, p-Ar), 2.98 (q, 2H, \(^3\)J\(_{HH}\): 4.8 Hz, Zr-CH\(_2\)), 2.43 (d of sept, 6H, \(^3\)J\(_{HH}\): 7.2 Hz, \(^3\)J\(_{HP}\): 3.0 Hz, P-CH), 2.22 (s, 18H, Ar-CH\(_3\)), 1.14 (dd, 18H, \(^3\)J\(_{HP}\): 16.0 Hz, \(^3\)J\(_{HH}\): 7.2 Hz, CH\(_3\)-i-Pr), 1.08 (dd, 18H, \(^3\)J\(_{HP}\): 15.0 Hz, \(^3\)J\(_{HH}\): 6.9 Hz, CH\(_3\)-i-Pr).

\(^{13}\)C\({\{^1}\text{H}\}}\) NMR (δ in ppm, C\(_6\)D\(_6\), 293 K, 100.6 MHz): 154.7 (s, C\(_{ipso}\)-Ph), 152.5 (d, \(^2\)J\(_{CP}\): 7.0 Hz, C\(_{ipso}\)-Ar), 137.4 (s, C\(_{meta}\)-Ar), 128.0 (s, Ph), 127.9 (s, Ph) 123.4 (s, C\(_{para}\)-Ar), 122.0 (br, C\(_{ortho}\)-Ar), 120.2 (s, Ph), 57.6 (s, Zr-CH\(_2\)), 28.0 (d, \(^1\)J\(_{CP}\): 5.9 Hz, P-CH), 21.6 (s, Ar-CH\(_3\)), 21.0 (d, \(^2\)J\(_{CP}\): 11.5 Hz, CH\(_3\)-i-Pr), 19.9 (d, \(^2\)J\(_{CP}\): 9.0 Hz, CH\(_3\)-i-Pr). For C\(_{49}\)H\(_{76}\)N\(_3\)P\(_3\)Zr\(_1\) EA (%, calc.): C, 66.03; H, 8.59; N, 4.71. EA (%, found): C, 65.15; H, 8.52; N, 4.99.

(ArNP\(^3\)Pr\(^2\))\(_3\)Zr(BH\(_4\)) (3.7)

Complex 3.2 (834 mg, 1.0 mmol) and NaBH\(_4\) (189 mg, 5.0 mmol) were weighed to a Teflon-sealed flask and 10 mL THF were added at room temperature. The reaction mixture was allowed to stir for 7 days, at which point the volatiles were removed in vacuo. The residues were extracted with 20 mL toluene and filtered through Celite, subsequent removal of the toluene in vacuo gave the desired product as a white solid, 690 mg, 85 % yield.

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$^{31}$P{$^1$H} NMR (δ in ppm, $C_6D_6$, 293 K, 162 MHz): 5.7 (s); $^{11}$B{$^1$H} NMR (δ in ppm, $C_6D_6$, 293 K, 90 MHz): -20.4 (s); $^1$H NMR (δ in ppm, $C_6D_6$, 293 K, 600 MHz): 6.92 (s, 6H, o-Ar), 6.49 (s, 3H, p-Ar), 2.45 (d of septet, 6H, $^3J_{HH}$: 7.6 Hz, $^3J_{HP}$: 2.0 Hz, P-CH), 2.23 (s, 12H, Ar-CH$_3$), 2.10-1.50 (very br d, 3H, BH), 1.19 (dd, 6H, $^3J_{HP}$: 16.4 Hz, $^3J_{HH}$: 7.2 Hz, CH$_3$-Pr), 1.09 (dd, 6H, $^3J_{HP}$: 14.8 Hz, $^3J_{HH}$: 6.8 Hz, CH$_3$-Pr); $^{13}$C{$^1$H} NMR (δ in ppm, $C_6D_6$, 293 K, 150.9 MHz): 152.2 (d, $^2J_{CP}$: 8.5 Hz, $C_{ipso}$-Ar), 137.4 (s, C-Ar), 123.5 (s, C-Ar), 122.1 (s, $C_{ortho}$-Ar), 28.0 (s, P-CH), 21.6 (s, Ar-CH$_3$), 21.0 (app t, $^2J_{CP}$: 5.9 Hz, CH$_3$-Pr), 19.8 (app t, $^2J_{CP}$: 4.2 Hz, CH$_3$-Pr). Samples were always contaminated with small amounts of 3.2, thus suitable EA could not be obtained.

(ArNP'Pr$_2$)$_3$Zr(PHPH) (3.8)

PhPH$_2$ (0.91 mmol, 0.10 mL) was added via syringe to a Schlenk flask containing 10 mL of Et$_2$O, then a 1.6 M solution of nBuLi (0.91 mmol, 0.56 mL) was added via syringe dropwise at room temperature. The solution was stirred for one hour at room temperature and was then cooled to -78 °C (dry ice / acetone bath). (ArNP'Pr$_2$)ZrCl dissolved in 15 mL Et$_2$O was then added dropwise via cannula. Upon completion of the addition, the solution was warmed to room temperature and was stirred for 30 minutes, and then the volatiles were removed in vacuo. The residues were extracted with 40 mL of pentane and were filtered through Celite, and the volatiles were again removed in vacuo to give bright yellow solid, yield: 545 mg (72 %). X-ray quality crystals were grown from a concentrated hexanes solution at -35 °C. $^{31}$P{$^1$H} NMR (δ in ppm, $C_6D_6$, 293 K, 162 MHz): 2.4 (d, 3P, $^2J_{PP}$: 27.9 Hz, N-PPr$_2$), -38.8 (quart, 1P, $^2J_{PP}$: 27.8 Hz, PHPH); $^1$H NMR (δ in ppm, $C_6D_6$, 293 K, 400 MHz): 7.74 (ov dd or apparent t, 2H, $^3J_{HH}$: 8.0 Hz, $^3J_{HP}$: 7.2 Hz, o-PPh) 7.12 (t, 2H, $^3J_{HH}$: 7.2 Hz, m-PPh), 6.91 (t, 1H, $^3J_{HH}$: 7.2 Hz, p-PPh), 6.81 (s, 6H, o-NPh), 6.48 (s, 3H, p-NPh), 4.66 (d of quart, 1H, $^1J_{HP}$: 214 Hz, $^3J_{HP}$: 9.2 Hz, PhPH), 2.46 (d of septets, 6H, $^2J_{HP}$: 2.8 Hz, $^3J_{HH}$: 7.2 Hz, PCH), 2.19 (s, 18H, Ar-CH$_3$), 1.20 (dd, 18H, $^3J_{HH}$: 7.6 Hz).
Hz, $^{3}J_{HP}$: 16.4 Hz, $CH_{3}^{-}\text{iPr}$), 1.12 (dd, $^{3}J_{HH}$: 6.8 Hz, $^{3}J_{HP}$: 15.2 Hz, $CH_{3}^{-}\text{iPr}$); $^{13}C\{^{1}H\}$ NMR (δ in ppm, $C_{6}D_{6}$, 100.6 MHz): 151.8 (d, $^{2}J_{CP}$: 9.0 Hz PN-C), 149.9 (dd, $^{1}J_{CP}$: 26.5 Hz, $^{3}J_{CP}$: 6.1 Hz, HP-$C_{ph}$), 137.4 (s, $C_{Ar}$-CH$_{3}$), 132.6 (d, $^{2}J_{CP}$: 11.6 Hz, $C_{ortho}$-PPh), 127.7 (d, $^{3}J_{CP}$: 19.8 Hz $C_{meta}$-PPh), 123.6 (s, $C_{para}$-NAr), 122.9 (s, $C_{para}$-PPh), 121.9 (d, $^{3}J_{CP}$: 4.9 Hz, $C_{ortho}$-NAr)), 28.4 (d, $^{1}J_{CP}$: 3.8 Hz), 21.5 (s, Ar-CH$_{3}$), 21.0 (d, $^{2}J_{CP}$: 9.6 Hz), 20.0 (d, $^{2}J_{CP}$: 8.3 Hz). For $C_{4}H_{75}N_{3}P_{4}Zr_{1}$ EA (%, calc.): C, 63.41; H, 8.31; N, 4.62. EA (%, found): C, 61.42; H, 8.60; N, 4.52, repeated analyses were low in carbon.

7.2.3 Complexes pertaining to Chapter 4

$fc(NP^{i}Pr_{2})Zr(NMe_{2})_{2}$ (4.1)

Solid samples of $fc$($NHP^{i}Pr_{2}$)$_{2}$ (0.335 mmol, 150 mg) and Zr($NMe_{2}$)$_{4}$ (0.335 mmol, 90 mg) were weighed to the same Schlenk flask. At room temperature 5 mL of hexanes was added via cannula and the mixture was allowed to stir for 6 hours. The volatiles were removed in vacuo to give 200 mg (yield: 91%) of orange powder. The product can be recrystallized from hexanes at -35°C and x-ray quality crystals were obtained in this manner. $^{31}P\{^{1}H\}$ NMR (δ in ppm, $C_{6}D_{6}$, 293 K, 162 MHz): 29.4 (s), $^{1}H$ NMR (δ in ppm, $C_{6}D_{6}$, 293 K, 400 MHz); 4.09 (s, 4H, Cp-H), 3.90 (s, 4H, Cp-H), 3.27 (s, 12H, N-CH$_{3}$), 2.00 (septet of d, 4H, $^{2}J_{HP}$: 1.9 Hz, $^{3}J_{HH}$: 7.2 Hz, P-CH), 1.09 (dd, 12H, $^{2}J_{HP}$: 13.2 Hz, $^{3}J_{HH}$: 7.2 Hz, CH$_{3}^{-}\text{iPr}$), 1.04 (dd, 12H, $^{2}J_{HP}$: 15.0 Hz, $^{3}J_{HH}$: 7.2 Hz, CH$_{3}^{-}\text{iPr}$), $^{13}C\{^{1}H\}$ NMR (δ in ppm, $C_{6}D_{6}$, 100.6 MHz): 112.1 (s, (Cp)C-N), 67.4 (s, (Cp)C), 65.1 (s, (Cp)C), 46.7 (t, $^{3}J_{CP}$: 5.4 Hz, N-CH$_{3}$), 25.4 (t, $^{2,4}J_{CP}$: 4.6 Hz, P-CH), 19.1 (t, $^{2,4}J_{CP}$: 3.6 Hz, CH$_{3}^{-}\text{iPr}$), 18.8 (t, $^{2,4}J_{CP}$: 3.6 Hz, CH$_{3}^{-}\text{iPr}$). For $C_{28}H_{54}N_{4}P_{2}Fe_{1}Zr_{1}$ EA (%, calc.): C, 51.28; H, 8.30; N, 8.54. EA (%, found): C, 50.17; H, 7.96; N, 8.78; repeated analyses were low in carbon.
(fc(NP\textsuperscript{i}Pr\textsubscript{2})ZrCl\textsubscript{2})\textsubscript{2} (4.2)

fc(NHP\textsuperscript{i}Pr\textsubscript{2})\textsubscript{2} (2.5) (5.35 mmol, 2.400 g) and Zr(NMe\textsubscript{2})\textsubscript{4} (5.35 mmol, 1.432 g) were weighed to the same Schlenk flask. At room temperature 80 mL of hexanes was added via cannula and the mixture was allowed to stir for 4 hours. The volatiles were removed \textit{in vacuo} and the residue was dissolved in 30 mL toluene, and TMSCl (42.8 mmol, 5.4 mL) was added via syringe. After the addition the reaction mixture was heated at 65 °C for 17 hours, and the volatiles were removed \textit{in vacuo}. The yellow solids were washed onto a glass frit with 25 mL hexanes and the solids were dried \textit{in vacuo}, yield: 2.950 g (91 %).

\textsuperscript{31}P\textsuperscript{1}{\textsubscript{1}H} NMR (δ in ppm, C\textsubscript{6}D\textsubscript{6}, 293 K, 162 MHz): 19.2 (s); \textsuperscript{1}H NMR (δ in ppm, C\textsubscript{6}D\textsubscript{6}, 293 K, 400 MHz); 4.21 (s, 4H, Cp-H), 3.79 (s, 4H, Cp-H), 2.15 (br, 4H, P-CH\textsubscript{3}), 1.21 (br m, 12H, C\textsubscript{8}H\textsubscript{3}-iPr), 1.06 (br m, 12H, CH\textsubscript{3}-Pr). The solubility of the complex in C\textsubscript{6}D\textsubscript{6} or toluene-d\textsubscript{8} was too low to obtain suitable \textsuperscript{13}C NMR data. Repeated attempts to obtain acceptable elemental analysis were unsuccessful, a typical result is: for C\textsubscript{24}H\textsubscript{42}N\textsubscript{2}P\textsubscript{2}Cl\textsubscript{2}Fe\textsubscript{i}Zr\textsubscript{i} EA (%, calc.): C, 45.14; H, 6.63; N, 4.39. EA (%, found): C, 43.57; H, 6.00; N, 5.17.

fc(NP\textsuperscript{i}Pr\textsubscript{2})ZrCl\textsubscript{2}(THF) (4.3)

Complex 4.2 was dissolved in THF and the volatiles were then removed in vacuo to give a yellow powder in quantitative yield. \textsuperscript{31}P\textsuperscript{1}{\textsubscript{1}H} NMR (δ in ppm, C\textsubscript{6}D\textsubscript{6}, 293 K, 162 MHz): 20.5 (s); \textsuperscript{1}H NMR (δ in ppm, C\textsubscript{6}D\textsubscript{6}, 293 K, 400 MHz); 4.50 (s, 4H, Cp-H), 4.10 (br, 4H, THF), 3.93 (s, 4H, Cp-H), 2.39 (septet of d, 4H, \textsuperscript{2}J\textsubscript{HP}: 3.6 Hz, \textsuperscript{3}J\textsubscript{HH}: 7.2 Hz, P-CH\textsubscript{3}), 1.42 (br, 4H, THF), 1.33 (dd, 12H, \textsuperscript{2}J\textsubscript{HP}: 16.8 Hz, \textsuperscript{3}J\textsubscript{HH}: 7.2 Hz, CH\textsubscript{3}-Pr), 1.08 (dd, 12H, \textsuperscript{2}J\textsubscript{HP}: 14.8 Hz, \textsuperscript{3}J\textsubscript{HH}: 7.2 Hz, CH\textsubscript{3}-Pr). \textsuperscript{13}C\textsuperscript{1}{\textsubscript{1}H} NMR (δ in ppm, C\textsubscript{6}D\textsubscript{6}, 75.5 MHz): 115.0 (s, (Cp)C-N), 73.0 (s, THF), 67.6 (s, (Cp)C), 65.2 (s, (Cp)C), 26.7 (s P-CH), 25.8 (s, THF), 20.8 (t, \textsuperscript{2,4}J\textsubscript{CP}: 4.7 Hz, CH\textsubscript{3}-Pr), 19.3 (t, \textsuperscript{2,4}J\textsubscript{CP}: 2.5 Hz, CH\textsubscript{3}-Pr). Repeated attempts to obtain acceptable elemental analysis were
unsuccessful, a typical result is: for C_{48}H_{84}N_{4}P_{4}Cl_{4}Fe_{2}Zr_{2} EA (%, calc.): C, 45.14; H, 6.63; N, 4.39. EA (%, found): C, 43.80; H, 5.84; N, 4.64.

**fc(NP^iPr_2)ZrMe_2 (4.4)**

Complex 4.3 (304 mg, 0.25 mmol) was suspended in 10 mL of Et_2O in a Schlenk flask and was cooled to -78 °C. A solution of MeLi (0.7 mL of a 1.4 M in Et_2O, 1.0 mmol) was added via syringe, upon addition the cold bath was removed and the solution was warmed to room temperature and was allowed to stir for 1 hour. The volatiles were removed *in vacuo* and the residues were extracted with 10 mL toluene. The suspension was filtered through Celite and was dried *in vacuo* to give 240 mg of pale yellow powder (yield = 85 %).

^31^P\{^1^H\} NMR (δ in ppm, C_6D_6, 293 K, 121.5 MHz): 23.0 (s); ^1^H NMR (δ in ppm, C_6D_6, 293 K, 300 MHz); 4.16 (t, 4H, ^3^J_{HH}: 1.8 Hz; Cp-H), 3.85 (t, 4H, ^3^J_{HH}: 1.8 Hz; Cp-H), 2.13 (septet of d, 4H, ^2^J_{HP}: 2.7 Hz, ^3^J_{HH}: 7.2 Hz, P-CH), 1.11 (dd, 12H, ^2^J_{HP}: 10.2 Hz, ^3^J_{HH}: 7.2 Hz, CH_3-Pr), 1.07 (dd, 12H, ^2^J_{HP}: 12.3 Hz, ^3^J_{HH}: 6.9 Hz, CH_3-Pr), 0.75 (t, 6H, ^3^J_{HP}: 4.2 Hz, CH_3-Zr). ^1^H NMR (δ in ppm, C_6D_6, 75.5 MHz): 114.9 (s, (Cp)C-N), 67.4 (s, (Cp)C), 64.9 (s, (Cp)C), 38.4 (s, Zr-CH_3), 26.6 (s P-CH), 20.8 (s), 19.3 (t, ^2^J_{CP}: 5.4 Hz, CH_3-Pr). For C_{24}H_{42}N_{2}P_{2}Fe_{1}Zr_{1} EA (%, calc.): C, 50.78; H, 7.46; N, 4.94. EA (%, found): C, 51.10; H, 7.63; N, 7.63.

**fc(NP^iPr_2)Zr(CH_2Ph)_2 (4.5)**

**Method A**: Complex 4.2 (608 mg, 1.00 mmol) was dissolved in 40 mL of THF and solid KCH_2Ph (260 mg, 2.00 mmol) was added portionwise to the stirring solution at room temperature. After stirring for 2 hours at room temperature the volatiles were removed *in vacuo*. The residues were extracted with 20 mL of toluene and the solution was filtered through Celite. The filtrate was dried in vacuo to give 450 mg of yellow powder (yield = 60 %).
Method B: fc(NHP^iPr)_2 (2.5) (359 mg, 0.80 mmol), Zr(CH_2Ph)_4 (365 mg, 0.80 mmol), and KO^iBu (1 mg, 0.008 mmol) were all weighed to a Schlenk flask with stir bar. Toluene (15 mL) was added at room temperature and the solution was stirred for 2.5 hours at which point the volatiles were removed in vacuo. Conversion to 4.5 was quantitative as ascertained by NMR spectroscopy.

^{31}P\{^1H\} NMR (δ in ppm, C_6D_6, 293 K, 162 MHz): 15.7 (s); ^1H NMR (δ in ppm, C_6D_6, 293 K, 400 MHz): 7.28 (ov m, 4H, Ph), 7.25 (ov m, 4H, Ph), 7.05 (t, 2H, ^3J_{HH}: 5.4 Hz, H_{ortho}) 4.14 (t, 4H, ^3J_{HH}: 2.4 Hz, Cp-H), 3.77 (t, 4H, ^3J_{HH}: 2.4 Hz, Cp-H), 1.91 (t, 4H, ^2J_{HP}: 6.0 Hz, Zr-CH_2), 1.76 (septet of d, 4H, ^2J_{HP}: 3.2 Hz, ^3J_{HH}: 9.6 Hz, P-CH), 0.96 (dd, 12H, ^2J_{HP}: 21.2 Hz, ^3J_{HH}: 9.6 Hz, CH_3-{^3}Pr), 0.84 (dd, 12H, ^2J_{HP}: 19.6 Hz, ^3J_{HH}: 9.6 Hz, CH_3-{^3}Pr), ^13C\{^1H\} NMR (δ in ppm, C_6D_6, 100.6 MHz): 144.7 (s, Ph_{ipso}), 128.9 (s, Ph), 128.7 (t, J_{CP}: 2.0 Hz, C_{ortho}), 122.2 (s, Ph), 114.8 (t, ^3J_{CP}: 3.4 Hz, (Cp)C-N), 67.0 (s, (Cp)C), 65.0 (s, (Cp)C), 56.4 (s, Zr-CH_2), 26.6 (br, P-CH), 20.2 (t, ^2J_{CP}: 5.8 Hz, CH_3-{^3}Pr), 18.9 (t, ^2J_{CP}: 4.3 Hz). For C_{38}H_{56}N_2P_2Fe_iZr_i EA (%, calc.): C, 60.68; H, 7.53; N, 3.74. EA (%, found): C, 59.94; H, 7.04; N, 4.28.

(4.5-d_{14})

Was prepared following the protocol in method A using complex 4.3 and benzylpotassium-{^7}D.

^{31}P\{^1H\} NMR (δ in ppm, C_6D_6, 293 K, 162 MHz): 15.8 (s); ^1H NMR (δ in ppm, C_6D_6, 293 K, 400 MHz): 4.26 (br, Cp-H), 3.89 (br, Cp-H), 1.88 (septet of d, 4H, ^2J_{HP}: 2.0 Hz, ^3J_{HH}: 7.8 Hz, P-CH), 1.08 (dd, 12H, ^2J_{HP}: 16.0 Hz, ^3J_{HH}: 7.2 Hz, CH_3-{^3}Pr), 0.95 (dd, 12H, ^2J_{HP}: 14.4 Hz, ^3J_{HH}: 7.2 Hz, CH_3-{^3}Pr), ^13C\{^1H\} NMR (δ in ppm, C_6D_6, 100.6 MHz): 144.4 (s, C_{ipso}), 114.8 (t, ^3J_{CP}: 2.8 Hz, (Cp)C-N), 67.0 (s, (Cp)C), 65.0 (s, (Cp)C), 26.6 (s, P-CH), 20.1 (t, ^2J_{CP}: 4.3 Hz, CH_3-{^3}Pr), 18.9 (t, ^2J_{CP}: 3.3 Hz, CH_3-{^3}Pr).
fc(NP\textsuperscript{iPr\textsubscript{2}})Zr(CH\textsubscript{2}CMe\textsubscript{3})\textsubscript{2} (4.6)

A solution of LiCH\textsubscript{2}CMe\textsubscript{3} (156 mg, 2.0 mmol) in 10 mL of Et\textsubscript{2}O was added dropwise to a stirring suspension of complex 4.3 (608 mg, 1.0 mmol) in 20 mL of Et\textsubscript{2}O. The reaction mixture was allowed to stir for 3 hours at room temperature. The volatiles were removed in vacuo and the residues were extracted with 20 mL pentane. The suspension was filtered through Celite and the filtrate was dried in vacuo to give 520 mg of yellow powder (yield = 73 %).

\textsuperscript{31}P\{\textsuperscript{1}H\} NMR (δ in ppm, C\textsubscript{6}D\textsubscript{6}, 293 K, 162 MHz): 18.7 (s); \textsuperscript{1}H NMR (δ in ppm, C\textsubscript{6}D\textsubscript{6}, 293 K, 400 MHz): 4.20 (t, 4H, \textsuperscript{3}J\textsubscript{HH}: 2.0 Hz, Cp-H), 3.87 (t, 4H, \textsuperscript{3}J\textsubscript{HH}: 2.0 Hz, Cp-H), 2.21 (septet of d, 4H, \textsuperscript{2}J\textsubscript{HP}: 2.0 Hz, \textsuperscript{3}J\textsubscript{HH}: 7.2 Hz, CH\textsubscript{3}-Pr), 0.84 (dd, 12H, \textsuperscript{2}J\textsubscript{HP}: 14.0 Hz, \textsuperscript{3}J\textsubscript{HH}: 7.2 Hz, CH\textsubscript{3}-Pr), 0.88 (ov dd, 4H, \textsuperscript{3}J\textsubscript{HH}: 7.0 Hz, CH\textsubscript{3}-Pr).

\textsuperscript{13}C\{\textsuperscript{1}H\} NMR (δ in ppm, C\textsubscript{6}D\textsubscript{6}, 75.5 MHz): 113.4 (s, (Cp)C-N), 82.5 (s, Zr-CH\textsubscript{2}), 67.0 (s, (Cp)C), 65.1 (s, (Cp)C), 36.1 (s, CH\textsubscript{2}CCH\textsubscript{3}), 35.8 (s, CH\textsubscript{2}CCH\textsubscript{3}), 27.4 (t, \textsuperscript{1,3}J\textsubscript{CP}: 3.4 Hz, P-CH), 20.4 (t, \textsuperscript{2,4}J\textsubscript{CP}: 5.1 Hz, CH\textsubscript{3}-Pr), 19.0 (t, \textsuperscript{2,4}J\textsubscript{CP}: 3.7 Hz). For C\textsubscript{32}H\textsubscript{38}N\textsubscript{2}P\textsubscript{2}Fe\textsubscript{1}Zr\textsubscript{1} EA (%, calc.): C, 56.53; H, 8.60; N, 4.12. EA (%, found): C, 56.06; H, 8.28; N, 5.76.

fc(NP\textsuperscript{iPr\textsubscript{2}})Zr''Bu\textsubscript{2} (4.7)

Complex 4.3 was suspended in 40 mL Et\textsubscript{2}O and the solution was cooled to -78 °C. A 1.7 M solution of 'BuLi in pentane was added via syringe and the solution was stirred at -78 °C for 0.5 hours. The solution was then allowed to warm to room temperature, at which point the volatiles were removed in vacuo. The residues were extracted in 25 mL of hexanes and were filtered through a Celite plug, and the hexanes were removed in vacuo. X-ray quality crystals were obtained from a concentrated hexanes solution at -35 °C. \textsuperscript{31}P\{\textsuperscript{1}H\} NMR (δ in ppm, C\textsubscript{6}D\textsubscript{6}, 293 K, 162 MHz): 22.7 (s); \textsuperscript{1}H NMR (δ in ppm, C\textsubscript{6}D\textsubscript{6}, 293 K, 400 MHz): 4.06 (t, 4H, \textsuperscript{3}J\textsubscript{HH}: 2.0 Hz, Cp-H), 3.90 (t, 4H, \textsuperscript{3}J\textsubscript{HH}: 2.0 Hz, Cp-H), 2.10 (septet of d, 4H, \textsuperscript{2}J\textsubscript{HP}: 1.2 Hz, \textsuperscript{3}J\textsubscript{HH}: 7.6 Hz, P-CH),
1.65 (s, 18H, Zr–C\(\text{CH}_3\)), 1.16 (dd, 12H, \(^2J_{\text{HP}}\): 16.0 Hz, \(^3J_{\text{HH}}\): 7.2 Hz, CH\(_3\)-iPr), 1.01 (dd, 12H, \(^2J_{\text{HP}}\): 12.8 Hz, \(^3J_{\text{HH}}\): 7.2 Hz, CH\(_3\)-iPr). \(^{13}\text{C}\{^1\text{H}\}\) NMR (δ in ppm, C\(_6\)D\(_6\), 75.5 MHz): 67.1 (s, (Cp)\text{C}), 66.1 (s, (Cp)\text{C}), 32.8 (t, \(^3J_{\text{HH}}\): 5.4 Hz, Zr-C-CH\(_3\)), 27.1 (d, \(^2J_{\text{CP}}\): 12.0 Hz, P-CH), 20.1 (d, \(^2J_{\text{CP}}\): 14.3 Hz, CH\(_3\)-iPr), 18.9 (d, \(^2J_{\text{CP}}\): 8.2 Hz, CH\(_3\)-iPr); due to room temperature decomposition, short experiment times were used and therefore did not observe resonances for Zr-C, or (Cp)C-N. For C\(_{30}\)H\(_{54}\)N\(_2\)P\(_2\)Fe\(_1\)Zr\(_1\) EA (%, calc.): C, 55.28; H, 8.35; N, 4.30. EA (%, found): C, 55.00; H, 8.50; N, 4.69.

\(\text{fc(NP}^i\text{Pr}_2)\text{Zr(}\kappa^2-\text{CH}_2\text{CMe}_2\) (4.8)\)

A C\(_6\)D\(_6\) solution of 4.7 was allowed to stand at room temperature for 12 hours, which results in conversion to 4.8 and was analyzed by \(^1\text{H NMR spectroscopy. Samples of 4.8 are thermally sensitive both in the solid-state and in solution.}\)

\(^{31}\text{P}\{^1\text{H}\}\) NMR (δ in ppm, C\(_6\)D\(_6\), 293 K, 162 MHz): 35.7 (s); \(^1\text{H NMR (δ in ppm, C}\_6\text{D}_6\), 293 K, 400 MHz) 7.07 (ov s, 3H, Ar), 4.73 (s, 2H, Cp-H), 4.33 (s, 2H, Cp-H), 3.93 (m, 4H, Cp-H), 2.30 (ov s, 6H, Ar-CH\(_3\)), 2.29 (ov, s, 3H, Zr-C\(_{2}\)CH\(_3\)), 2.15 (septet, 4H, \(^3J_{\text{HH}}\): 2.4 Hz, P-CH), 1.26 (d, 12H, \(^3J_{\text{HP}}\): 12.8 Hz, CH\(_3\)-iPr), 1.22 (d, 12H, \(^3J_{\text{HP}}\): 13.2 Hz, CH\(_3\)-iPr), 0.68 (s, 3H, Zr-C\(_3\)H). \(^{13}\text{C}\{^1\text{H}\}\) NMR (δ in ppm, C\(_6\)D\(_6\), 75.5 MHz): 67.4 (s, (Cp)\text{C}), 67.2 (s, (Cp)\text{C}), 65.0 (ov s, (Cp)\text{C}), 65.0 (ov s, (Cp)\text{C}), 29.4 (m, Zr-CH\(_2\)), 27.7 (s, Zr-C\(_3\)CH\(_3\)), 27.2 (br m, P-CH), 26.4 (br m, P-CH), 19.7 (ov m, CH\(_3\)-iPr), 19.0 (ov m, CH\(_3\)-iPr), due to room temperature decomposition, short experiment times were used and therefore did not observe resonances for Zr-C, or (Cp)C-N. Additionally, due to the thermal sensitivity of 4.8 satisfactory EA could not be obtained.

\(\text{fc(NP}^i\text{Pr}_2)\text{Zr(CH}_3\)\(\kappa^2-(\text{NC})-\text{ArNCCH}_3\) (4.9)\)

A 2 mL toluene solution containing (2,6-dimethyl)isocyanide (24 mg, 0.18 mmol) was added dropwise at room temperature to a stirring solution of 4.5 (110 mg, 0.18 mmol) in 5 mL toluene.
After 1 hour the volatiles were removed \textit{in vacuo}. The yellow solids were washed onto a glass frit with 3 mL pentane, and were dried \textit{in vacuo}, yield: 77%.

$^{31}$P-$^{1}$H NMR (δ in ppm, C$_{6}$D$_{6}$, 293 K, 162 MHz): 35.7 (s); $^{1}$H NMR (δ in ppm, C$_{6}$D$_{6}$, 293 K, 400 MHz) 7.07 (ov s, 3H, Ar), 4.73 (s, 2H, Cp-Pr), 4.33 (s, 2H, Cp-Pr), 3.93 (m, 4H, Cp-Pr), 2.30 (ov s, 6H, Ar-CH$_{3}$), 2.29 (ov s, 3H, Zr-CCH$_{3}$), 2.15 (septet, 4H, $^{3}$J$_{HH}$: 2.4 Hz, P-CH$_{2}$), 1.26 (d, 12H, $^{3}$J$_{HH}$: 12.8 Hz, CH$_{3}$-Pr), 1.22 (d, 12H, $^{3}$J$_{HH}$: 13.2 Hz, CH$_{3}$-Pr), 0.68 (s, 3H, Zr-CH$_{3}$);

$^{13}$C-$^{1}$H NMR (δ in ppm, C$_{6}$D$_{6}$, 100.6 MHz): 242.8 (s, Zr-C), 147.6 (s, Ar), 137.4 (s, Ar), 130.3 (t, $^{3}$J$_{CP}$: 3.4 Hz, Ar$_{ips}$), 128.3 (s, Ar), 124.6 (s, Ar), 115.0 (t, $^{2,4}$J$_{CP}$: 3.4 Hz, Cp-C(N)), 69.0 (s, Cp-C), 66.9 (s, Cp-C), 64.6 (s, Cp-C), 64.4 (s, Cp-C), 37.7 (d, $^{1}$J$_{CP}$: 15.0 Hz, P-CH), 35.9 (d, $^{1}$J$_{CP}$: 17.7 Hz, P-CH), 33.7 (s, Ar-CH$_{3}$), 30.7 (t, $^{2,4}$J$_{CP}$: 4.8 Hz, CH$_{3}$-Pr), 30.6 (t, $^{2,4}$J$_{CP}$: 4.5 Hz, CH$_{3}$-Pr), 23.9 (s, Zr-CCH$_{3}$), 19.5 (t, $^{2,4}$J$_{CP}$: 3.0 Hz, Zr-CH$_{3}$). For C$_{33}$H$_{51}$N$_{3}$P$_{2}$Fe$_{1}$Zr$_{1}$ EA (%, calc.): C, 56.72; H, 7.36; N, 6.01. EA (%, found): C, 57.56; H, 7.55; N, 7.01.

\textbf{fc(NP$_{2}$Pr$_{2}$)Zr(CH$_{2}$Ph)(κ$^{2}$-(NC)-ArNCCH$_{2}$Ph) (4.10)}

A 2 mL toluene solution containing (2,6-dimethyl)isocyanide (26 mg, 0.20 mmol) was added dropwise at room temperature to a stirring solution of 4.5 (150 mg, 0.20 mmol) in 5 mL toluene. After 1 hour the volatiles were removed \textit{in vacuo}. The yellow solids were washed onto a glass frit with 3 mL pentane, and were dried \textit{in vacuo}, yield: 65%.

$^{31}$P-$^{1}$H NMR (δ in ppm, C$_{6}$D$_{6}$, 293 K, 162 MHz): 25.2 (s); $^{1}$H NMR (δ in ppm, C$_{6}$D$_{6}$, 293 K, 400 MHz); 7.23 (s, 1H, Ar), 7.21 (s, 1H, Ar), 7.13-7.01 (ov m, 10H, Ar), 6.77 (t, 1H, $^{3}$J$_{HH}$: 7.2 Hz, Ar), 4.47 (s, 2H, Cp-Pr), 4.15 (s, 2H, Cp-Pr), 3.97 (m, 4H, Cp-Pr), 3.75 (s, 2H, Zr-CCH$_{2}$), 2.77 (s, 2H, Zr-CH$_{2}$), 2.17 (s, 6H, Ar-CH$_{3}$), 1.87 (ov septet of d, 4H, P-CH$_{2}$), 1.12 (dd, 6H, $^{3}$J$_{HH}$: 15.6 Hz, $^{3}$J$_{HH}$: 7.6 Hz, CH$_{3}$-Pr), 1.02 (dd, 6H, $^{3}$J$_{HH}$: 12.4 Hz, $^{3}$J$_{HH}$: 7.6 Hz, CH$_{3}$-Pr), 0.86 (dd, 6H, $^{3}$J$_{HH}$: 15.2 Hz, $^{3}$J$_{HH}$: 7.2 Hz, CH$_{3}$-Pr), 0.80 (dd, 6H, $^{3}$J$_{HH}$: 14.8 Hz, $^{3}$J$_{HH}$: 7.2 Hz, CH$_{3}$-Pr);
$^{13}$C ($^1$H) NMR (δ in ppm, C$_6$D$_6$, 100.6 MHz): 246.4 (s, Zr-C), 151.6 (s, Ar), 146.9 (s, Ar), 137.4 (s, Ar), 130.5 (s, Ar), 128.5 (s, Ar), 128.4 (s, Ar), 126.6 (s, Ar), 125.3 (s, Ar), 119.7 (s, Ar), 110.7 (s, Ar), 68.0 (s, Cp-C), 66.6 (s, Cp-C), 65.6 (s, Cp-C), 65.2 (s, Cp-C), 55.0 (Zr-CH$_2$), 45.2 (Zr-C-CH$_2$), 28.2 (t, $^{13}$J$_{CP}$: 4.9 Hz, P-CH), 24.5 (t, $^{13}$J$_{CP}$: 4.6 Hz, P-CH), 20.4 (t, $^{2,4}$J$_{CP}$: 4.9 Hz, CH$_3$-Pr), 20.1 (t, $^{2,4}$J$_{CP}$: 4.9 Hz, CH$_3$-Pr), 19.0 (t, $^{2,4}$J$_{CP}$: 2.1 Hz, CH$_3$-Pr), 18.6 (t, $^{2,4}$J$_{CP}$: 6.2 Hz, CH$_3$-Pr). For C$_{45}$H$_{59}$N$_3$P$_2$Fe$_1$Zr$_1$ EA (%, calc.): C, 63.51; H, 6.99; N, 4.94. EA (%, found): C, 63.30; H, 6.88; N, 5.34.

(4.10-$d_{14}$)

Was prepared from 4.5-$d_{14}$ in a manner identical to that for 4.10.

$^{31}$P ($^1$H) NMR (δ in ppm, C$_6$D$_6$, 293 K, 162 MHz): 25.2 (s); $^1$H NMR (δ in ppm, C$_6$D$_6$, 293 K, 400 MHz): 7.09-7.05 (m, 3H, Ar), 4.46 (s, 2H, Cp-H), 4.15 (s, 2H, Cp-H), 3.96 (m, 4H, Cp-H), 3.21 (t, 6H, Ar-C=H), 1.87 (ov septet of d, 4H, P-CH), 1.07 (dd, 6H, $^3$J$_{HP}$: 15.6 Hz, $^3$J$_{HH}$: 7.6 Hz, CH$_3$-Pr), 0.98 (dd, 6H, $^3$J$_{HP}$: 12.4 Hz, $^3$J$_{HH}$: 7.6 Hz, CH$_3$-Pr), 0.82 (dd, 6H, $^3$J$_{HP}$: 15.2 Hz, $^3$J$_{HH}$: 7.2 Hz, CH$_3$-Pr), 0.76 (dd, 6H, $^3$J$_{HP}$: 14.8 Hz, $^3$J$_{HH}$: 7.2 Hz, CH$_3$-Pr); $^{13}$C ($^1$H) NMR (δ in ppm, C$_6$D$_6$, 100.6 MHz): 146.9 (s, Ar), 130.6 (s, Ar), 128.5 (s, Ar), 128.4 (s, Ar), 125.3 (s, Ar), 110.7 (s, Ar), 68.0 (s, Cp-C), 66.6 (s, Cp-C), 65.6 (s, Cp-C), 65.2 (s, Cp-C), 28.2 (t, $^{13}$J$_{CP}$: 4.9 Hz, P-CH), 24.5 (t, $^{13}$J$_{CP}$: 4.6 Hz, P-CH), 20.4 (t, $^{2,4}$J$_{CP}$: 4.9 Hz, CH$_3$-Pr), 20.1 (t, $^{2,4}$J$_{CP}$: 4.9 Hz, CH$_3$-Pr), 19.0 (t, $^{2,4}$J$_{CP}$: 2.1 Hz, CH$_3$-Pr), 18.6 (t, $^{2,4}$J$_{CP}$: 6.2 Hz, CH$_3$-Pr).

fc(NP$^8$Pr$_2$Zr(CH$_2$CMe$_3$)(κ$^2$-(NC)-ArNCCH$_2$CMe$_3$) (4.11)

$^{31}$P ($^1$H) NMR (δ in ppm, C$_6$D$_6$, 293 K, 162 MHz): 46.5 (s); $^1$H NMR (δ in ppm, C$_6$D$_6$, 293 K, 400 MHz): 7.02 (ov m, 3H, Ph-H), 4.17 (s, 2H, Cp-H), 4.07 (s, 2H, Cp-H), 3.99 (s, 2H, Cp-H), 3.87 (s, 2H, Cp-H), 2.60 (s, 2H, Zr-C-CH$_2$), 2.45 (s, 6H, Ar-C=H), 2.09 (septet, 2H, $^3$J$_{HH}$: 6.4 Hz, P-CH), 1.91 (septet, 2H, $^3$J$_{HH}$: 7.2 Hz, P-CH), 1.57 (s, 2H, Zr-CH$_2$), 1.28 (s ov, 9H, $^3$Bu-H), 1.27
(dd ov, 3H, J_HH: 16.0 Hz, J_HH: 7.2 Hz, CH_3^−Pr), 1.11 (dd ov, 3H, J_HH: 15.6 Hz, J_HH: 7.2 Hz, CH_3^−Pr), 0.97 (dd ov, 3H, J_HH: 10.8 Hz, J_HH: 7.2 Hz, CH_3^−Pr), 0.90 (dd ov, 3H, J_HH: 12.0 Hz, J_HH: 7.2 Hz, CH_3^−Pr); ^13C(^1H) NMR (δ in ppm, C_6D_6, 75.5 MHz): 252.1 (s, Zr-C=N), 149.4 (s, Ar), 130.8 (s, Ar), 128.5 (s, Ar), 125.9 (s, Ar), 97.2 (d, J_CP: 8.5 Hz, Cp-CN), 70.8 (s), 68.7 (s, Cp-C), 68.4 (s, Cp-C), 67.4 (s, Cp-C), 67.1 (s, Cp-C), 52.3 (Zr-CH_2CMe_3), 35.9 (Zr-C-CH_2), 35.5 (s, CMe_3), 32.2 (s, CMe_3), 31.0 (s), 27.5 (d, J_CP: 19.7 Hz), 26.0 (d, J_CP: 19.8 Hz), 21.8 (d, J_CP: 14.9 Hz), 21.6 (d, J_CP: 13.6 Hz), 21.2 (d, J_CP: 16.5 Hz), 18.7 (d, J_CP: 7.6 Hz), 18.5 (d, J_CP: 11.9 Hz). For C_{41}H_{67}N_3P_2FeZr_1 EA (% calc.): C, 60.72; H, 8.33; N, 5.18. EA (% found): C, 60.53; H, 8.24; N, 6.10.

fc(NP^3Pr_2)Zr(′Bu)(κ^2-(NC)-ArNC′Bu) (4.12)

^31P(^1H) NMR (δ in ppm, C_6D_6, 293 K, 162 MHz): 55.3 (s); ^1H NMR (δ in ppm, C_6D_6, 293 K, 400 MHz): 7.02 (s ov, 3H, Ph-H), 4.11 (s, 2H, Cp-H), 4.00 (s, 2H, Cp-H), 3.85 (s, 2H, Cp-H), 3.68 (s, 2H, Cp-H), 2.58 (s, 6H, Ar-CH_3), 1.93 (septet, 2H, J_HH: 5.2 Hz, P-CH), 1.78 (septet, 2H, J_HH: 6.8 Hz, P-CH), 1.65 (s, 9H, Zr-C-CCH_3), 1.24 (dd, 6H, J_HH: 15.6 Hz, J_HH: 7.2 Hz, CH_3^−Pr), 1.17 (s, 9H, Zr-C-CCH_3), 1.13 (ov dd, 6H, J_HH: 16.4 Hz, J_HH: 7.2 Hz, CH_3^−Pr), 0.94 (ov dd, 6H, J_HH: 10.4 Hz, J_HH: 7.6 Hz, CH_3^−Pr), 0.93 (ov dd, 6H, J_HH: 14.8 Hz, J_HH: 7.6 Hz, CH_3^−Pr); ^13C(^1H) NMR (δ in ppm, C_6D_6, 100.6 MHz): 255.2 (s, Zr-C=N), 150.2 (s, Ar), 130.0 (s, Ar), 128.6 (s, Ar), 125.7 (s, Ar), 90.0 (d, J_CP: 9.7 Hz, Cp-CN), 69.5 (s, Cp-C), 68.5 (s, Cp-C), 68.1 (s, Cp-C), 68.0 (s, Cp-C), 54.4 (Zr-CMe), 41.0 (Zr-C-CH_2), 33.1 (app t, J_CP: 4.7 Hz), 28.3 (s), 26.9 (d, J_CP: 24.4 Hz), 26.6 (d, J_CP: 24.4 Hz), 22.4 (s), 22.2 (d, J_CP: 25.3 Hz), 21.8 (d, J_CP: 21.6 Hz), 18.5 (d, J_CP: 11.5 Hz), 18.3 (d, J_CP: 9.3 Hz). For C_{48}H_{84}N_4P_4Cl_4Fe_2Zr_2 EA (% calc.): C, 60.57; H, 8.55; N, 5.17. EA (% found): C, 58.57; H, 8.39; N, 5.93; the analysis is low in carbon.
fc(NP′Pr2)Zr(CCH2Ph)(ArNCH=CHPh) (4.13)

Complex 4.10 (25 mg, 0.03 mmol) was dissolved in 5 mL toluene in a teflon-sealed flask, and the solution was heated at 90 °C for 24 hours. Removal of the volatiles in vacuo gave the desired complex in quantitative yield.

\[\text{\textsuperscript{31}P\{\textsuperscript{1}H\} NMR (}\delta\text{ in ppm, C}_6\text{D}_6, 293 \text{ K}, 121.6 \text{ MHz}): 15.9 \text{ (s); }\text{\textsuperscript{1}H NMR (}\delta\text{ in ppm, C}_6\text{D}_6, 293 \text{ K}, 300 \text{ MHz}): 8.22 \text{ (d, 1H, } J_{HH} : 13.5 \text{ Hz, Zr-N-CH), 7.58 \text{ (d, 2H, } J_{HH} : 7.5 \text{ Hz, Ar-H), 7.35 \text{ (t, 2H, } J_{HH} : 7.5 \text{ Hz, Ar-H), 7.15 \text{ (ov m, 2H, Ar-H), 7.05 \text{ (ov, 2H, Ar-H), 6.96 \text{ (ov m, 3H, Ar-H), 4.84 \text{ (d, 1H, } J_{HH} : 13.5 \text{ Hz, C=CH}, 4.22 \text{ (s, 2H, Cp-H), 4.14 \text{ (s, 2H, Cp-H), 3.87 \text{ (ov, 4H, Cp-H), 2.87 \text{ (t, 2H, } J_{HP} : 5.4 \text{ Hz, Zr-CH}, 2.46 \text{ (s, 6H, Ar-CH}, 2.19 \text{ (d of septets, 2H, } J_{HP} : 4.8 \text{ Hz, } J_{HH} : 7.2 \text{ Hz, P-CH), 1.37 \text{ (septet, 2H, } J_{HH} : 7.2 \text{ Hz, P-CH), 1.18 \text{ (dd, 6H, } J_{HP} : 15.6 \text{ Hz, } J_{HH} : 7.2 \text{ Hz, CH}_3^{-}\text{Pr), 1.03 \text{ (dd, 6H, } J_{HP} : 15.2 \text{ Hz, } J_{HH} : 7.2 \text{ Hz, CH}_3^{-}\text{Pr), 0.88 \text{ (ov dd, 6H, } J_{HP} : 12.6 \text{ Hz, } J_{HH} : 7.5 \text{ Hz, CH}_3^{-}\text{Pr), 0.84 \text{ (ov dd, 6H, } J_{HP} : 12.6 \text{ Hz, } J_{HH} : 7.6 \text{ Hz, CH}_3^{-}\text{Pr); }\text{\textsuperscript{13}C\{\textsuperscript{1}H\} NMR (}\delta\text{ in ppm, toluene-}d_8, 75.5 \text{ MHz}): 148.1 \text{ (s, Ar-C}_i\text{pso), 146.9 \text{ (s, Ar-C}_i\text{pso), 140.2 \text{ (s, Ar-C}_i\text{pso), 137.9 \text{ (t, } J_{CP} : 5.6 \text{ Hz, Ar), 134.9 \text{ (s, Ar-C}_i\text{pso), 128.8 \text{ (s, Ar), 128.4 \text{ (s, Ar), 128.3 \text{ (s, Ar), 124.6 \text{ (s, Ar), 124.3 \text{ (s, Ar), 123.3 \text{ (s, Ar), 121.5 \text{ (s, Ar), 113.9 \text{ (s, Cp-CN), 97.7 \text{ (s, CH), 67.9 \text{ (s, Cp-C), 66.5 \text{ (s, Cp-C), 65.2 \text{ (s, Cp-C), 65.0 \text{ (s, Cp-C), 64.3 \text{ (s, Ar-CH}, 60.2 \text{ (s, Zr-CH}, 59.5 \text{ (d, } J_{CP} : 6.1 \text{ Hz, Zr-NCH), 28.4 \text{ (s, PCH), 26.9 \text{ (d, } J_{CP} : 19.8 \text{ Hz, PCH), 25.8 \text{ (s, 18.9 \text{ (d, } J_{CP} : 6.0 \text{ Hz), 18.2 \text{ (s, 17.4 \text{ (d, } J_{CP} : 6.5 \text{ Hz). For } C_{45}H_{59}N_3P_2FeZr_1 \text{ EA (%), calc.: } C, 63.51; H, 6.99; N, 4.94. EA (%), found): } C, 62.98; H, 6.86; N, 5.91.\]}

(4.13-\textit{d}_{14})

Was prepared from 4.10-\textit{d}_{14} in a manner identical to that for 4.10.

\[\text{\textsuperscript{31}P\{\textsuperscript{1}H\} NMR (}\delta\text{ in ppm, toluene-}d_8, 293 \text{ K}, 121.6 \text{ MHz}): 16.3 \text{ (s); }\text{\textsuperscript{1}H NMR (}\delta\text{ in ppm, C}_6\text{D}_6, 293 \text{ K}, 300 \text{ MHz): 7.15-7.00 \text{ (ov m, 3H, Ar-H), 4.22 \text{ (m, 2H, Cp-H), 4.14 \text{ (m, 2H, Cp-H), 3.87}}\]
(ov m, 4H, Cp-H), 2.47 (s, 6H, Ar-CH3), 2.19 (d of septets, 2H, $^2J_{HH}$: 4.8 Hz, $^3J_{HH}$: 7.2 Hz, P-CH), 1.37 (septet, 2H, $^3J_{HH}$: 7.2 Hz, P-CH), 1.18 (dd, 6H, $^2J_{HP}$: 15.6 Hz, $^3J_{HH}$: 7.2 Hz, CH3-iPr), 1.03 (dd, 6H, $^2J_{HP}$: 15.2 Hz, $^3J_{HH}$: 7.2 Hz, CH3-iPr), 0.88 (ov dd, 6H, $^2J_{HP}$: 12.6 Hz, $^3J_{HH}$: 7.5 Hz, CH3-iPr), 0.84 (ov dd, 6H, $^2J_{HP}$: 12.6 Hz, $^3J_{HH}$: 7.6 Hz, CH3-iPr); $^{13}$C{\textsuperscript{1}H} NMR (δ in ppm, C\textsubscript{6}D\textsubscript{6}, 75.5 MHz): 148.1 (s, Ar-Cipso), 146.9 (s, Ar-Cipso), 140.2 (s, Ar-Cipso), 134.9 (s, Ar-Cipso), 128.8 (s, Ar), 128.4 (s, Ar), 124.6 (s, Ar), 113.9 (s, Cp-CN), 93.0 (s, CH), 67.9 (s, Cp-C), 66.5 (s, Cp-C), 65.2 (s, Cp-C), 65.0 (s, Cp-C), 54.3 (s, Ar-CH3), 28.4 (s, PCH), 26.9 (d, $J_{CP}$: 19.8 Hz, PCH), 25.8 (s), 18.9 (d, $J_{CP}$: 6.0 Hz), 18.2 (s), 17.4 (d, $J_{CP}$: 6.5 Hz).

7.2.4 Complexes pertaining to Chapter 5

fc(NP\textsuperscript{i}Pr\textsubscript{2})\textsubscript{2}Li\textsubscript{2} (5.1)

Complex 2.7 (448 mg, 1.00 mmol) was dissolved in 25 mL of Et\textsubscript{2}O and 1.6 M n\textsubscript{BuLi solution in hexanes (1.4 mL, 2.2 mmol) was added via syringe. The reaction mixture was allowed to stir for 2 hours and the volatiles were removed via vacuum. The solids were washed with 4 mL hexanes onto a glass frit and were dried via vacuum to give 340 mg of a colorless powder (64 % yield). $^{31}$P{\textsuperscript{1}H} NMR (δ in ppm, C\textsubscript{6}D\textsubscript{6}, 293 K, 162 MHz): 62.1 (br s); \textsuperscript{1}H NMR (δ in ppm, C\textsubscript{6}D\textsubscript{6}, 293 K, 400 MHz): 4.18 (s, 4H, Cp-H), 3.98 (s, 4H, Cp-H), 2.36 (d of septets, 4H, $^2J_{HP}$: 7.2 Hz, $^3J_{HH}$: 7.2 Hz, P-CH), 1.38 (dd, 12H, $^2J_{HP}$: 7.2 Hz, $^3J_{HH}$: 7.2 Hz, CH3-iPr), 1.07 (dd, 12H, $^2J_{HP}$: 7.2 Hz, $^3J_{HH}$: 7.2 Hz, CH3-iPr), 1.38 (dd, 12H, $^2J_{HP}$: 7.2 Hz, $^3J_{HH}$: 7.2 Hz, CH3-iPr), 1.07 (dd, 12H, $^2J_{HP}$: 7.2 Hz, $^3J_{HH}$: 7.2 Hz, CH3-iPr), 1.38 (dd, 12H, $^2J_{HP}$: 7.2 Hz, $^3J_{HH}$: 7.2 Hz, CH3-iPr), 1.07 (dd, 12H, $^2J_{HP}$: 7.2 Hz, $^3J_{HH}$: 7.2 Hz, CH3-iPr), 1.38 (dd, 12H, $^2J_{HP}$: 7.2 Hz, $^3J_{HH}$: 7.2 Hz, CH3-iPr), 1.07 (dd, 12H, $^2J_{HP}$: 7.2 Hz, $^3J_{HH}$: 7.2 Hz, CH3-iPr); $^{13}$C{\textsuperscript{1}H} NMR (δ in ppm, C\textsubscript{6}D\textsubscript{6}, 75.5 MHz): 106.1 (d, $^2J_{CP}$: 13.8 Hz, (Cp)C-N), 66.0 (s, (Cp)C), 65.4 (d, $^3J_{CP}$: 5.9 Hz, (Cp)C), 27.3 (d, $^1J_{CP}$: 16.5 Hz, P-CH), 22.7 (d, $^2J_{CP}$: 17.7 Hz, CH3-iPr), 19.2 (d, $^2J_{CP}$: 20.6 Hz, CH3-iPr). For C\textsubscript{22}H\textsubscript{36}N\textsubscript{2}P\textsubscript{2}Fe\textsubscript{i}Li\textsubscript{2} EA (%, calc.): C, 57.42; H, 7.88; N, 6.09. EA (%, found): C, 56.00; H, 7.82; N, 5.99.
7.2.5 Complexes pertaining to Chapter 6

PhP(o-C₆H₄-NHCO'Bu)₂ (6.1)

PhNHCO'Bu (3.54 g, 0.020 mol) was weighed to a schlenk flask and was dissolved in 120 mL Et₂O and the solution was cooled to -20 °C. A solution of t-BuLi in pentane (1.50 M) was added via syringe dropwise (29.3 mL, 0.044 mol), and the solution was stirred maintaining the temperature at -20 °C for 2 hours. The solution was then cooled to -78 °C and PhPCl₂ was added (1.78 g, 0.010 mol) in 50 mL Et₂O via addition funnel dropwise. The reaction mixture was warmed to room temperature and was stirred for 8 hours, at which time Me₃NHCl was added as a solid. After further stirring for 1 hour, the volatiles were removed in vacuo. The residues were extracted with toluene and filtered through Celite. The toluene was removed in vacuo and the solids were recrystallized from hexanes at -35 °C (Yield: 1.79 g, 21 %).

³¹P{¹H} NMR (δ in ppm, CDCl₃, 293 K, 162 MHz): -32.3 (s); ¹H NMR (δ in ppm, CDCl₃, 293 K, 400 MHz): 8.17 (dd, 2H, JₚH: 8.4 Hz, JₜH: 8.0 Hz, Ar-H), 7.95 (d, 2H, JₚH: 6.4 Hz, NH), 7.41 (ov m, 5H, Ar-H), 7.33 (t, 2H, JₜH: 8.4 Hz, Ar-H), 7.05 (t, 2H, JₜH: 7.6 Hz, Ar-H), 6.82 (t, 2H, JₜH: 6.0 Hz, Ar-H), 1.08 (s, 18H, CCH₃). ¹³C{¹H} NMR (δ in ppm, CDCl₃, 100.6 MHz): 176.5 (s, NC=O), 141.1 (d, JₚC: 17.9 Hz, Cipso-Ar), 134.4 (d, JₚC: 19.6 Hz, C-Ar), 133.4 (s, C-Ar), 131.4 (s, Cipso-Ar), 130.9 (s, C-Ar), 130.3 (s, C-Ar), 129.5 (d, JₚC: 7.7 Hz, C-Ar), 125.1 (d, JₚC: 1.4 Hz, C-Ar), 123.9 (d, JₚC: 4.5 Hz, Cipso-Ar), 122.8 (d, JₚC: 2.3 Hz, C-Ar), 40.1 (s, CCH₃), 27.5 (s, CCH₃).

fc(NHP'Bu₂) (6.2)

Both fc(NH₂)₂ (35.0 mmol, 7.56 g) and LiN(SiMe₃)₂ (70.0 mmol, 11.71 g) were weighed to a schlenk flask, THF (250 mL) was added via cannula. ClP'Bu₂ (73.5 mmol, 14.0 mL) was added
via syringe at room temperature. After stirring at room temperature for 19 hours the volatiles were removed in vacuo. The residues were extracted with hexanes (200 mL) and filtered through Celite. The filtrate was cooled to -78°C for 2 hours to produce a precipitate, the mother liquor was decanted, and the red-orange solids were dried in vacuo, yield: 14.32 g, (81 %). \(^{31}\)P\(^{1}\)H NMR (\(\delta\) in ppm, C\(_6\)D\(_6\), 293 K, 162 MHz): 70.7 (s); \(^1\)H NMR (\(\delta\) in ppm, C\(_6\)D\(_6\), 293 K, 400 MHz); 4.20 (s, 4H, Cp-\(H\)), 3.93 (s, 4H, Cp-\(H\)), 2.74 (d, \(^2\)J\(_{HP}\): 10.4 Hz, 2H, N-\(H\)), 1.07 (d, \(^3\)J\(_{HP}\): 11.2 Hz, 36H, P-C-CH\(_3\)); \(^{13}\)C\(^{1}\)H NMR (\(\delta\) in ppm, C\(_6\)D\(_6\), 100.6 MHz): 111.3 (d, \(^2\)J\(_{CP}\): 25.3 Hz, (Cp)C-N), 64.5 (s, (Cp)C), 60.2 (d, \(^3\)J\(_{CP}\): 8.5 Hz, (Cp)C), 34.2 (d, \(^1\)J\(_{CP}\): 22.2 Hz, P-CCH\(_3\)), 28.5 (d, \(^2\)J\(_{CP}\): 15.7 Hz, P-CCH\(_3\)). For C\(_{26}\)H\(_{46}\)Fe\(_1\)N\(_2\)P\(_2\) EA (%, calc.): C, 61.90; H, 9.19; N, 5.55. EA (%, found): C, 61.71; H, 9.26; N, 5.43.
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Appendices

Appendix A

$^{13}$C-APT (attached proton test) NMR spectrum (150 MHz, 298K, C$_6$D$_6$) of a solution of 3:1 (YR$_3$(THF)$_2$: Y(ArNP$^i$Pr$_2$)$_3$(THF)) which displays quarternary carbons and methylene carbons in a negative phase, and methine and methyl carbons in a positive phase.
Appendix B

Comparison of the X-ray diffraction patterns obtained for 2.10, from the single crystal data (labeled simulated) and from the bulk powder.
Appendix C

In a sealed J-Young NMR tube 20 mM solutions of 4.10 in toluene-$d_8$ containing an internal standard of trimethoxybenzene were lowered into a preheated NMR spectrometer (95, 101 or 110 °C), or alternatively were lowered into an oil bath (80 °C) and removed and cooled to room temperature for spectroscopic analysis. The samples were allowed to equilibrate during routine shimming and $^1$H NMR spectra were recorded at regular intervals. The rate of consumption of 4.10 was obtained as a ratio of the integrals of 2 resonances ($A / (A+B)$), both normalized against the internal standard, is shown below: a portion of the $^1$H NMR spectra taken during a kinetic run at 80 °C: $S =$ arene resonance for trimethoxybenzene standard, $A =$ Cp resonance for 4.10, $B =$ Cp resonance for 4.13.
The decay of 4.10 was found to follow first order kinetics using the integrated rate law method, a representative plot (80 °C) of ln(A / (A+B)) against time is shown below.

The temperature dependent rate constants were obtained using linear regression and the error for each value was taken from the least-squares analysis. The rate constants obtained are as follows: $k_{80} = 1.18(2) \times 10^{-5} \text{ s}^{-1}$, $k_{95} = 5.61(9) \times 10^{-5} \text{ s}^{-1}$, $k_{101} = 1.21(4) \times 10^{-4} \text{ s}^{-1}$, $k_{110} = 2.11(11) \times 10^{-4} \text{ s}^{-1}$. For the benzyl-group deuterated analog 4.13-$d_{14}$ a rate constant $k_{110} = 4.75(11) \times 10^{-5} \text{ s}^{-1}$ was obtained.

The plotting the ln(k / T) vs (1 / T), where T is in Kelvin, allows us to obtain thermodynamic data of the transition state of the transformation from the Eyring equation:

$$\ln(k / T) = (-\Delta H^\ddagger / R)(1 / T) + \ln(K_B / h) + (\Delta S^\ddagger / R).$$

The Eyring plot is shown in Figure 4.6 and from the regression analysis the slope of the line is $-1.34(11) \times 10^4$ and the intercept is 21(3). Temperature error values were estimated to be ± 1 K, and the error in the ln(k / T) values were determined statistically. Rearrangement of the Eyring plot gives values of $\Delta H^\ddagger = 26.7 \pm 2.1$ (kcal / mol) and $\Delta S^\ddagger = -5.7 \pm 0.7$ (cal / K mol).
Appendix D

Highest occupied molecular orbital (HOMO) diagrams for complexes 2.8 and 3.1 obtained from DFT calculations.
## Appendix E

### E1: Crystal structure and refinement data

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<th>Chemical formula</th>
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$R1 = \Sigma ||Fo|-|Fc|| / \Sigma |Fo|; \ wR2 = [ \Sigma (w(Fo^2 - Fc^2)^2) / \Sigma w(Fo^2)^2]^{1/2}$
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$R1 = \Sigma ||Fo|-|Fc|| / \Sigma |Fo|$; $wR2 = [ \Sigma (w(Fo^2 - Fe^2)^2) / \Sigma w(Fo^2)^2 ]^{1/2}$
### E3: Crystal structure and refinement data

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$R1 = \Sigma ||F_o|-|F_c||/\Sigma |F_o|; \ wR2 = [\Sigma (w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$
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$R1 = \Sigma ||Fo|-|Fc|| / \Sigma |Fo|; \ wR2 = [ \Sigma (w(Fo^2 - Fc^2)^2) / \Sigma w(Fo^2)^2]^{1/2}$
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<td>Crystal size / mm&lt;sup&gt;3&lt;/sup&gt;</td>
<td>0.20 x 0.24 x 0.26</td>
<td>0.10 x 0.18 x 0.20</td>
</tr>
<tr>
<td>Wavelength / Å</td>
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<td>0.71073</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>65092</td>
<td>19322</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>8940 [R&lt;sub&gt;int&lt;/sub&gt; = 0.0473]</td>
<td>5208 [R&lt;sub&gt;int&lt;/sub&gt; = 0.0305]</td>
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<td>Data / restraints / parameters</td>
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<td>5208 / 0 / 319</td>
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<tr>
<td>Goodness-of-fit on F&lt;sup&gt;2&lt;/sup&gt;</td>
<td>1.043</td>
<td>1.049</td>
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<tr>
<td>R indices [I&gt;2σ(I)] (R1, wR2)</td>
<td>0.0303, 0.0695</td>
<td>0.0253, 0.0664</td>
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<tr>
<td>R indices [all data] (R1, wR2)</td>
<td>0.0404, 0.0733</td>
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<tr>
<td>Completeness to theta max</td>
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<td>0.969</td>
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<td>Min. and max. transmission</td>
<td>0.9082 and 0.9283</td>
<td>0.8351 and 0.9123</td>
</tr>
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<td>Theta range for data collection</td>
<td>1.63 - 25.07</td>
<td>1.22 - 24.92</td>
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R1 = \( \Sigma ||Fo||-|Fc|| / \Sigma|Fo| \); wR2 = \( \Sigma (w(Fo^2 - Fc^2)^2) / \Sigma w(Fo^2)^2 \)^{1/2}
### E6: Crystal structure and refinement data

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<td>Monoclinic</td>
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<td><strong>Space group</strong></td>
<td>P -1</td>
<td>C 2/c</td>
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<td><strong>a / Å</strong></td>
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<td>12.7839(7)</td>
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<td><strong>b / Å</strong></td>
<td>12.6740(8)</td>
<td>19.2894(10)</td>
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<td><strong>c / Å</strong></td>
<td>12.8007(7)</td>
<td>12.8641(7)</td>
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<td><strong>α /°</strong></td>
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<td>90.00</td>
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<tr>
<td><strong>β /°</strong></td>
<td>104.526(2)</td>
<td>104.6010(10)</td>
</tr>
<tr>
<td><strong>γ /°</strong></td>
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<td>90.00</td>
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<td><strong>Volume / Å$^3$</strong></td>
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<td>3069.8(3)</td>
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<td><strong>T / K</strong></td>
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<td>140(2)</td>
</tr>
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<td><strong>Z</strong></td>
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<td>4</td>
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<td><strong>μ / mm$^{-1}$</strong></td>
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<td>1.112</td>
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<td><strong>ρ (calcd) / g/cm$^3$</strong></td>
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<td>1.473</td>
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<td><strong>F(000)</strong></td>
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<td>1408</td>
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<td><strong>Absorption Correction</strong></td>
<td>Multi-scan</td>
<td>Multi-scan</td>
</tr>
<tr>
<td><strong>Crystal size / mm$^3$</strong></td>
<td>0.22 x 0.24 x 0.28</td>
<td>0.12 x 0.16 x 0.18</td>
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<tr>
<td><strong>Wavelength / Å</strong></td>
<td>0.71073</td>
<td>0.71073</td>
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<tr>
<td><strong>Reflections collected</strong></td>
<td>16012</td>
<td>9716</td>
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<td><strong>Independent reflections</strong></td>
<td>4439 [R$_{int}$ = 0.0286]</td>
<td>2695 [R$_{int}$ = 0.0197]</td>
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<td>4439 / 0 / 327</td>
<td>2695 / 0 / 240</td>
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<td><strong>Goodness-of-fit on F$^2$</strong></td>
<td>1.301</td>
<td>1.091</td>
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<tr>
<td><strong>R indices [I&gt;2σ(I)] (R1, wR2)</strong></td>
<td>0.0188, 0.0658</td>
<td>0.0210, 0.0545</td>
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<tr>
<td><strong>R indices [all data] (R1, wR2)</strong></td>
<td>0.0251, 0.1027</td>
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<tr>
<td><strong>Completeness to theta max</strong></td>
<td>0.964</td>
<td>1.000</td>
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<td><strong>Min. and max. transmission</strong></td>
<td>0.7118 and 0.7626</td>
<td>0.8249 and 0.8781</td>
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<td><strong>Theta range for data collection</strong></td>
<td>1.89 - 25.05</td>
<td>1.96 - 24.95</td>
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R1 = Σ ||Fo|-|Fc|| / Σ|Fo|; wR2 = [ Σ (w(Fo$^2$ - Fe$^2$)$^2$) / Σ w(Fo$^2$)$^2$]$^{1/2}$
### E7: Crystal structure and refinement data

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<td>$C_{36}H_{50}Fe_1N_2P_1Zr_1\cdot C_6H_6$</td>
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<td>Triclinic</td>
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<td><strong>Space group</strong></td>
<td>P 2(1)/n</td>
<td>P -1</td>
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<td>$a$ / Å</td>
<td>10.671(3)</td>
<td>10.7135(13)</td>
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<td>$b$ / Å</td>
<td>22.035(5)</td>
<td>10.7916(13)</td>
</tr>
<tr>
<td>$c$ / Å</td>
<td>16.918(4)</td>
<td>17.012(2)</td>
</tr>
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<td>$\alpha$ / °</td>
<td>90.00</td>
<td>82.547(6)</td>
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<tr>
<td>$\beta$ / °</td>
<td>100.116(8)</td>
<td>80.239(6)</td>
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<tr>
<td>$\gamma$ / °</td>
<td>90.00</td>
<td>65.230(5)</td>
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<td><strong>Volume / Å³</strong></td>
<td>3916.1(2)</td>
<td>1756.2(4)</td>
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<td><strong>T / K</strong></td>
<td>100(2)</td>
<td>100(2)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
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<td>2</td>
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<td>$\mu$ / mm$^{-1}$</td>
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<td>$\rho$ (calcd) / g/cm$^3$</td>
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<td>720</td>
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<td>Multi-scan</td>
<td>Multi-scan</td>
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<td><strong>Crystal size / mm$^3$</strong></td>
<td>0.10 x 0.18 x 0.20</td>
<td>0.16 x 0.20 x 0.22</td>
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<td><strong>Wavelength / Å</strong></td>
<td>0.71073</td>
<td>0.71073</td>
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<td><strong>Reflections collected</strong></td>
<td>23988</td>
<td>21658</td>
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<td><strong>Independent reflections</strong></td>
<td>6827 [R$_{int} = 0.0373$]</td>
<td>6056 [R$_{int} = 0.0319$]</td>
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<td>2695 / 0 / 421</td>
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<td><strong>Goodness-of-fit on F$^2$</strong></td>
<td>1.033</td>
<td>1.196</td>
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<td>R indices [I&gt;2σ(I)] (R1, wR2)</td>
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<td>R indices [all data] (R1, wR2)</td>
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<td>0.985</td>
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<td>Min. and max. transmission</td>
<td>0.8646 and 0.9288</td>
<td>0.8397 and 0.8796</td>
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<td>Theta range for data collection</td>
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<td>2.08 - 25.02</td>
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</table>

R1 = Σ ||Fo|−|Fc|| / Σ|Fo|; wR2 = [ Σ (w(Fo$^2$ - Fe$^2$)$^2$) / Σ w(Fo$^2$)$^2$]$^{1/2}$
### E8: Crystal structure and refinement data

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<td>Space group</td>
<td>C 2/c</td>
<td>P -1</td>
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<td>$a$ / Å</td>
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<td>$c$ / Å</td>
<td>20.3050(19)</td>
<td>25.177(5)</td>
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<td>$\alpha$ / °</td>
<td>90.00</td>
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<td>$\gamma$ / °</td>
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<td>79.964(5)</td>
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<td>100(2)</td>
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<td>Multi-scan</td>
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<tr>
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<td>Independent reflections</td>
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<td>28895 [R$_{int}$ = 0.0453]</td>
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<td>28895 / 0 / 1435</td>
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<td>Goodness-of-fit on F$^2$</td>
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<td>R indices [I&gt;2\sigma(I)] (R1, wR2)</td>
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<td>0.0495, 0.1223</td>
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<tr>
<td>R indices [all data] (R1, wR2)</td>
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<td>Completeness to theta max</td>
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<td>0.994</td>
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<tr>
<td>Min. and max. transmission</td>
<td>0.7939 and 0.9823</td>
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<tr>
<td>Theta range for data collection</td>
<td>2.05 – 30.52</td>
<td>1.24 – 27.52</td>
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</table>

$R1 = \Sigma ||Fo||-|Fc|| / \Sigma |Fo|; wR2 = [ \Sigma (w(Fo^2 - Fe^2)^2) / \Sigma w(Fo^2)^2 ]^{1/2}$
### E9: Crystal structure and refinement data

#### 4.12

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<td>17.012(5)</td>
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<td>$\gamma$ / °</td>
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<td>Multi-scan</td>
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<td>Crystal size / mm$^3$</td>
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<td>Independent reflections</td>
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<td>R indices [I&gt;$2\sigma$(I)] (R1, $wR2$)</td>
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<td>Min. and max. transmission</td>
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<td>Theta range for data collection</td>
<td>1.21 – 27.50</td>
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</table>

R1 = $\sum ||\text{Fo}| - |	ext{Fc}|| / \sum |\text{Fo}|$; $wR2 = [\sum (w(\text{Fo}^2 - \text{Fc}^2)^2) / \sum w(\text{Fo}^2)^2]^{1/2}$
NRH collected all X-ray data with the exception of data for complex 4.7, for which data was collected by Ms. Alyssa Yeo under the supervision of Dr. Brian Patrick.

A disordered Et₂O or pentane molecule was identified in the solid-state structure of 2.2 but no satisfactory model could be obtained. For further refinement, the contribution of this solvent molecule was subtracted from the reflection data using the SQUEEZE routine in the PLATON program package.

Additionally, crystals of 2.6 were non-merohedrally twinned. Both twin domains are related by a 180° rotation about the c-axis (1 0 0 axis). Out of 41335 measured reflections, 14258 data (4642 unique) involved domain 1 only, 14249 data (4674 unique) involved domain 2 only and 12828 data (4403 unique) were part of both domains. The twinned structure was solved by direct methods using the non-overlapping reflections in an HKL4 formatted data set and refined using an HKL5 formatted data set that also included the overlapping reflections. The reflection data were prepared for refinement using the TWINABS program.