AMIDOPHOSPHINE COMPLEXES OF ZIRCONIUM AND TITANIUM FOR DINITROGEN ACTIVATION

by

LARA MORELLO

B. Sc., University of Calgary, 1998

A thesis submitted in partial fulfillment of
the requirements for the degree of
DOCTOR OF PHILOSOPHY
in
THE FACULTY OF GRADUATE STUDIES
(CHEMISTRY)

THE UNIVERSITY OF BRITISH COLUMBIA

December 2005

© Lara Morello, 2005
ABSTRACT

The preparation and reactivity of zirconium and titanium complexes with the macrocyclic $P_2N_2$ ligand (where $P_2N_2 = \text{PhP(CH}_2\text{SiMe}_2\text{NSiMe}_2\text{CH}_2)_2\text{PPh}$) or the chelating NPN ligand (where NPN = \text{PhP(CH}_2\text{SiMe}_2\text{NPh})_2) are presented.

The zirconium dinitrogen complex ($[P_2N_2]\text{Zr}_2(\mu-\eta^2:\eta^2-N_2)$) reacts with ($p$-methyl)phenylacetylene and ($p$-tert-butyl)phenylacetylene to afford ($[P_2N_2]\text{Zr}_2(\mu-\eta^2:\eta^2-N_2\text{CH}=\text{CH}(p-\text{Me-CH}_3\text{H}_4))(\mu-\text{C}=(p-\text{Me-CH}_3\text{H}_4))$ and ($[P_2N_2]\text{Zr}_2(\mu-\eta^2:\eta^2-N_2\text{CH}=\text{CH}(p-\text{Bu-CH}_3\text{H}_4))(\mu-\text{C}=(p-\text{Bu-C}_6\text{H}_4))$, respectively. In both complexes, the bridging alkenylhydrazido unit has a trans-configuration across the C-C double bond. The formation of this new N-C bond is only observed for reactions between ($[P_2N_2]\text{Zr}_2(\mu-\eta^2:\eta^2-N_2)$ and terminal arylalkynes. A simple kinetic analysis of the reaction indicates that the rate-determining step does not involve C-H bond cleavage or N-H bond formation.

The reduction of $[\text{NPN}]\text{ZrCl}_2(\text{THF})$ under an atmosphere of $N_2$ with two equivalents of K$_8$ gives ($[\text{NPN}]\text{ZrTHF}_2(\mu-\eta^2:\eta^2-N_2)$. The THF ligand is labile and can be displaced in solution by pyridine, from which ($[\text{NPN}]\text{Zrpy}_2(\mu-\eta^2:\eta^2-N_2)$ can be isolated. A third complex, ($[\text{NPN}]\text{ZrTHF}_2(\mu-\eta^2:\eta^2-N_2)(\text{pyZr}[\text{NPN}])$, is only observed in situ by $^{31}P\{^1H\}$ and $^1H$ NMR spectroscopy.

The reduction of $[P_2N_2]\text{TiCl}_2$ with two equivalents of K$_8$ under an atmosphere of $N_2$ affords the dinitrogen complex ($[P_2N_2]\text{Ti}_2(\mu-\eta^1:\eta^1-N_2)$. This complex does not react with hydrogen or ($p$-methyl)phenylacetylene. The reaction of $[\text{NPN}]\text{Li}_2(\text{THF})_2$ with TiCl$_4$(THF)$_2$ or TiCl$_3$(THF)$_3$ produces $[\text{NPN}]\text{TiCl}_2$ or $[\text{NPN}]\text{TiCl}(\text{THF})$, respectively. Upon reduction of $[\text{NPN}]\text{TiCl}(\text{THF})$ or $[\text{NPN}]\text{TiCl}_2$ with the appropriate number of equivalents of K$_8$ under $N_2$, a phosphinimide complex, ($[\text{N(PN)N}]\text{Ti}_2$, can be isolated, suggesting that the N≡N bond of $N_2$ is cleaved and a new N-P bond is formed as a result of the reduction reaction. This is supported by mass spectrometric data and $^{31}P\{^1H\}$ NMR spectroscopic data obtained for the reduction of $[\text{NPN}]\text{TiCl}_2$ under an atmosphere of $^{15}N_2$.
TABLE OF CONTENTS

ABSTRACT .......................................................................................................................... ii
TABLE OF CONTENTS ......................................................................................................... iii
LIST OF TABLES .................................................................................................................. vii
LIST OF FIGURES ............................................................................................................... ix
GLOSSARY OF TERMS ....................................................................................................... xiii
ACKNOWLEDGEMENTS ..................................................................................................... xvii
DEDICATION ...................................................................................................................... xviii

Chapter 1: The Role of Metal Complexes in the Activation and Functionalization of Dinitrogen ......................................................... 1

1.1 Dinitrogen in the Environment ...................................................................................... 1
1.2 Industrial Nitrogen Fixation ......................................................................................... 5
1.3 Dinitrogen as a Ligand in Transition Metal Complexes .............................................. 9
1.4 Reactivity of Coordinated Dinitrogen ......................................................................... 14
1.5 Amidophosphine Ligands for \( \text{N}_2 \) Activation and Functionalization .................. 16
1.6 Scope of this Thesis ..................................................................................................... 21
1.7 References .................................................................................................................. 23

Chapter 2: Formation of C-N Bonds from Molecular Nitrogen and Arylalkynes ................................................................. 29

2.1 Introduction .................................................................................................................. 29
2.2 Modified Synthesis of \( ([P_2N_2]Zr)_2(\mu-\eta^2:\eta^2-N_2) \) (1) ..................................... 34
2.3 Synthesis and Characterization of \( ([P_2N_2]Zr)_2(\mu-\eta^2:\eta^2-N_2CH=CHR)(\mu-C=CR), \)
   where R = \( (\rho-\text{Me-C}_6\text{H}_4) \) (8), \( (\rho-\text{Bu-C}_6\text{H}_4) \) (9) ........................................ 37
   (i) Molecular Structures of Complexes 8 and 9 from Single Crystal X-ray Diffraction ......................................................................................................................... 38
   (ii) Solution Characterization of Complexes 8 and 9 by NMR Spectroscopy .......... 43
   (iii) Proposed Mechanism for Fluxional Behaviour .................................................. 46
2.4 Proposed Mechanism for the Formation of Complexes 4, 8 and 9 .........................47
2.5 Reactivity of Complexes 8 and 9 ................................................................. 52
2.6 Reactivity of 1 with Other Alkynes and Miscellaneous Compounds ..................54
2.7 Summary and Conclusions ........................................................................... 56
2.8 Experimental .................................................................................................. 57
2.8.1 General Procedures .................................................................................... 57
2.8.2 Materials .................................................................................................... 58
2.8.3 Attempted Procedures for the Synthesis of 1 in High Yield and Purity ........ 58
2.8.4 Synthesis and Characterization of Complexes 8 and 9 ............................... 60
2.8.5 Reactivity of Complexes 8 and 9 ............................................................... 63
2.8.6 Additional Reactions of 1 with Terminal Alkynes ..................................... 64
2.8.7 Miscellaneous Reactions of 1 ................................................................. 67
2.8.8 Isotopic Labeling Experiment .................................................................. 68
2.9 References .................................................................................................... 69

Chapter 3: Synthesis and Reactivity of ([NPN]ZrY)_2(\mu-\eta^2:\eta^2-N_2),
where Y = THF, Pyridine, Benzonitrile ....................................................... 73
3.1 Introduction .................................................................................................... 73
3.2 Synthesis of [NPN]ZrCl_2(THF) (11) and ([NPN]ZrTHF)_2(\mu-\eta^2:\eta^2-N_2) (12) .. 79
3.3 Adduct Exchange: Replacement of THF in 12 with Pyridine and Benzonitrile ... 83
   (i) Synthesis and Characterization of ([NPN]Zrpy)_2(\mu-\eta^2:\eta^2-N_2) (13) ............ 83
   (ii) Synthesis and Characterization of ([NPN]Zr(PhCN))_2(\mu-\eta^2:\eta^2-N_2) (14) .... 85
3.4 Evidence for the Formation of a Mixed-Adduct Intermediate
   ([NPN]ZrTHF)(\mu-\eta^2:\eta^2-N_2)(pyZr[NPN]) (15) ........................................ 86
3.5 Reactivity of Complexes 12 and 13 .............................................................. 92
3.6 Reduction of 11 under Various Conditions .................................................. 93
3.7 Summary and Conclusions ........................................................................... 94
3.8 Experimental .................................................................................................. 96
   3.8.1 General Procedures ............................................................................... 96
Chapter 4: Amidophosphine Complexes of Titanium for the Activation of Dinitrogen

4.1 Introduction

4.2 Titanium and the P2N2 Ligand
   (i) Synthesis and Characterization of \([\text{P}_2\text{N}_2]\text{TiCl}_2\) (16) ........................................ 116
   (ii) Synthesis and Characterization of \((\text{P}_2\text{N}_2\text{Ti})_2(\text{µ-η}^1,\eta^1\text{-N}_2)\) (17) ........ 117
   (iii) Reactivity of 17 ................................................. 120
   (iv) Reduction of 16 under Nitrogen-Free Conditions ...................... 121

4.3 Titanium and the NPN Ligand
   (i) Synthesis and Characterization of \([\text{NPN}]\text{TiCl}_2\) (18) ......................... 122
   (ii) Synthesis and Characterization of \([\text{NPN}]\text{TiCl(THF)}\) (19) ............... 124

4.4 Synthesis and Characterization of a Titanium Phosphinimide Complex, \([\text{N}(\text{PN})\text{N}]\text{Ti}_2\) (20) ........................................ 125
   (i) Reduction of 18 or 19 under \text{N}_2: Isolation of 20 ...................... 125
   (ii) Molecular Structure of 20 from Single Crystal X-ray Diffraction .... 126
   (iii) Identification of the Nitrogen-Source within 20 ....................... 129

4.5 Evidence for an Intermediate Dinitrogen Complex, \([\text{NPN}]\text{Ti}_2(\text{µ-N}_2)\) (21) ....... 129

4.6 Proposed Mechanism for the Formation of 20 from 21 .................... 132

4.7 Summary and Conclusions ........................................... 136

4.8 Experimental .................................................................. 138
   4.8.1 General Procedures ............................................. 138
   4.8.2 Materials .......................................................... 138
   4.8.3 Synthesis and Characterization of Complexes 16 and 17 ............ 138
4.8.4 Reactivity of 17 ................................................................. 140
4.8.5 Reduction of 16 under Different Conditions ...................... 141
4.8.6 Synthesis and Characterization of Complexes 18, 19, 20 and 21 .. 142
4.8.7 Additional Reduction Reactions of 18 and 19 ....................... 144

4.9 References ........................................................................ 146

Appendix 1: X-ray Crystal Structure Data .................................. 150

Appendix 2: Isotopic Labeling Experiment: Reaction of 1 with
              PhC≡CH or PhC≡CD ......................................................... 154
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Table 1.1</strong> N-N Stretching Frequencies and Bond Lengths for Selected Compounds</td>
<td>11</td>
</tr>
<tr>
<td><strong>Table 2.1</strong> Selected Bond Lengths and Angles in [([P_2N_2]Zr)_2(\mu-\eta^2:\eta^2-N_2CH=CH(p-Me-C_6H_4)) (\mu-C=C(p-Me-C_6H_4)), 8 ]</td>
<td>40</td>
</tr>
<tr>
<td><strong>Table 2.2</strong> Selected Bond Lengths and Angles in [([P_2N_2]Zr)_2(\mu-\eta^2:\eta^2-N_2CH=CH(p-tBu-C_6H_4)) (\mu-C=C(p-tBu-C_6H_4)), 9 ]</td>
<td>42</td>
</tr>
<tr>
<td><strong>Table 3.1</strong> Selected Bond Lengths and Angles in [([NPN]ZrTHF)_2(\mu-\eta^2:\eta^2-N_2), 12 ]</td>
<td>82</td>
</tr>
<tr>
<td><strong>Table 3.2</strong> Comparison of (N_2) Bond Lengths for Zr Complexes with a Planar (Zr_2N_2) Core and a Side-On Bridged (N_2) Unit</td>
<td>82</td>
</tr>
<tr>
<td><strong>Table 3.3</strong> Selected Bond Lengths and Angles in [([NPN]Zrpy)_2(\mu-\eta^2:\eta^2-N_2), 13 ]</td>
<td>85</td>
</tr>
<tr>
<td><strong>Table 3.4</strong> Relative Integration Values for a Solution Containing Complexes 12, 13 and 15</td>
<td>90</td>
</tr>
<tr>
<td><strong>Table 4.1</strong> Bond Lengths and Angles for Ti Complexes with an End-On Bridging (N_2) Unit</td>
<td>114</td>
</tr>
<tr>
<td><strong>Table 4.2</strong> Selected Bond Lengths and Angles in [([P_2N_2]Ti)_2(\mu-\eta^1:\eta^1-N_2), 17 ]</td>
<td>120</td>
</tr>
</tbody>
</table>
Table 4.3  Selected Bond Lengths and Angles in [NPN]TiCl$_2$, 18  

Table 4.4  Selected Bond Lengths and Angles in ([N(PN)N]Ti)$_2$, 20  

Table A1.1  Summary of Crystallographic Data Collection and Refinement for  
([P$_2$N$_2$]Zr)$_2$($\mu$-$\eta^2$-$\eta^2$-N$_2$CH=CH(p-Me-C$_6$H$_4$))(\mu-C=C(p-Me-C$_6$H$_4$)), 8;  
([P$_2$N$_2$]Zr)$_2$($\mu$-$\eta^2$-$\eta^2$-N$_2$CH=CH(p-$^t$Bu-C$_6$H$_4$))(\mu-C=C(p-$^t$Bu-C$_6$H$_4$)), 9;  
and ([NPN]Zrpy)$_2$(\mu-$\eta^2$-$\eta^2$-N$_2$), 13  

Table A1.2  Summary of Crystallographic Data Collection and Refinement for  
([P$_2$N$_2$]Ti)$_2$(\mu-$\eta^1$-$\eta^1$-N$_2$), 17; [NPN]TiCl$_2$, 18;  
and ([N(PN)N]Ti)$_2$, 20  

Table A1.3  File Name for the Crystallographic Data of each Complex  

Table A2.1  Concentration of ([P$_2$N$_2$]Zr)$_2$($\mu$-$\eta^2$-$\eta^2$-N$_2$), 1, and PhCCH  
(or PhCCD) in a Solution of d$_8$-Toluene  

Table A2.2  Integration Values for 1 in Solution A and Solution B from  
$^{31}$P{$^1$H} NMR (121 MHz) Spectra Obtained over a Period  
of 5 Hours
# List of Figures

<table>
<thead>
<tr>
<th>Figure 1.1</th>
<th>Representation of the FeMo cofactor in the MoFe protein of the nitrogenase enzyme in <em>Azotobacter vinelandii</em>.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1.2</td>
<td>The first example of a transition metal complex with a coordinated N\textsubscript{2} ligand, where ( \text{X}^- = \text{Br}^-, \Gamma, \text{BF}_4^- \text{ and PF}_6^- ).</td>
</tr>
<tr>
<td>Figure 1.3</td>
<td>Dewar-Chatt-Duncanson representation of synergistic bonding between the ( d )-orbitals of a metal centre and the molecular orbitals of N\textsubscript{2}.</td>
</tr>
<tr>
<td>Figure 1.4</td>
<td>Representations of the known coordination modes for dinitrogen: end-on, side-on and side-on/end-on.</td>
</tr>
<tr>
<td>Figure 1.5</td>
<td>Orbital orientations that are suitable for side-on bonding of N\textsubscript{2} between two metal centres: interaction of the ( d )-orbitals of the metals with the ( \pi )-orbital and ( \pi^* )-orbitals of dinitrogen.</td>
</tr>
<tr>
<td>Figure 1.6</td>
<td>The zirconium dinitrogen complex, \textbf{1}, supported by the P\textsubscript{2}N\textsubscript{2} ligand set.</td>
</tr>
<tr>
<td>Figure 2.1</td>
<td>Mo and W phosphine complexes with (a) \textit{trans}-end-on or (b) \textit{cis}-end-on coordinated N\textsubscript{2} ligands and (c) a depiction of the charge disparity on N\textsubscript{2} resulting from synergistic bonding.</td>
</tr>
</tbody>
</table>
Figure 2.2 ORTEP representation (ellipsoid probability 50%) of the molecular structure of 
([P_2N_2]Zr)_2(μ-η^2:η^2-N_2CH=CH(p-Me-C_6H_4))(μ-C=C(p-Me-C_6H_4)), 8, as determined by single crystal X-ray diffraction. Hydrogen atoms and silylmethyl groups are omitted for clarity and only ipso carbons of the P_2N_2 ligand phenyl rings are shown.

Figure 2.3 ORTEP representation (ellipsoid probability 50%) of the molecular structure of 
([P_2N_2]Zr)_2(μ-η^2:η^2-N_2CH=CH(p-1Bu-C_6H_4))(μ-C=C(p-1Bu-C_6H_4)), 9, as determined by single crystal X-ray diffraction. Hydrogen atoms and silylmethyl groups are omitted for clarity and only ipso carbons of the P_2N_2 ligand phenyl rings are shown.

Figure 2.4 Alternative ORTEP representation (ellipsoid probability 50%) of the molecular structure of 
([P_2N_2]Zr)_2(μ-η^2:η^2-N_2CH=CH(p-Me-C_6H_4))(μ-C=C(p-Me-C_6H_4)), 8, when viewed along the Zr-Zr axis. All the P_2N_2 ligand atoms, except for phosphorus, have been excluded for clarity. The visible Zr atom eclipses the other.

Figure 2.5 $^{31}$P{H} NMR (121 MHz) spectra of complex 8 at room temperature and low temperature: A and A', or B and B', are pairs of doublets corresponding to phosphorus nuclei within the same P_2N_2 ligand set, which are coupling to each other. A coupling constant of 74.3 Hz is observed for A and A' ($^2J_{pp} = 66.8$ Hz for B and B'). Small signals in the spectra are attributed to the presence of unidentified impurities in the sample.
Figure 3.1  ORTEP representation (ellipsoid probability 50%) of the molecular structure of ([NPN]ZrTHF)$_2$(μ-η$^2$:η$^2$-N$_2$), 12, as determined by single crystal X-ray diffraction. Hydrogen atoms and silylmethyl groups are omitted for clarity and only ipso carbons of the NPN ligand phenyl rings are shown. Crystals of 12 were grown by Dr. P. Yu.

Figure 3.2  ORTEP representation (ellipsoid probability 50%) of the molecular structure of ([NPN]Zrpy)$_2$(μ-η$^2$:η$^2$-N$_2$), 13, as determined by single crystal X-ray diffraction. Hydrogen atoms and silylmethyl groups are omitted for clarity and only ipso carbons of the NPN ligand phenyl rings are shown.

Figure 3.3  $^{31}$P$^{'1}$H (121 MHz) and $^1$H NMR (300 MHz) spectra of a solution containing approximately equimolar amounts of 12 and 13.

Figure 4.1  Titanium complexes with a) a side-on/end-on N$_2$ unit bridging three Ti atoms and b) two Ti atoms bridged by two side-on N$_2$ units.

Figure 4.2  ORTEP representation (ellipsoid probability 50%) of the molecular structure of ([P$_2$N$_2$]Ti)$_2$(μ-η$^2$:η$^2$-N$_2$), 17, as determined by single crystal X-ray diffraction. Hydrogen atoms and silylmethyl groups are omitted for clarity and only ipso carbons of the P$_2$N$_2$ ligand phenyl rings are shown.

Figure 4.3  ORTEP representation (ellipsoid probability 50%) of the molecular structure of [NPN]TiCl$_2$, 18, as determined by single crystal X-ray diffraction. Hydrogen atoms and silylmethyl groups are omitted for clarity.
Figure 4.4 ORTEP representation (ellipsoid probability 50%) of the molecular structure of \([\text{N(PN)N}]\text{Ti}_2\), 20, as determined by single crystal X-ray diffraction. Hydrogen atoms and silylmethyl groups are omitted for clarity.

Figure 4.5 A titanium complex with two bridging phosphinimide ligands. Bond lengths and angles for the \(R = \text{^1Pr}\) derivative are listed.

Figure A2.1 Decrease in the integrated area for the \(^{31}\text{P}\{^1\text{H}\}\) NMR signal of 1 over time following the addition of PhCCH (Solution A) or PhCCD (Solution B).

Figure A2.2 A first-order plot of the integration data for the depletion of 1 over time following the addition of PhCCH (Solution A) or PhCCD (Solution B).
GLOSSARY OF TERMS

The following abbreviations, most of which are commonly found in the literature, are used in this thesis.

Å  Angström
A  absorbance
Anal.  Analysis
Ar  aryl (or argon)
atm  atmosphere
BASF  Badische Anilin & Soda Fabrik
Bp  Me₂Si(η⁵-C₅H₂-2-SiMe₃-4-CMe₃)₂ ligand
br  broad
"Bu  n-butyl group, -CH₂CH₂CH₂CH₃
'Bu  tertiary butyl group, -C(CH₃)₃
Cα  carbon atom in the α position
Cβ  carbon atom in the β position
Calcd.  calculated
CCD  charge coupled device
cm  centimetre
Cp  cyclopentadienyl, C₅H₅
Cp*  pentamethylcyclopentadienyl group, C₅Me₅
°C  degrees Celsius
d  doublet
D or ²H  deuterium
deg (or °)  degrees
dppe  1,2-bis(diphenylphosphino)ethane
DME  1,2-dimethoxyethane
dₙ  n-deuterated
dₓᵧ, dₓz, dᵧz, dₓ²₋ᵧ², dₓ²  d-orbitals of appropriate symmetry
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>“entgegen” or trans</td>
</tr>
<tr>
<td>EI-MS</td>
<td>electro spray ionization mass spectrometry</td>
</tr>
<tr>
<td>eq.</td>
<td>equivalents</td>
</tr>
<tr>
<td>eV</td>
<td>electron Volt</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl group, -CH$_2$CH$_3$</td>
</tr>
<tr>
<td>Et$_2$O</td>
<td>diethyl ether</td>
</tr>
<tr>
<td>$^{19}$F</td>
<td>fluorine-19</td>
</tr>
<tr>
<td>g</td>
<td>grams</td>
</tr>
<tr>
<td>Gof</td>
<td>goodness of fit</td>
</tr>
<tr>
<td>HIPT</td>
<td>hexaisopropylterphenyl, $(3,5-(2,4,6,-^{1}Pr$_3$-C$_6$H$_2$)$_2$C$_6$H$_3$)</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>$h\nu$</td>
<td>photon</td>
</tr>
<tr>
<td>$^1$H</td>
<td>proton</td>
</tr>
<tr>
<td>${^1$H$}$</td>
<td>proton decoupled</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz, seconds$^{-1}$</td>
</tr>
<tr>
<td>IPA</td>
<td>isopropyl alcohol, $(CH$_3$)$_2$CHOH</td>
</tr>
<tr>
<td>$^{n}$J$_{AB}$</td>
<td>coupling constant between nuclei A and B over n bonds</td>
</tr>
<tr>
<td>k or $k$</td>
<td>rate constant</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>$m$</td>
<td>meta position</td>
</tr>
<tr>
<td>m</td>
<td>multiplet (NMR spectroscopy)</td>
</tr>
<tr>
<td>M</td>
<td>metal atom (or molar, when referring to concentration)</td>
</tr>
<tr>
<td>M$^+$</td>
<td>parent atom or molecular ion</td>
</tr>
<tr>
<td>Me</td>
<td>methyl group, -CH$_3$</td>
</tr>
<tr>
<td>MgADP</td>
<td>adenosine diphosphate, magnesium salt</td>
</tr>
<tr>
<td>MgATP</td>
<td>adenosine triphosphate, magnesium salt</td>
</tr>
<tr>
<td>MHz</td>
<td>megahertz</td>
</tr>
<tr>
<td>mL</td>
<td>millilitre</td>
</tr>
<tr>
<td>mmol</td>
<td>millimole</td>
</tr>
<tr>
<td>mol</td>
<td>mole</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>m/z</td>
<td>mass/charge (mass spectrometry)</td>
</tr>
<tr>
<td>n</td>
<td>normal (as in n-butyl)</td>
</tr>
<tr>
<td>$^{15}$N</td>
<td>nitrogen-15</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>NPN</td>
<td>diamidophosphine ligand, PhP(CH$_2$SiMe$_2$NPh)$_2$</td>
</tr>
<tr>
<td>o</td>
<td>ortho position</td>
</tr>
<tr>
<td>ORTEP</td>
<td>Oakridge Thermal Ellipsoid Plotting Program</td>
</tr>
<tr>
<td>p</td>
<td>para position</td>
</tr>
<tr>
<td>$^{31}$P</td>
<td>phosphorus-31</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl group, -C$_6$H$_5$</td>
</tr>
<tr>
<td>PNP</td>
<td>amidodiphosphine ligand, N(SiMe$_2$CH$_2$PPh)$_2$</td>
</tr>
<tr>
<td>P$_2$N$_2$</td>
<td>diamidodiphosphine ligand, PhP(CH$_2$SiMe$_2$NSiMe$_2$CH$_2$)$_2$PPh</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>Pr$_1$ or Pr$^i$</td>
<td>isopropyl group, -CH(CH$_3$)$_2$</td>
</tr>
<tr>
<td>Pr$^i$NON</td>
<td>tridentate diamido ligand, (i-PrN-o-C$_6$H$_4$)$_2$O</td>
</tr>
<tr>
<td>P$_i$</td>
<td>inorganic phosphate, PO$_4^{3-}$</td>
</tr>
<tr>
<td>py</td>
<td>pyridine</td>
</tr>
<tr>
<td>q</td>
<td>quartet</td>
</tr>
<tr>
<td>R</td>
<td>hydrocarbon substituent</td>
</tr>
<tr>
<td>R$^2$</td>
<td>coefficient of determination for a linear regression</td>
</tr>
<tr>
<td>R$_1$, R$_w$</td>
<td>residual errors (X-ray crystallography)</td>
</tr>
<tr>
<td>reflns</td>
<td>reflections (X-ray crystallography)</td>
</tr>
<tr>
<td>s</td>
<td>singlet or seconds</td>
</tr>
<tr>
<td>S</td>
<td>solvent, donor atom or sulfur (depending on context)</td>
</tr>
<tr>
<td>SiMe$_3$</td>
<td>trimethylsilyl group, Si(CH$_3$)$_3$</td>
</tr>
<tr>
<td>T</td>
<td>temperature in Kelvin or °C</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran (C$_4$H$_8$O)</td>
</tr>
<tr>
<td>TMS</td>
<td>trimethylsilyl group, Si(CH$_3$)$_3$</td>
</tr>
<tr>
<td>TMEDA</td>
<td>N, N', N'-tetramethylethylenediamine</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>V</td>
<td>unit cell volume</td>
</tr>
</tbody>
</table>
VT: variable temperature
$\Delta w_{1/2}$: width at half height
$Z$: formula units in the unit cell
$Z$: "zusammen" or cis
$\sigma, \pi, \delta$: notations for bond symmetry
$\eta^n$: hapticity of order $n$
$\mu$: bridging
$\mu$ (Mo K$\alpha$): absorption coefficient (X-ray crystallography)
$\mu$L: microlitre
$\rho$: density
$\rho_{\text{calc}}$: calculated density
$\nu_{\text{NN}}$: stretching frequency of N-N bond
$\delta$: chemical shift in ppm
$\delta^+$ or $\delta^-$: partial positive or negative charge
ACKNOWLEDGMENTS

First, I would like to thank my supervisor, Professor Michael Fryzuk, for his guidance and patience throughout the course of this work, but especially in these last few months. I thank my lab mates, both past and present, for their friendship and the many helpful suggestions they offered over the years. Many thanks go to Drs. Samuel Johnson, Michael Petrella, Scott Winston and Bruce MacKay, for freely sharing their expertise. I am particularly thankful for the many insightful discussions and good times I enjoyed in the company of Erin MacLachlan and Sharonna Greenberg; I am indebted to both of them for editing this thesis.

The assistance I received from the staff in the Department of Chemistry is also appreciated: Dr. Nick Burlinson, Marietta Austria and Liane Darge (NMR), Mr. P. Borda and Mr. M. Lakha (elemental analysis), Mr. M. Lapawa (EI-MS), Steve Rak and Brian Ditchburn (glassblowing), as well the staff in the Mechanical and Electronics shop. I thank Drs. Brian Patrick and Chris Carmichael for solving the crystal structures in this thesis.

I thank Anna Johnston, Monica Kovacs, Jenn Wong, Anne Co, Leah Thompson, Iona Sham, Keri Kwong, Tracey Stott and Carolyn Moorlag for their friendship and encouragement. I also wish to thank the Bruschetta family for welcoming me into their home when I first arrived in Vancouver.

Most importantly, I am grateful to my parents, my sister Luana and my niece Chiara, whose constant support and words of encouragement carried me through the most difficult times.
To my Mom and Dad,
who always had faith
Chapter 1: The Role of Metal Complexes in the Activation and Functionalization of $N_2$

1.1 Dinitrogen in the Environment

Molecular nitrogen, or $N_2$, is the most abundant gas in our atmosphere, comprising 78% of the air we breathe. In the early 1770s, several scientists independently isolated dinitrogen from the air; however, Daniel Rutherford is usually given most of the credit for the discovery. Rutherford was interested in separating the various components of air in order to study their individual properties. In one experiment, mice were exposed to a limited supply of air and their exhaled CO$_2$ was removed with KOH to precipitate potash, K$_2$CO$_3$. The mice eventually died from asphyxiation and the residual air, dinitrogen, became appropriately known as 'azote', meaning 'no life' in Greek. By performing combustion experiments, Rutherford was also able to determine another interesting property of the residual air: the ability to extinguish a flame. A French chemist, Jean A. C. Chaptal, recognized the presence of nitrogen in nitrate salts, known as nitre, and so named $N_2$ gas nitrogène in 1790. For clarity, the term nitrogen is now used when referring to the lone atom, N, and $N_2$ is molecular nitrogen or dinitrogen.
Dinitrogen is generally considered an inert molecule, as it is involved in neither respiration nor combustion at ambient temperatures. For this reason, food products and reactive chemicals are often infused or purged with dinitrogen to preserve the quality of the product after packaging. Dinitrogen is also used as a refrigerant and as an inert atmosphere in industrial processes to avoid the oxidation or combustion of sensitive materials.

Several factors contribute to the inert nature of dinitrogen. The N\textsubscript{2} molecule has a strong triple bond and lacks a dipole moment. The energy gap between the highest occupied molecular orbital (−15.6 eV) and the lowest unoccupied molecular orbital (7.3 eV) in N\textsubscript{2} is large; thus, difficulty is encountered when attempting to reduce or oxidize dinitrogen.

Nitrogen is essential to life on Earth, but only a few organisms are able to absorb this nutrient from the vast supply of N\textsubscript{2} available in the atmosphere. The nitrogen cycle illustrates how dinitrogen is incorporated into living things, cycled through the environment and returned to the atmosphere. A simplified version of the \textit{biological} nitrogen cycle is shown in Scheme 1.1. Certain bacteria, known as diazotrophs, are the only organisms capable of converting N\textsubscript{2} into ammonia. This process is nitrogen fixation: the formation of nitrogenous products directly from dinitrogen. Symbiotic diazotrophs are attracted to the roots or stem of certain plants. For example, the \textit{Rhizobium} bacteria enter the roots of leguminous plants (such as clover, soy, and alfalfa), forming nodules in which the bacteria grow. In turn, the roots of the plant have direct access to the ammonia produced by the diazotroph.

Although plants are able to absorb ammonia, nitrates are relatively more soluble in water than NH\textsubscript{3} and, as a result, are more accessible to plant roots in soil. Nitrification is the oxidation of ammonia to nitrites and nitrates by nitrifying bacteria. These forms of fixed nitrogen (i.e., nitrites, nitrates and ammonia) are then assimilated by plants and used to build the biological material, such as proteins, that are necessary for life. Nitrates and nitrites are also depleted from the soil by various microorganisms that use the oxygen in these compounds for their respiration. This denitrification process returns dinitrogen to the atmosphere. The decomposition of biological material returns fixed nitrogen to the cycle in the form of NH\textsubscript{3} and is aptly named ammonification. In turn, this ammonia may be reabsorbed by plants or oxidized to nitrates, which can either be incorporated into plant material or consumed by the denitrification process to complete the cycle.
Chapter 1: The Role of Metal Complexes in the Activation and Functionalization of $N_2$

Lightning also contributes to the total amount of fixed $N_2$ in the atmosphere.\textsuperscript{2,11-13} The electrical discharge from lightning generates the high temperature and pressure necessary to react $N_2$ with $O_2$ and form nitrogen oxides, such as NO and NO$_2$. However, the amount of fixed nitrogen produced in this fashion is minor in comparison to that resulting from the biological fixation of dinitrogen. Further, only a small portion of this fixed nitrogen is deposited onto the ground in the form of nitrates.

Diazotrophs are of particular interest to chemists for their unique ability to fix $N_2$ under ambient temperature and pressure. The nitrogenase enzyme in a diazotroph is responsible for facilitating the energy intensive reaction required to produce ammonia from $N_2$.\textsuperscript{14-17} In particular, sixteen equivalents of MgATP are needed for the reduction of one equivalent of $N_2$ to ammonia (Equation 1.1). The nitrogenase enzyme consists of two proteins: the Fe protein uses ATP to generate the electrons necessary for the reduction of $N_2$ and the MoFe protein contains the active site for $N_2$ binding and reactivity, known as the FeMo cofactor.

References begin on page 23
Chapter 1: The Role of Metal Complexes in the Activation and Functionalization of $N_2$

$$N_2 + 8 H^+ + 8 e^- + 16 \text{MgATP} \xrightarrow{\text{nitrogenase}} 2 \text{NH}_3 + H_2 + 16 \text{MgADP} + 16 P_i \quad [1.1]$$

The structure of the FeMo cofactor in the nitrogenase enzyme of the *Azotobacter vinelandii* bacterium has been reported.\textsuperscript{18-22} The FeMo cofactor consists of a MoFe\textsubscript{7}S\textsubscript{9} cluster, where a histidine and a cysteine ligand on Mo and Fe, respectively, anchor the cofactor to the protein (Figure 1.1). The octahedral Mo atom also has a homocitrate ligand and three bridging sulfide ligands, which link Mo to three iron centres. Six Fe atoms have a distorted trigonal geometry and are connected through $\mu_3$-S and $\mu_2$-S bridging sulfide ligands to form a cavity in the centre of the cluster. Conceptually, dinitrogen could bind to any of the Fe and Mo atoms. However, the Mo atom has a relatively saturated coordination sphere, whereas the iron cavity is less congested and generally viewed as the most favourable site for $N_2$ activation.\textsuperscript{22} Improved resolution of the structure of the FeMo cofactor has shown the presence of an interstitial ligand within the central cavity of the metallic cluster.\textsuperscript{22} The ligand is a light atom that is coordinated to the six trigonal iron atoms. The identity of the atom, referred to as X, could not be determined unambiguously based on crystallographic data; however, the authors proposed that X is possibly a carbon, oxygen or nitrogen atom. Given the function of the nitrogenase enzyme, X was assumed to be an N atom that originated from dinitrogen. However, spectroscopic evidence contradicts this assertion; X is not a nitrogen atom.\textsuperscript{23,24} As a result, the significance of X in $N_2$ activation is not obvious.

References begin on page 23
Chapter 1: The Role of Metal Complexes in the Activation and Functionalization of $N_2$

Figure 1.1. Representation of the FeMo cofactor in the MoFe protein of the nitrogenase enzyme in *Azotobacter vinelandii*.18-22

The site for $N_2$ coordination and activation within the MoFe$_7$S$_9$ cluster is uncertain.14-17 The reported structure is only representative of the FeMo cofactor when the enzyme is not catalytically active. During catalysis, the structural features of the cluster probably change to effect the necessary transformation of dinitrogen. Nonetheless, the presence of several transition metals in the FeMo cofactor is a clear indication that metal atoms are important contributors to the catalytic functionalization of dinitrogen. Consequently, this knowledge has inspired the research of iron and molybdenum complexes, in addition to other transition metal complexes, as synthetic models of nitrogenase.17,25-28

1.2 Industrial Nitrogen Fixation

The availability of fixed nitrogen is often the limiting factor controlling plant growth.2,10 A balance between the processes that fix nitrogen and those that release dinitrogen is vital for maintaining a healthy ecosystem.29,30 All plants and animals on Earth are mutually dependent on the nitrogen cycle for growth, whether it is through the direct or indirect absorption of dinitrogen.

Prior to the twentieth century, agricultural productivity was limited by the availability of natural sources of fixed dinitrogen.2 Traditional farming included the cultivation and rotation of leguminous crops, as well as the addition of organic waste, to enrich the nitrogen
content in the soil. Peruvian guano was introduced as a fertilizer to Europe and the United States in the early 1800s, but the high demand for nitrogen-rich guano exhausted its limited supply by the end of that century. Chilean caliche (NaNO₃) and ammonium sulfate, a by-product from the coking of coal, were the most important commercial sources of fixed nitrogen by the 1890s. Even with these sources of fixed nitrogen, an imminent food shortage was predicted for an ever-increasing human population at the turn of the century.³¹,³² As a result, research was directed toward developing a method of deriving fixed nitrogen directly from N₂; an effective chemical process had to be economical and simple for it to have widespread utility.

The first commercial method for nitrogen fixation was the Birkeland-Eyde arc process, which was put into practice in Norway by 1905.²,³³ Similar to the effect of lightning in the atmosphere, an electric arc furnace produces a high temperature of 2000-3000°C and N₂ combines with O₂ to form nitric oxide (Scheme 1.2). The resulting nitric oxide has to be cooled down quickly to inhibit the reversible reaction. Nitric oxide is further oxidized by O₂ and then reacts with water to produce nitric acid, from which calcium nitrate can be isolated and used directly for fertilizer. However, a major drawback to this method is the large amount of electrical energy needed to produce a small amount of fixed nitrogen: the reacted air has an NO content of only 1.5-2%, by volume.² In practice, the process was limited to regions where cheap electricity, such as that provided by hydro electrical power stations, was available. Even then, the process was uneconomical and replaced by more efficient methods.

\[ 3 \text{N}_2 + 3 \text{O}_2 \xrightarrow{2000-3000^\circ \text{C}} 6 \text{NO} \xrightarrow{<1000^\circ \text{C}} 6 \text{NO}_2 \]

- \( \xrightarrow{2 \text{H}_2\text{O}} (-2 \text{NO}) \)
- \( \xrightarrow{2 \text{CaO}} (-2 \text{H}_2\text{O}) \)
- \( 2 \text{Ca(NO}_3)_2 \xrightarrow{4 \text{HNO}_3} \)

**Scheme 1.2**
Chapter 1: The Role of Metal Complexes in the Activation and Functionalization of \( \text{N}_2 \)

The Frank-Caro cyanamide process was more widespread than the Birkland-Eyde process, with commercial plants operating in several countries, including Canada, by 1909.\(^2,33\) The cyanamide process requires calcium carbide, which is derived from the reaction of lime, \( \text{CaO} \), with coke, \( \text{C} \), at high temperatures. The production of \( \text{CaC}_2 \) consumes less electrical power than the Birkland-Eyde arc process and, as a result, the Frank-Caro cyanamide process became the relatively more economical method for nitrogen fixation at that time. Pure dinitrogen is necessary for the reaction and obtained from the liquefaction of air. Dinitrogen is then reacted with finely ground calcium carbide at high temperatures to give calcium cyanamide (Equation 1.2). The product, \( \text{CaNCN} \), may be used directly as a fertilizer or reacted with steam to generate ammonia (Equation 1.3). By 1914, this was the major industrial process used for nitrogen fixation.\(^33\)

\[
\text{CaC}_2 + \text{N}_2 \xrightarrow{1000^\circ\text{C}} \text{CaNCN} + \text{C} \quad [1.2]
\]

\[
\text{CaNCN} + 3 \text{H}_2\text{O} \longrightarrow 2 \text{NH}_3 + \text{CaCO}_3 \quad [1.3]
\]

The most significant industrial method for nitrogen fixation is the Haber-Bosch process (Equation 1.4).\(^33,34\) In 1909, Fritz Haber and his assistant, Robert Le Rossignol, demonstrated that ammonia could be isolated from the reaction of \( \text{N}_2 \) and \( \text{H}_2 \) at high temperatures and pressure over a metal catalyst.\(^2,35\) As a result, Haber was awarded the Nobel Prize for Chemistry in 1918 for the synthesis of ammonia from its elements. Carl Bosch developed the methods that would be necessary to perform the high-pressure reaction on an industrial scale and, with Friedrich Bergius, was awarded the Nobel Prize for Chemistry in 1931. The industrial process was developed by BASF, under the direction of Bosch, and the first plant was opened in Oppau, Germany in 1913. A large investment was needed to put the Haber-Bosch process into practice; at the time, the high-pressure equipment was novel and the plant was expensive to build.\(^33\) However, over time the Haber-Bosch process proved to be the most economical method for fixing dinitrogen and a return on the initial investment was anticipated after two years of continuous operation. The Haber-Bosch
process has two major advantages over the Birkeland-Eyde and Frank-Caro processes: 1) it consumes much less electricity and 2) dinitrogen is abundant and inexpensive. Currently, the Haber-Bosch process is very efficient and ammonia is produced economically from an Fe- or Ru-based catalyst system.\textsuperscript{36}

\[ \text{Fe or Ru catalyst} \begin{array}{c}
\text{500-600}^\circ\text{C} \\
\sim 200 \text{ atm}
\end{array} \] \[ \text{N}_2 + 3 \text{H}_2 \rightarrow 2 \text{NH}_3 \] [1.4]

The Haber-Bosch synthesis of ammonia provides an abundance of fixed nitrogen for a variety of purposes.\textsuperscript{2} Ammonia is used in agriculture as a fertilizer and in other industries as a starting material for the synthesis of nitrogenous products. As a direct result, agricultural productivity is high and the human population has grown dramatically in the last 100 years. This industrial process is now widespread and generates about half as much ammonia as all the bacteria in the world. It is worth noting that this increase in the total amount of fixed nitrogen has somewhat disrupted the natural balance of the nitrogen cycle. Some of the adverse effects on the environment have been recognized;\textsuperscript{29,30} for example, in heavily fertilized regions the soil is saturated with fixed nitrogen, which then leaches into and pollutes groundwater and aquifers. Nonetheless, the synthesis of ammonia from its elements is considered one of the most important discoveries ever made.\textsuperscript{2}

Nitrogenase and the Haber-Bosch process each operate under different conditions, yet both are able to produce fixed nitrogen in the form of ammonia. The common factor in both biological and industrial fixation is the presence of a metal catalyst. Clearly, metal catalysts have a critical role in nitrogen fixation and a greater understanding of how they function is of interest. Further, the otherwise inert dinitrogen molecule can be made reactive under the appropriate conditions and, as a result, new products might be catalytically accessible using this abundant feedstock. In particular, one aspect of dinitrogen research is focused on discovering and investigating new transformations for coordinated N\textsubscript{2} in metal complexes.\textsuperscript{8,9,28,37-39}
1.3 Dinitrogen as a Ligand in Transition Metal Complexes

The first dinitrogen complex was reported by Bert Allen and Caesar Senoff in 1965 (Figure 1.2).\textsuperscript{40,41} When the complex was first identified, it was prepared by the reaction of RuCl\textsubscript{3}·3H\textsubscript{2}O with hydrazine; however, later experiments showed that the same product could be obtained by bubbling N\textsubscript{2} through a solution of Ru(NH\textsubscript{3})\textsubscript{5}Cl\textsubscript{3} in the presence of a reducing agent, such as zinc.\textsuperscript{42} The discovery of [Ru(NH\textsubscript{3})\textsubscript{5}N\textsubscript{2}]\textsuperscript{2+} clearly showed that dinitrogen could coordinate to a metal centre, which is believed to be the first step in fixing dinitrogen from the atmosphere. As a result, this knowledge inspired further research into the chemistry of dinitrogen complexes, the properties of coordinated N\textsubscript{2} and different methods for preparing N\textsubscript{2} complexes.\textsuperscript{43}

\[\begin{array}{c}
\text{N} \\
\text{N} \\
\text{NH}_3 \text{Ru} \text{NH}_3 \\
\text{NH}_3 \\
\text{NH}_3 \\
2^+ \\
2X^- \\
\end{array}\]

\textbf{Figure 1.2.} The first example of a transition metal complex with a coordinated N\textsubscript{2} ligand, where X\textsuperscript{−} = Br\textsuperscript{−}, I\textsuperscript{−}, BF\textsubscript{4}\textsuperscript{−} and PF\textsubscript{6}\textsuperscript{−}.\textsuperscript{40}

Dinitrogen is considered a poor ligand for transition metal complexes. The N\textsubscript{2} molecule is neither a good σ-donor nor a good π-acceptor ligand due to the same factors that contribute to its inertness.\textsuperscript{4,5,8,9} Based on the Dewar-Chatt-Duncanson model for bonding, a synergistic interaction between the frontier orbitals of the N\textsubscript{2} ligand and the d-orbitals of the metal contribute to the stability of the complex (Figure 1.3).\textsuperscript{44,45} For example, a σ-bond is formed by donation from the HOMO (3σ\textsubscript{e}) of N\textsubscript{2} into the empty d\textsubscript{x\textsuperscript{2}−y\textsuperscript{2}} orbital of the metal; the simultaneous back-donation from a filled d\textsubscript{xy}, d\textsubscript{xz} or d\textsubscript{yz} orbital of the metal into the
LUMO ($1\pi_g$) of N\textsubscript{2} creates a bond with $\pi$-symmetry. Alternatively, a $\sigma$-bond could also result from the overlap between the $d_{z^2}$ orbital of the metal and $3\sigma_g$ orbital of N\textsubscript{2}.

![Diagram showing Dewar-Chatt-Duncanson representation of synergistic bonding between the $d$-orbitals of a metal centre and the molecular orbitals of N\textsubscript{2}.

Figure 1.3. Dewar-Chatt-Duncanson representation of synergistic bonding between the $d$-orbitals of a metal centre and the molecular orbitals of N\textsubscript{2}.

Back-donation from the metal $d$-orbitals into the degenerate $\pi^*$-orbitals of N\textsubscript{2} serves to weaken the N-N triple bond and effectively reduce, or activate, the N\textsubscript{2} ligand.\textsuperscript{8,9,26} The extent of N\textsubscript{2} activation in the complex is often evident by infrared or Raman spectroscopy: an activated N\textsubscript{2} unit has a lower energy stretching frequency, $\nu_{\text{NN}}$, than free molecular nitrogen (Table 1.1). The molecular structure of the complex, as determined by X-ray or neutron diffraction, also gives some indication regarding the degree of N\textsubscript{2} activation: an elongated N-N bond distance compared to that of free N\textsubscript{2} suggests activation in the bound N\textsubscript{2} unit.
Table 1.1. N-N Stretching Frequencies and Bond Lengths for Selected Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>N-N (Å)</th>
<th>$v_{\text{NN}}$ (cm$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{N}=\text{N}$</td>
<td>1.0975</td>
<td>2331</td>
<td>46,47</td>
</tr>
<tr>
<td>Ph$\text{N}=\text{NPh}$</td>
<td>1.255</td>
<td>1442</td>
<td>47-50</td>
</tr>
<tr>
<td>$\text{H}_2\text{N}–\text{NH}_2$</td>
<td>1.460</td>
<td>1111</td>
<td>47,51,52</td>
</tr>
</tbody>
</table>

Certain formalisms have been developed to describe the oxidation state for a coordinated $\text{N}_2$ unit.\textsuperscript{8,26} For instance, a bound $\text{N}_2$ unit with a bond length approximating that of hydrazine is considered strongly activated and referred to as a hydrazido or $(\text{N}_2)^{4-}$ ligand. Similarly, a diazenido ligand, $(\text{N}_2)^{2-}$, displays properties that resemble those of a compound with an N-N double bond. However, the formal oxidation state on the metal centre must also be considered when determining the level of $\text{N}_2$ activation. Consequently, formalisms assigned to the $\text{N}_2$ unit should not be based solely on the N-N bond length or the stretching frequency.

The dinitrogen ligand can bridge two or more metal centres; however, monometallic and bimetallic complexes are most common.\textsuperscript{6,8,9,26} In the majority of such complexes, the dinitrogen ligand is coordinated to the metal in an end-on fashion (Figure 1.4). The side-on, or lateral, coordination mode for dinitrogen is less common and is usually observed as a bridging ligand between two or more metal centres. With the exception of a few examples,\textsuperscript{53,54} there is often insufficient evidence for monometallic complexes with a side-on $\text{N}_2$ unit.\textsuperscript{55-58} Complexes with a strongly activated $\text{N}_2$ unit are generally bimetallic.
Chapter 1: The Role of Metal Complexes in the Activation and Functionalization of N₂

<table>
<thead>
<tr>
<th>Strong Activation</th>
<th>Side-on</th>
<th>Side-on/End-on</th>
</tr>
</thead>
<tbody>
<tr>
<td>End-on</td>
<td><img src="image1.png" alt="Diagram" /></td>
<td><img src="image2.png" alt="Diagram" /></td>
</tr>
<tr>
<td>Weak Activation</td>
<td><img src="image3.png" alt="Diagram" /></td>
<td><img src="image4.png" alt="Diagram" /></td>
</tr>
</tbody>
</table>

Figure 1.4. Representations of the known coordination modes for dinitrogen: end-on, side-on and side-on/end-on.

For an N₂ unit that is bound side-on, the overlap between the π*-orbitals of N₂ (1π₉) and the available d-orbitals of a metal forms molecular orbitals with π- and δ-symmetry (Figure 1.5).\(^{59,60}\) In the end-on coordinated N₂ unit, overlap between the appropriate d-orbitals and π*-orbitals gives two possible π-bonding interactions: one of these is shown in Figure 1.3. However, for a side-on N₂ unit, only one d-orbital has the appropriate orientation and symmetry to form a π-bond. The π-orbital of N₂ (1π₉) and a vacant dₓ² or dₓ²₋ᵧ² orbital on the metal have the proper symmetry for the formation of a σ-bond.
Figure 1.5. Orbital orientations that are suitable for side-on bonding of N$_2$ between two metal centres: interaction of the $d$-orbitals of the metals with the $\pi$-orbital and $\pi^*$-orbitals of dinitrogen.

Synthetic methods that directly use N$_2$ gas to prepare dinitrogen complexes are the most desirable since they imitate biological and industrial fixation.$^{6,8,9,26}$ However, the preparation of dinitrogen complexes is difficult and unpredictable. One method involves the reduction of a transition metal complex under an atmosphere of dinitrogen.$^{61-66}$ In some cases, dinitrogen spontaneously coordinates to a metal centre without the need for an external reducing agent.$^{67-73}$ Some dinitrogen complexes are formed when N$_2$ displaces a weakly coordinated ligand.$^{74-78}$
1.4 Reactivity of Coordinated Dinitrogen

The synthesis of ammonia by nitrogenase and via the Haber-Bosch process both involve the formation of N-H bonds and the cleavage of the N-N triple bond. As a result, the protonation of coordinated dinitrogen, for the purpose of evolving ammonia or hydrazine, has been studied for many dinitrogen metal complexes. Complexes capable of breaking the N-N bond to form reactive metal nitrides are also of interest. Selected examples of N-H bond formation and N-N bond cleavage are shown below.

The synthesis of ammonia from a well-characterized dinitrogen complex was first reported by Joseph Chatt; the protonation of cis-[M(N₂)₂(PMe₂Ph)₄] or trans-[M(N₂)₂(PMePh₂)₄], where M = Mo or W, produced a stoichiometric amount of ammonia. Recently, the synthesis of ammonia by the stepwise reduction and protonation of dinitrogen has been reported for a molybdenum triamidoamine complex (Scheme 1.3). Several of the intermediates were identified and support the mechanisms that were originally proposed by Joseph Chatt. An interesting aspect of this catalytic system is that dinitrogen is fixed under ambient conditions; thus, parallels have been drawn between this Mo catalyst and the function of the lone Mo atom in the FeMo cofactor in nitrogenase.

Scheme 1.3

References begin on page 23
The three-coordinate Mo complex depicted in Scheme 1.4 is capable of spontaneously binding \( \text{N}_2 \) at low temperatures and eventually severing the N-N triple bond at room temperature.\textsuperscript{84-86} The N-N cleavage proceeds through a bis-molybdenum dinitrogen complex that distorts to a ‘zig-zag’ geometry in the transition state, from which a Mo nitrido complex can be isolated.\textsuperscript{85}

\begin{align*}
\text{Ar(R)N-Mo} & \overset{\text{N}_2}{\longrightarrow} \text{N(R)Ar} \quad \text{N}_2 \rightarrow \text{N}=\text{Mo} \\
\text{R} = \text{C(CD}_3^2\text{CH}_3} \quad \text{Ar} = \text{3,5-C}_6\text{H}_3\text{Me}_2
\end{align*}

Scheme 1.4

The reactivity of coordinated dinitrogen is not limited to protonation and cleavage. The formation of N-C bonds and the synthesis of organonitrogen products from \( \text{N}_2 \) have also been reported;\textsuperscript{37,87} this topic is explored further in Chapters two and four.
1.5 Amidophosphine Ligands for \textit{N}_2 Activation and Functionalization

The nature of the ancillary ligand contributes to the ability of a metal complex to bind dinitrogen. Often the metal is supported by ligands that have phosphorus\textsuperscript{5,88} or nitrogen donors\textsuperscript{89,90} or are cyclopentadienyl-based.\textsuperscript{91} However, some ligands are more suitable for a specific type of metal.\textsuperscript{92,93} For instance, phospine donors are well known to bind to late transition metals while amido donors are less common. The opposite is observed for early transition metals, where amido donors are extremely common and phosphine donors are quite rare. A mixed donor, multidentate ligand that is capable of coordinating to different types of metal centres would be more versatile and would likely be able to support a range of oxidation states in a given metal. Research in the Fryzuk group has employed this strategy to design effective ligands for promoting dinitrogen activation and functionalization.\textsuperscript{59,63,64,77,78,94-101} In particular, ligands containing both phosphine and amido donors have been prepared and are referred to herein as \textit{amidophosphine} ligands.

The \textit{P}_2\textit{N}_2 ligand, [PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh]^-, is a 12-membered macrocycle with two phosphine and two amido donors. The synthesis of the ligand precursor, [P_2N_2]Li_2(dioxane), is detailed in Scheme 1.5.\textsuperscript{102} One equivalent of \textit{n}-butyllithium is reacted with phenylphosphine\textsuperscript{103} to give LiPHPh, which is added to the silylamine arm, HN(SiMe_2CH_2Cl)_2, to generate HN(SiMe_2CH_2PHPh)_2. The macrocycle is closed by the reaction of HN(SiMe_2CH_2PHPh)_2 with another equivalent of the silylamine and 4 equivalents of \textit{n}-butyllithium. The lithium salt of the ligand is isolated as a 1,4-dioxane adduct. Through the judicious choice of solvent and reaction temperature, the stereochemistry at the trigonal phosphorus is controlled; Li acts as a template and directs the preferential formation of the \textit{syn}-isomer of the ligand precursor, where the phenyl groups are \textit{cis} to each other as shown in Scheme 1.5.
Chapter 1: The Role of Metal Complexes in the Activation and Functionalization of $N_2$

In general, the $P_2N_2$ ligand is transferred to a transition metal by a salt metathesis reaction with the appropriate starting material. For example, the reaction of $[P_2N_2]Li_2$(dioxane) with NbCl$_3$(DME) gives the Nb(III) complex $[P_2N_2]NbCl$ (Scheme 1.6). Reduction of this niobium complex under an atmosphere of $N_2$ generates $([P_2N_2]Nb)_2(\mu_{\cdot\cdot\cdot\cdot\cdot\cdot}-\eta^1:\eta^1-N_2)$, where the N-N bond distance of the bridging $N_2$ unit is 1.272(5) Å. Based on this N-N bond length, it might be assumed that the bridging $N_2$ unit is a diazenido ligand, $(N_2)^2-$, since it is only slightly longer than the N-N bond distance in diazobenzene (Table 1.1). As a result, the complex would consist of two Nb(III) centres. However, the EPR spectrum and magnetic susceptibility measurements indicate that both Nb centres have a formal oxidation state of 4+. Consequently, the $N_2$ unit is considered a hydrazido ligand, $(N_2)^4$.

References begin on page 23
The reactivity of \([\text{P}_2\text{N}_2]\text{Nb}_2(\eta^1:\eta^1-\text{N}_2)\) was also investigated. In an attempt to cleave the N-N bond, the complex was heated to reflux in a toluene solution; it was thought that the two electrons needed to sever the N-N single bond could be provided by the two Nb(IV) centres under suitable conditions. The N-N bond was broken, but the predicted product, a Nb complex with a terminal nitride, did not form. Instead, one of the N atoms of the former \(\text{N}_2\) unit had inserted into a \(\text{P}_2\text{N}_2\) ligand set, while the other N atom became a bridging nitride (Scheme 1.6). Overall, the thermolysis reaction resulted in the functionalization of \(\text{N}_2\); the niobium complex facilitated the formation of new N-Si and N-P bonds.
bonds from molecular nitrogen. However, the N$_2$ unit was not functionalized when ([P$_2$N$_2$]Nb)$_2$(μ-η$^1$:η$^1$-N$_2$) was reacted with H$_2$, $n$-butylsilane or phenylacetylene.

The second ligand of interest is known as NPN or [PhP(CH$_2$SiMe$_2$NPh)$_2$]$^{2-}$. The synthesis of the ligand precursor, [NPN]Li$_2$(THF)$_2$, is outlined in Scheme 1.7.$^{77,78}$ Conceptually, NPN is a tridentate variation of P$_2$N$_2$, where one of the phosphine arms has been removed from P$_2$N$_2$ to give a ligand that is also dianionic but in an acyclic configuration with relatively less steric bulk. Lithiated aniline is reacted with ClCH$_2$SiMe$_2$Cl to give ClCH$_2$SiMe$_2$NHPh. Two equivalents of the silylated aniline are then reacted with one equivalent of phenylphosphine$^{103}$ and four equivalents of $n$-butyllithium to produce the dilithium ligand precursor, which is isolated as an adduct with a tetrahydrofuran molecule coordinated to each lithium ion.

Scheme 1.7
Similar to P₂N₂, the NPN ligand is transferred onto the desired metal centre by a salt metathesis reaction. The Ta complex, [NPN]TaMe₃, is prepared in this manner (Equation 1.5). Hydrogenation of [NPN]TaMe₃ gives a bimetallic complex that is bridged by four hydride ligands (Scheme 1.8). Attempts to crystallize this complex under an N₂ atmosphere led to the discovery of a dinitrogen complex, ([NPN]Ta(µ-H))₂(µ-η¹:η²-N₂), with the uncommon side-on/end-on coordination mode for the N₂ unit. The long N-N bond distance of 1.319(4) Å, together with the spectroscopic data, is consistent for an N₂ unit that is a hydrazido moiety, (N₂)₄⁻.

In addition to the rare N₂ binding mode, this system is interesting for several reasons; 1) N₂ is activated without the need for an external reducing agent, 2) the reaction proceeds at a moderate temperature (15°C) and, most importantly, 3) the N₂ unit is susceptible to functionalization. For example, the addition of n-butylsilane to ([NPN]Ta(µ-H))₂(µ-η¹:η²-N₂) results in cleavage of the N-N bond and the formation of new N-Si bonds. The unique reactivity of this complex suggests that novel transformations for molecular nitrogen might be possible with the appropriate catalyst.
1.6 Scope of this Thesis

A better understanding of the fundamental processes that are involved in the activation and functionalization of N\textsubscript{2} would be beneficial and could potentially be used to develop new catalytic N\textsubscript{2}-fixing systems. As a small contribution to this ambitious goal, the activation of molecular nitrogen by amidophosphine complexes of zirconium and titanium
Chapter 1: The Role of Metal Complexes in the Activation and Functionalization of \( \text{N}_2 \)

was investigated and is the focus of this thesis. The ability to functionalize the activated \( \text{N}_2 \) unit within these complexes was also explored.

A zirconium dinitrogen complex with the \( \text{P}_2\text{N}_2 \) ligand set has been previously reported (Figure 1.6).\(^{96}\) The \( \text{N}_2 \) moiety in \( \text{I} \), \([\text{P}_2\text{N}_2\text{Zr}]_2(\mu-\eta^2:\eta^2-\text{N}_2)\), is reactive toward small molecules, such as \( \text{H}_2 \) and \( n \)-butylsilane. Chapter 2 details the reactivity of \( \text{I} \) with \( p \)-substituted phenylacetylenes, where a new N-C bond is formed at the bound \( \text{N}_2 \) unit of complex \( \text{I} \).

![Figure 1.6. The zirconium dinitrogen complex, \( \text{I} \), supported by the \( \text{P}_2\text{N}_2 \) ligand set.](image)

Chapter 3 investigates the reactivity of the dinitrogen complex \((\text{NPN})\text{ZrTHF})_2(\mu-\eta^2:\eta^2-\text{N}_2)\), \( \text{II} \). Although no complexes with a functionalized \( \text{N}_2 \) unit were isolated, the THF adduct was exchanged \textit{in situ} with other donor ligands, such as pyridine, to generate a new dinitrogen complex.

The synthesis and reactivity of titanium complexes, supported by NPN or \( \text{P}_2\text{N}_2 \) ligands, are presented in Chapter 4. Dinitrogen activation by these Ti complexes is notably different than that observed for the zirconium analogues; an unusual transformation was discovered for dinitrogen.

\textit{References} begin on page 23
Chapter 1: The Role of Metal Complexes in the Activation and Functionalization of $\text{N}_2$

1.7 References


Chapter 1: The Role of Metal Complexes in the Activation and Functionalization of $N_2$


Chapter 1: The Role of Metal Complexes in the Activation and Functionalization of $N_2$


Chapter 1: The Role of Metal Complexes in the Activation and Functionalization of $N_2$


References begin on page 23
Chapter 1: The Role of Metal Complexes in the Activation and Functionalization of $N_2$


References begin on page 23
References begin on page 23
Chapter 2

Reactivity of ([P₂N₂]Zr)₂(μ-η²:η²-N₂): Formation of C-N Bonds from Molecular Nitrogen and Arylalkynes

2.1 Introduction

Ammonia is the primary reagent used for the production of all organonitrogen materials.¹ An alternative route to these materials could be advantageous as it would not be dependent on the energy intensive production of ammonia. For this reason, a catalytic process that can directly use nitrogen gas for the synthesis of amines and N-containing heterocycles is a worthy goal.²⁻³ An important step in the production of such materials is the formation of carbon-nitrogen bonds, where the N-source is likely dinitrogen coordinated to a transition metal complex. Therefore, research into the reactivity of bound dinitrogen with various substrates is necessary for developing and understanding new methods for the synthesis of N-containing materials.

Numerous examples of C-N bond formation from dinitrogen complexes are known.³⁻⁴ In most cases, the resulting organonitrogen material is either the product of a well characterized dinitrogen complex⁵⁻⁸ or an ill-defined complex in a ‘one-pot’ reaction mixture.⁹⁻¹¹
Chapter 2: Formation of C-N Bonds from Molecular Nitrogen and Arylalkynes

Figure 2.1. Mo and W phosphine complexes with (a) trans-end-on or (b) cis-end-on coordinated N$_2$ ligands and (c) a depiction of the charge disparity on N$_2$ resulting from synergistic bonding.

The Mo and W complexes shown in Figure 2.1a and 2.1b are known to react with a variety of electrophilic substrates to form new N-H, N-Si and N-C bonds. An accepted explanation for this reactivity is that the terminal-N atom of an end-on coordinated N$_2$ ligand is partially negatively charged, making it susceptible to electrophilic attack. The lone pair electrons of the proximal-N atom can σ-donate to form a bond with the metal centre, while back-donation of d-electrons from the metal into the π$^*$ orbital of N$_2$, as shown in Figure 1.3, distributes electron density over both N atoms and results in a disparity of charge (Figure 2.1c). The reaction of the N$_2$ moiety within the trans-Mo/W complex, Figure 2.1a, with organic acid chlorides (RCOCl where R = Me, Et, Ph, p-MeO-C$_6$H$_4$) results in the formation of complexes with new organonitrogen ligands, rather than yielding discrete organonitrogen products. The formation of new N-C bonds from the cis-Mo/W complex, Figure 2.1b, cannot be achieved by a direct reaction of the N$_2$ moiety with organic compounds. Rather, an indirect route for the formation of N-C bonds is necessary, which first requires the protonation of coordinated N$_2$ to form a hydrazido ligand. Namely, cis-[W(N$_2$)$_2$(PMe$_2$Ph)$_4$] reacts with MeOH to form an intermediate hydrazido complex, [W(OCH$_3$)$_2$(NNH$_2$)(PMe$_2$Ph)$_3$], which reacts with ketones to form a diazoalkane complex.

References begin on page 69
Further reaction of this organonitrogen ligand with MeOH releases a hydrazone, \( R^1R^2C=NNH_2 \), that reacts with ketones to form ketazines of the general formula, \( R^1R^2C=NN=CR^2R^1 \).

![Scheme 2.1]

Similarly, the \( N_2 \) ligand of the \( trans \)-Mo/W complexes may also be converted to a hydrazido ligand with the addition of two equivalents of HBF\(_4\) (Scheme 2.1). Subsequent reaction with 2,5-dimethoxytetrahydrofuran forms a pyrrolylimido complex, which incorporates the terminal N of the original \( N_2 \) ligand. Pyrrole, N-aminopyrrole and \([MH_4(dppe)_2]\) are liberated from the cation following reduction with LiAlH\(_4\).\(^5\) Pyrrole is the major product when either metal complex is used; however, the W-based system produces a larger yield (\( \sim 80\% \)). The tetrahydride of the Mo system is recovered in higher yield than that

References begin on page 69
of the W system (~45% vs. 18%). The tetrahydride complex is converted back to the original dinitrogen complex by irradiation under an N₂ atmosphere, thus completing the proposed cycle.²²

Recent success in the synthesis of N-heterocyclic compounds has been a result of reactions where the nitrogen source is a dinitrogen complex formed in situ.⁹¹¹³⁴ The nature of the catalytic species is uncertain; however, the nitrogen source is derived from the reduction of TiCl₄ with Li in the presence of trimethylsilylchloride and N₂ gas. The resulting mixture of black products, “N₂-TiCl₄-Li-TMSCl”, may be added to a variety of ketone containing substrates to form indoles, quinolines, pyrroles, pyrrolizines and indolizines. Although these dinitrogen complexes have useful applications, details pertaining to N-N bond cleavage and C-N bond formation are unknown.

![Scheme 2.2](image)

Previous work in the Fryzuk group has shown that the N₂ ligand of ([P₂N₂]Zr₂(μ-η²:η²-N₂), 1, is highly reactive towards H₂ and "BuSiH₃ (Scheme 2.2).²⁴ One equivalent of H₂, or "BuSiH₃, is incorporated into the complex with the formation of a new N-H, or N-Si bond. A single crystal neutron diffraction study of 2 supports the spectroscopic evidence for
a bridging hydride. Solution NMR spectroscopy and single crystal X-ray analysis of 3 shows that this complex is similar to 2. The formation and isolation of 2 is remarkable considering N₂ ligands are known to be easily displaced by hydrogen. Density functional studies of 2 have shown that the addition of a second H₂ molecule should be feasible.

The reaction of 1 with phenylacetylene generates 4 (Equation 2.1). Complex 4 is unusual in that two molecules of PhCCH have been incorporated into the original dinitrogen complex, 1. This is unlike complexes 2 and 3, which possess only one equivalent of H₂ or nBuSiH₃, respectively. Also, an acetylide bridges the two Zr centres in 4, rather than a hydride. The proton of this bridging acetylide is presumably transferred to another PhCCH molecule to form the alkenylhydrazido bridging moiety. The reaction between strong electrophiles and N₂ complexes is known to produce N-C bonds. In contrast, alkynes are relatively weak electrophiles and, thus, this represents a completely new kind of transformation. Also, an example of C-N bond formation that originates from a side-on bound and bridging N₂ ligand is rare and worthy of further study.

The reactivity of ([P₂N₂]Zr)₂(μ-η²:η²-N₂), 1, with various terminal alkynes and saturated molecules is the focus of this chapter. In particular, new Zr-alkenylhydrazido complexes that are analogous to 4 have been prepared and characterized. Further, a possible mechanism for the synthesis of these new complexes was investigated.
2.2 Modified Synthesis of ([P₂N₂]Zr)₂(μ-η²:η²-N₂), 1

Since the synthesis of 1 was first reported,²⁴ various attempts have been made to improve the purity and yield of this complex. Originally, 1 was synthesized by the addition of toluene to a 1:2 mixture of [P₂N₂]ZrCl₂ and KC₈ under one (or four) atmosphere of N₂ at room temperature. The reaction is instantaneous, as suggested by the immediate formation of a blue-green solution that is characteristic for the presence of complex 1. However, additional resonances in the ³¹P{'H} NMR spectrum of the crude reaction mixture indicate that other products are formed under these reducing conditions as shown in Equation 2.2.

Subsequently, two of the minor products, 5 and 6, were identified, synthesized independently and characterized by NMR spectroscopy and X-ray crystallography.³⁰,³¹ Complexes 5 and 6 are believed to be side-products resulting from reactions of an intermediate Zr(II) species, which is formed initially from the reduction of the Zr(IV) starting material by KC₈. The Zr(II) species appears to reduce, or activate, one of the P-phenyl groups of another [P₂N₂]Zr fragment or attack the phenyl group of solvent toluene to produce complexes 5 and 6, respectively. Under a nitrogen atmosphere, the amount of 5 formed is small (~5%). However, 5 can be isolated in good yield when the reduction is carried out under static vacuum or under an argon atmosphere.

\[
[P₂N₂]ZrCl₂ + KC₈ \xrightarrow{N₂ \text{toluene}} 1 + 5 + 6
\]

References begin on page 69
Chapter 2: Formation of C-N Bonds from Molecular Nitrogen and Arylalkynes

Complex 6 also forms under dinitrogen-free conditions (5-15% yield)\(^\text{30}\) or may be prepared in moderate yield (58%) from the exposure of a toluene/THF solution of ZrMe\(_2\)[P\(_2\)N\(_2\)] to H\(_2\) gas.\(^\text{31}\) The formation of 6 can clearly be avoided by using an alternative solvent to toluene for the reduction of [P\(_2\)N\(_2\)]ZrCl\(_2\).

Other impurities are also associated with the synthesis of 1. Even small amounts of moisture can promote the decomposition of 1 to varying degrees. Occasionally, trace amounts of 7 are detected in the synthesis of 1, which is probably due to the introduction of adventitious water during the workup. When 1 is exposed to one equivalent of H\(_2\)O, the Zr-oxo complex 7 is formed as shown in Equation 2.3; complex 7 has been isolated and characterized by NMR spectroscopy and X-ray crystallography.\(^\text{31}\) When excess H\(_2\)O is added to 1, only the protonated ligand, [P\(_2\)N\(_2\)]H\(_2\), can be detected spectroscopically. These two major decomposition products can readily be identified by singlets at \(\delta -12.5\) and \(-36.8\) in the \(^{31}\)P\{\(^1\)H\} NMR spectrum and correspond to 7 and [P\(_2\)N\(_2\)]H\(_2\), respectively.

Attempts to isolate 1 from a crude reaction mixture that consists of 5, 6, 7 and [P\(_2\)N\(_2\)]H\(_2\), are complicated by the similar solubilities of the desired product and the impurities. Complex 1 is sufficiently soluble in a mixture of hexanes/toluene that it may be separated by extraction from 5, which is sparingly soluble in both solvents. However, 7 and [P\(_2\)N\(_2\)]H\(_2\) are also removed, along with 1, by the extraction process. A hexane rinse of the
crude blue-green powder removes $[\text{P}_2\text{N}_2]\text{H}_2$ from complex 1. However, a significant amount of 7 remains in both the washed product and the discarded filtrate, based on $^{31}\text{P}\{^{1}\text{H}\}$ NMR spectroscopy. A portion of 1 is also sacrificed with each washing. Also, recrystallization of 1 from the slow evaporation of a toluene solution is tedious and is an unreliable means of purification. To offset these problems, an alternative method for preparing complex 1 in higher yield and purity was sought.

An improvement in the synthesis of 1 was achieved by changing the solvent to THF and initiating the reduction reaction at a low temperature. Conditions that promote the reaction of the reduced Zr species with $\text{N}_2$, and hinder the side-reaction that produces 5, are vital for the preparation of 1. This is achieved by transferring the solvent to a cold mixture of $[\text{P}_2\text{N}_2]\text{ZrCl}_2$ and $\text{KC}_8$, in vacuo, such that the solvent freezes immediately and, as a result, no side-reactions occur. Dinitrogen is then introduced as the frozen mixture thaws. Maintaining a cold temperature ($\sim-78^\circ\text{C}$) for several hours, while the solution is stirred vigorously, gives the highest yield and purity of 1: 95% with no evidence of 5, 6 or 7. Tetrahydrofuran was found to be more effective than toluene or cyclohexane as a solvent.

The study of nitrogen fixation is often motivated by the desire to develop new catalytic processes that use atmospheric nitrogen, an abundant feedstock. However, dinitrogen complexes have also been prepared by using N sources other than molecular nitrogen, such as hydrazine. For example, the addition of TMS-substituted hydrazine to $\text{NbCl}_5$ in THF/$\text{CH}_2\text{Cl}_2$ forms $\{[\text{NbCl}_3(\text{THF})_2]_2(\mu-\text{N}_2)\}$, without the need for additional reducing agents (Equation 2.4). Also, a dilithiated hydrazine can be isolated by the reaction of a bis(silyl)hydrazine with two equivalents of $^8\text{BuLi}$ (Equation 2.5).

$$\text{NbCl}_5 + (\text{Me}_3\text{Si})_2\text{NN}(\text{SiMe}_3)_2 \xrightarrow{\text{THF/CH}_2\text{Cl}_2} \{\text{NbCl}_3(\text{THF})_2\}_2(\mu-\text{N}_2) \quad [2.4]$$

$$\{(\text{Bu}_2\text{MeSi})\text{NHNH(SiMe}_4\text{Bu}_2)\} + 2^8\text{BuLi} \xrightarrow{\text{THF}} \text{Me}^8\text{Bu}_2\text{Si} \quad [2.5]$$
Chapter 2: Formation of C-N Bonds from Molecular Nitrogen and Arylalkynes

With this chemistry in mind, the metathesis reaction of N,N'-dilithium hydrazine with \([P_2N_2]ZrCl_2\) was thought to be an alternative pathway for the formation of 1. Two approaches were taken: \(^{t}BuLi\) was added to a cold solution of hydrazine followed by the addition of \([P_2N_2]ZrCl_2\), or \(^{t}BuLi\) was added to a cold solution containing both \(N_2H_4\) and \([P_2N_2]ZrCl_2\). In the former case, a yellow residue was isolated and \(^{31}P\{^1H\}\) NMR analysis of the crude reaction mixture showed multiple resonances, including the signal attributed to \([P_2N_2]H_2\). Green residues were isolated using the second approach and multiple resonances, including those associated with \([P_2N_2]H_2\) and \([P_2N_2]Li_2(THF)\), were observed in the \(^{31}P\{^1H\}\) NMR spectrum. None of the attempted reactions formed complex 1 (Equation 2.6) and, as a result, this approach was not pursued further.

\[
2 [P_2N_2]ZrCl_2 + N_2H_4 \xrightarrow{^{t}BuLi, THF} 4 \text{ product}
\]

2.3 Synthesis and Characterization of \(((P_2N_2)Zr)_2(\mu-\eta^2:\eta^2-N_2CH=CHR)(\mu-C\equiv CR), \text{ where } R= (p-Me-C_6H_4), 8; (p-tBu-C_6H_4), 9\)

As shown in Equation 2.1, the reaction of phenylacetylene with 1 results in the formation of 4. In an effort to expand on this new carbon-nitrogen bond forming process, we examined the reactivity of a range of terminal alkynes with 1. When approximately two equivalents of \((p\text{-methyl})\text{phenylacetylene or } (p\text{-tert-butyl})\text{phenylacetylene are added to a toluene solution of } ((P_2N_2)Zr)_2(\mu-\eta^2:\eta^2-N_2), 1, a gradual colour change is observed over the
course of a week. The dark blue-green solution of complex 1 fades to a clear orange solution that yields an orange powder when the solvent is removed. The orange powder typically contains 8 (or complex 9) and some unidentified impurities. Purification of the product by recrystallization was unsuccessful due to the poor solubility of the powder in various solvents (e.g., toluene, benzene, THF, hexanes). Multiple attempts to remove the impurities by washing the product with various solvent combinations were also unproductive. However, crystals of 8 (or complex 9) can be isolated reproducibly in situ by the slow evaporation of the original toluene solution at room temperature. Crystals of 9, suitable for single crystal X-ray diffraction, were grown in this manner. Crystals of 8, suitable for single crystal X-ray diffraction, were isolated by first concentrating the orange solution to a brown oil, adding hexanes and then allowing this mixed-solvent solution to evaporate at room temperature.

(i) Molecular Structure of Complexes 8 and 9 from Single Crystal X-ray Diffraction

The molecular structures of 4, 8 and 9 were determined by X-ray diffraction and may be considered analogous. ORTEP representations of complexes 8 and 9 are shown in Figures 2.2 and 2.3, respectively. Tables 2.1 and 2.2 list selected bond lengths and angles for complexes 8 and 9, respectively. Crystallographic data of complex 4 has been reported elsewhere.29

The resulting compounds from these phenylacetylene reactions are highly unsymmetrical in the solid state. In complex 1, the phosphorus atoms of P$_2$N$_2$, both zirconium atoms and the bridging N$_2$ moiety are located in the same plane of symmetry.24 In complexes 4, 8 and 9 this planarity does not exist: the functionalized N$_2$ moiety bridges the two zirconium centres in a bent or hinged geometry and the phosphorus atoms of the P$_2$N$_2$ ligands no longer share the same plane of symmetry.
Chapter 2: Formation of C-N Bonds from Molecular Nitrogen and Arylalkynes

Figure 2.2. ORTEP representation (ellipsoid probability 50%) of the molecular structure of ([P2N2]Zr)2(μ-η2:N2CH=CH(p-Me-C6H4))(μ-C≡C(p-Me-C6H4)), 8, as determined by single crystal X-ray diffraction. Hydrogen atoms and silylmethyl groups are omitted for clarity and only ipso carbons of the P2N2 ligand phenyl rings are shown.

The bridging acetylide has a C≡C bond length of 1.202(6) Å and 1.223(5) Å in 8 and 9, respectively, which is common for the carbon-carbon triple bond of a coordinated alkynyl unit. In addition, the C49-C50-C51 angle in 8 (and C49-C50-C51 angle in 9) is nearly linear, and essentially unchanged from the original alkyne.
Table 2.1. Selected Bond Lengths and Angles in \((\{\text{P}_2\text{N}_2\}\text{Zr}_2(\mu-\eta^2:\eta^2-\text{N}_2\text{CH}==\text{CH}(\text{p-Me-C}_6\text{H}_4))\)(\mu-C==C(p-Me-C_6H_4)), 8

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atom</th>
<th>Distance (Å)</th>
<th>Atom</th>
<th>Atom</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(6)</td>
<td>N(5)</td>
<td>1.457(4)</td>
<td>Zr(1)</td>
<td>N(6)</td>
<td>2.197(3)</td>
</tr>
<tr>
<td>N(6)</td>
<td>C(58)</td>
<td>1.419(5)</td>
<td>Zr(1)</td>
<td>N(5)</td>
<td>2.094(3)</td>
</tr>
<tr>
<td>C(58)</td>
<td>C(59)</td>
<td>1.330(6)</td>
<td>Zr(2)</td>
<td>P(3)</td>
<td>2.732(1)</td>
</tr>
<tr>
<td>C(49)</td>
<td>C(50)</td>
<td>1.202(6)</td>
<td>Zr(2)</td>
<td>P(4)</td>
<td>2.767(1)</td>
</tr>
<tr>
<td>Zr(2)</td>
<td>C(49)</td>
<td>2.445(4)</td>
<td>Zr(2)</td>
<td>N(4)</td>
<td>2.176(3)</td>
</tr>
<tr>
<td>Zr(1)</td>
<td>C(49)</td>
<td>2.463(4)</td>
<td>Zr(2)</td>
<td>N(3)</td>
<td>2.306(3)</td>
</tr>
<tr>
<td>Zr(2)</td>
<td>N(6)</td>
<td>2.142(3)</td>
<td>Zr(1)</td>
<td>P(2)</td>
<td>2.756(1)</td>
</tr>
<tr>
<td>Zr(2)</td>
<td>N(5)</td>
<td>2.163(3)</td>
<td>Zr(1)</td>
<td>P(1)</td>
<td>2.785(1)</td>
</tr>
<tr>
<td>Zr(1)</td>
<td>N(1)</td>
<td>2.205(3)</td>
<td>Zr(1)</td>
<td>N(2)</td>
<td>2.306(4)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atom</th>
<th>Atom</th>
<th>Angle (°)</th>
<th>Atom</th>
<th>Atom</th>
<th>Atom</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)</td>
<td>Zr(1)</td>
<td>N(2)</td>
<td>91.8(1)</td>
<td>Zr(1)</td>
<td>N(6)</td>
<td>Zr(2)</td>
<td>103.35(1)</td>
</tr>
<tr>
<td>N(3)</td>
<td>Zr(2)</td>
<td>N(4)</td>
<td>95.7(1)</td>
<td>Zr(1)</td>
<td>N(5)</td>
<td>Zr(2)</td>
<td>106.2(1)</td>
</tr>
<tr>
<td>P(3)</td>
<td>Zr(2)</td>
<td>P(4)</td>
<td>145.22(4)</td>
<td>N(6)</td>
<td>C(58)</td>
<td>C(59)</td>
<td>126.2(4)</td>
</tr>
<tr>
<td>P(1)</td>
<td>Zr(1)</td>
<td>P(2)</td>
<td>154.52(4)</td>
<td>C(58)</td>
<td>C(59)</td>
<td>C(60)</td>
<td>126.2(5)</td>
</tr>
<tr>
<td>Zr(1)</td>
<td>C(49)</td>
<td>Zr(2)</td>
<td>87.8(2)</td>
<td>C(49)</td>
<td>C(50)</td>
<td>C(51)</td>
<td>177.7(5)</td>
</tr>
</tbody>
</table>

The C58-C59 distance in 8 (1.330(6) Å) and the C61-C62 distance in 9 (1.327(5) Å) are significantly longer than the C≡C bond length of the bridging acetylide, or even free acetylene. Further, the bond angle C58-C59-C60 in 8 is not linear, 126.2(5)°, and is slightly smaller than the same angle in 9, where C61-C62-C63 is 128.2(4)°. The geometry of these carbons does not reflect the sp-character of the carbon atoms in the original alkyne. Instead, they appear to be sp^2 hybridized and possess the geometry of an alkene with trans-disposed substituents. These bond lengths and angles are consistent with those for an alkenylhydrazido moiety.
Figure 2.3. ORTEP representation (ellipsoid probability 50%) of the molecular structure of 
\([\text{P}_2\text{N}_2]\text{Zr}_2(\mu-\eta^2:\eta^2\text{-N}_2\text{CH}=\text{CH}(p^{-1}\text{Bu-C}_6\text{H}_4))(\mu-\text{C}=\text{C}(p^{-1}\text{Bu-C}_6\text{H}_4)), \ 9, \text{ as determined by single crystal X-ray diffraction. Hydrogen atoms and silylmethyl groups are omitted for clarity and only ipso carbons of the P}_2\text{N}_2 \text{ligand phenyl rings are shown.}

The N-N bond distance of the bridging moiety (1.457(4) Å in 8 and 1.454(4) Å in 9) is only slightly lengthened from that of 1, where the distance is 1.43(1) Å.\textsuperscript{24} The distances about each Zr centre to the donors of the P\textsubscript{2}N\textsubscript{2} ligand remain essentially unchanged in 8 and 9, in relation to those of complex 1. The P atoms within each ligand set are positioned opposite of each other, with P-Zr-P angles of 145.22(4)\textdegree \text{ and 154.52(4)\textdegree for 8 (145.71(3)\textdegree and 152.52(3)\textdegree for 9). These are slightly larger than the P-Zr-P angle of 140.90(7)\textdegree found for 1. However, the Zr-Zr internuclear distance for 8 and 9 is shorter, with an average value of 3.41 Å, than that for 1 (3.75 Å Zr-Zr separation).}
Table 2.2. Selected Bond Lengths and Angles in ([P₂N₂]Zr₂(μ-η²:η²-N₂CH=CH(p⁻¹Bu-C₆H₄))(μ-C=CC(p⁻¹Bu-C₆H₄)), 9

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atom</th>
<th>Distance (Å)</th>
<th>Atom</th>
<th>Atom</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(6)</td>
<td>N(5)</td>
<td>1.454(4)</td>
<td>Zr(1)</td>
<td>N(6)</td>
<td>2.206(3)</td>
</tr>
<tr>
<td>N(6)</td>
<td>C(61)</td>
<td>1.416(4)</td>
<td>Zr(1)</td>
<td>N(5)</td>
<td>2.076(3)</td>
</tr>
<tr>
<td>C(61)</td>
<td>C(62)</td>
<td>1.327(5)</td>
<td>Zr(2)</td>
<td>P(3)</td>
<td>2.7361(11)</td>
</tr>
<tr>
<td>C(49)</td>
<td>C(50)</td>
<td>1.223(5)</td>
<td>Zr(2)</td>
<td>P(4)</td>
<td>2.7559(10)</td>
</tr>
<tr>
<td>Zr(2)</td>
<td>C(49)</td>
<td>2.446(4)</td>
<td>Zr(2)</td>
<td>N(4)</td>
<td>2.188(3)</td>
</tr>
<tr>
<td>Zr(1)</td>
<td>C(49)</td>
<td>2.473(3)</td>
<td>Zr(2)</td>
<td>N(3)</td>
<td>2.303(3)</td>
</tr>
<tr>
<td>Zr(2)</td>
<td>N(6)</td>
<td>2.161(3)</td>
<td>Zr(1)</td>
<td>P(1)</td>
<td>2.7693(10)</td>
</tr>
<tr>
<td>Zr(2)</td>
<td>N(5)</td>
<td>2.144(3)</td>
<td>Zr(1)</td>
<td>P(2)</td>
<td>2.7780(9)</td>
</tr>
<tr>
<td>Zr(1)</td>
<td>N(2)</td>
<td>2.214(3)</td>
<td>Zr(1)</td>
<td>N(1)</td>
<td>2.296(3)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atom</th>
<th>Atom</th>
<th>Angle (°)</th>
<th>Atom</th>
<th>Atom</th>
<th>Atom</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(2)</td>
<td>Zr(1)</td>
<td>N(1)</td>
<td>92.03(10)</td>
<td>Zr(1)</td>
<td>N(6)</td>
<td>Zr(2)</td>
<td>102.56(12)</td>
</tr>
<tr>
<td>N(3)</td>
<td>Zr(2)</td>
<td>N(4)</td>
<td>95.22(11)</td>
<td>Zr(1)</td>
<td>N(5)</td>
<td>Zr(2)</td>
<td>107.68(12)</td>
</tr>
<tr>
<td>P(3)</td>
<td>Zr(2)</td>
<td>P(4)</td>
<td>145.71(3)</td>
<td>N(6)</td>
<td>C(61)</td>
<td>C(62)</td>
<td>124.6(3)</td>
</tr>
<tr>
<td>P(2)</td>
<td>Zr(1)</td>
<td>P(1)</td>
<td>152.52(3)</td>
<td>C(61)</td>
<td>C(62)</td>
<td>C(63)</td>
<td>128.2(4)</td>
</tr>
<tr>
<td>Zr(1)</td>
<td>C(49)</td>
<td>Zr(2)</td>
<td>87.69(12)</td>
<td>C(49)</td>
<td>C(50)</td>
<td>C(51)</td>
<td>178.2(4)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atom</th>
<th>Atom</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(2)</td>
<td>Zr(1)</td>
<td>Zr(2)</td>
<td>-18.41(3)</td>
</tr>
<tr>
<td>P(1)</td>
<td>Zr(1)</td>
<td>Zr(2)</td>
<td>-18.68(4)</td>
</tr>
</tbody>
</table>
Chapter 2: Formation of C-N Bonds from Molecular Nitrogen and Arylalkynes

The alkynyl and alkenylhydrazido moieties that bridge the \([P_2N_2]Zr\) ends of the molecule impose the asymmetry seen in the complex. In the solid state, 4, 8 and 9 can be assigned to the \(C_1\) point group. This is clearly observed by considering the dihedral angles between phosphorus atoms of one \(P_2N_2\) ligand with respect to those of the other ligand. Figure 2.4 is an alternative view of the solid state molecular structure of complex 8. By viewing the molecule along an imaginary axis that connects the two \(Zr\) centres, and removing all extraneous atoms, the diastereotopic nature of the ligand phosphorus groups is apparent.\(^{40}\)

![Figure 2.4](image)

**Figure 2.4.** Alternative ORTEP representation (ellipsoid probability 50%) of the molecular structure of \(((P_2N_2)Zr)_2(\mu-\eta^2:\eta^2-N_2CH=CH(p-MeC_6H_4))(\mu-C=C(p-MeC_6H_4)), \ 8,\) when viewed along the \(Zr-Zr\) axis. All the \(P_2N_2\) ligand atoms, except for phosphorus, have been excluded for clarity. The visible \(Zr\) atom eclipses the other.

(ii) Solution Characterization of Complexes 8 and 9 by NMR Spectroscopy

At room temperature, one broad resonance accounts for all four phosphorus nuclei in the \(^{31}P\)\(^{1H}\) NMR spectra for each of the alkynyl complexes 4, 8 and 9. This suggests that the molecule is fluxional at room temperature on the NMR time scale. The resonance appears to be a very broad singlet, centred at \(\delta - 14.4\) with \(\Delta w_{1/2}\) (peak width at half height) = 14.9 Hz for

References begin on page 69
Chapter 2: Formation of C-N Bonds from Molecular Nitrogen and Arylalkynes

8 (δ -14.3 and Δν/Δν = 14.3 Hz for 9). However, this resonance is likely due to overlapping multiplets, for reasons that will be discussed in part (iii) of this section.

The 1H NMR at 300 K is complicated; however, some key features of the molecule can be identified. At least eight silylmethyl environments are evident as overlapping singlets for 8. Two sharp, distinct singlets corresponding to the tolylmethyl groups of the bridging alkyne and the alkenylhydrazido group appear at δ 1.97 and δ 2.14. The aromatic region is cluttered by overlapping multiplets, but a doublet at δ 6.34 can be assigned to one of the two trans-hydrogens of the alkenylhydrazido moiety (3JHH = 14.0 Hz). The spectrum for complex 9 is similar, but with fewer distinct silylmethyl resonances. The t-Bu groups appear as two different singlets at δ 1.09 and δ 1.26. One of the alkenylhydrazido protons appears as a doublet at δ 6.35 with a 3JHH of 13.9 Hz and supports the existence of a trans geometry across the carbon-carbon double bond.

As the temperature is lowered, the broad resonance observed in the 31P{1H} NMR spectra of these complexes sharpens to eight peaks that correspond to four unique phosphorus environments. Figure 2.5 depicts the NMR spectra for 8, but is representative of the spectra observed for 4 and 9, as well. The symmetry of the molecule in solution, as it is observed in the low temperature NMR spectrum at 240 K, is believed to approximate the geometry that the complex adopts in the solid state. Each phosphorus atom couples to the other phosphorus within the same ligand set, which results in four doublets. The coupling constants (2JPP = 66.8 Hz, 74.3 Hz for 8 and 2JPP = 65.6 Hz, 74.1 Hz for 9) are consistent with values observed for the phosphine groups of the P2N2 ligand in other complexes, such as 5. In particular, the P-Zr-P angle in complex 5 is 144.24(3)° and a JPP of 99 Hz is observed.30

References begin on page 69
Chapter 2: Formation of C-N Bonds from Molecular Nitrogen and Arylalkynes

Figure 2.5. $^{31}P\{^1H\}$ NMR (121 MHz) spectra of complex 8 at room temperature and low temperature: A and A', or B and B', are pairs of doublets corresponding to phosphorus nuclei within the same $P_2N_2$ ligand set, which are coupling to each other. A coupling constant of 74.3 Hz is observed for A and A' ($^2J_{PP} = 66.8$ Hz for B and B'). Small signals in the spectra are attributed to the presence of unidentified impurities in the sample.

The low temperature $^1H$ NMR spectra further supports the low symmetry of these complexes in solution. Almost all sixteen silylmethyl groups are observed as distinct singlets for both 8 and 9. Both of the trans-disposed protons on the alkenylhydrazido group (NCHCHR) are observed as doublets at $\delta$ 6.42 and 7.77, with a $^3J_{HH}$ of 14.0 Hz, for 8.
(δ 6.46 and δ 7.84, with $^{3}J_{HH}$ of 13.9 Hz, for 9) and are not masked by neighbouring phenyl proton peaks, as is the case for spectra obtained at room temperature.

(iii) Proposed Mechanism for Fluxional Behaviour

The flexible nature of the P$_2$N$_2$ ligand in solution has been observed in other early transition metal complexes. Namely, the singlet in the $^{31}$P-$^1$H NMR spectrum for [P$_2$N$_2$]TaMe$_3$ broadens and decoalesces into two doublets as the temperature is lowered. The broad singlet is a result of the exchange between the two phosphorus environments.$^{41,42}$ The mechanism for this fluxional behaviour is rationalized as the simultaneous pivoting of the phosphines and a ‘turnstile’ rotation of the three methyl groups, Scheme 2.3.

Scheme 2.3

The asymmetrical bridging centre of complexes 4, 8 and 9 is unlikely to rotate or shift considerably without requiring bonds to break and then re-form. Instead, the phosphine groups of the ligand could exchange environments by a simple ‘rocking’ motion of the ligand, which is tethered to each Zr centre by N- and P-donor atoms. Scheme 2.4 shows the proposed exchange mechanism from a perspective along the Zr-Zr axis of complex 8; the R group represents the styryl fragment, the bridging acetylide has been omitted and only the P atoms of P$_2$N$_2$ are shown for clarity. This illustration is modeled after the orientation of the phosphorus atoms in Figure 2.4, where the molecule has C$_1$ symmetry.
Chapter 2: Formation of C-N Bonds from Molecular Nitrogen and Arylalkynes

Scheme 2.4

The proposed motion would exchange the environment of P4 with that of P2 and, likewise, the P1 environment with that of P3. When the phosphines are eclipsed (P4 over P2; P3 over P1), there are two enantiotopic environments for phosphorus; a mirror plane bisects the Zr-Zr axis and the molecule has $C_5$ symmetry. It is unlikely that all four phosphorus nuclei would ever be equivalent because the interaction of the phosphorus-phenyl groups of $P_2N_2$ with the bulky bridging groups is expected to impede the full rotation of the ligand. For this reason, the broad ‘singlet’ observed at room temperature does not represent an equilibration of all phosphorus nuclei, but may result from overlapping broad doublets. Further, at higher temperatures (350 K for complex 8) this broad singlet begins to sharpen and take the shape of one doublet ($^2J_{pp} = 68.7$ Hz). This further supports the likelihood of at least two phosphorus environments at all temperatures.

2.4 Proposed Mechanism for the Formation of Complexes 4, 8 and 9

Complexes 4, 8 and 9 are a result of the reaction between $([P_2N_2]Zr)_2(\mu-$η$^2$:η$^2$-N$_2$), 1, and a terminal arylalkyne. Each of these complexes, 4, 8 and 9, are structurally similar and display the same fluxional behaviour in solution, as observed by NMR spectroscopy. This suggests that the $p$-substituent of phenylacetylene, whether it is H, methyl or tert-butyl, does not significantly affect the outcome of the reaction between these arylalkynes and 1. So, it is reasonable to assume that each of these complexes is formed by a common pathway or
mechanism. In an effort to study the mechanism, the simplest arylalkyne, PhCCH, was used to probe this reaction and the resulting data may be generalized to include analogous reactions involving the other two arylalkynes, (p-methyl)phenylacetylene and (p-tert-buty1)phenylacetylene. For the following discussion, the alkynyl carbon atoms of phenylacetylene are identified in relation to the terminal hydrogen of the molecule: Cα is bonded to H and Cβ is bonded to Ph. Two possible mechanistic pathways are proposed for this reaction.

The first pathway, shown in Scheme 2.5, proceeds through an intermediate that somewhat resembles complexes 2 and 3 (Scheme 2.2). The formation of complexes 4, 8 or 9 is unique in that two equivalents of the alkyne are required for the reaction with 1. This result is not entirely unexpected since a theoretical study suggests that an additional molecule of H₂ should react with 2 under appropriate conditions. In effect, 2 may be considered an intermediate in the activation of two molecules of hydrogen by 1. Further, there is evidence that the addition of an alkyne to a dinitrogen complex can result in the formation of N-H bonds: 

\[
[(\eta^5-C_5Me_4H)_2Zr]_2(\mu-\eta^2:\eta^2-N_2) \text{ reacts with terminal alkynes to generate the acetylide zirconocene complex, } [(\eta^5-C_5Me_4H)_2Zr(C=CR)]_2(\mu-\eta^2:\eta^2-N_2H_2) \text{ (where R = } ^{n}Bu, ^{t}Bu, Ph).]
\]
Chapter 2: Formation of C-N Bonds from Molecular Nitrogen and Arylalkynes

Scheme 2.5

The first step in Scheme 2.5 requires a concomitant scission of the Cα-Hα bond of phenylacetylene and the formation of a new N-Hα bond with the N₂ moiety of complex 1. The resulting acetylide becomes a bridging ligand, μ-C₆H₅Ph, between the two Zr centres to form an intermediate complex. The addition of N-Hα across the carbon-carbon triple bond of the second equivalent of phenylacetylene, PhC=CHb, in an anti-Markovnikov fashion produces complex 4.
The second proposed pathway is modeled after the mechanism for the intermolecular hydroamination of alkynes with Zr- or Ti-imido catalysts (Scheme 2.6). The first step involves the cycloaddition of phenylacetylene to Zr-N of complex 1, which results in the formation of an intermediate azazirconacyclobutene complex. The alkyne, PhCCH\(_a\), is added across the Zr-N bond such that C\(_\beta\) coordinates to the metal. This orientation is necessary to produce the resulting E stereochemistry across the C=C bond in the product, complex 4. An additional equivalent of phenylacetylene serves to cleave the Zr-C\(_\beta\) bond by protonation and upon rearrangement results in the formation of the bridging alkynyl unit, $\mu$-C\(_{a}$C\(_{\beta}\)Ph, and alkenylhydrazido unit, $\mu$-$\eta^2$:$\eta^2$-NN(H\(_a\)C=CPhH\(_b\)), of complex 4.
Both reaction pathways require the formation of intermediate complexes to effect the formation of 4. The reaction of 1 with PhCCH produces a significant amount of side-products, which is reflected in the moderate yield of 4 (and that of complexes 8 and 9 from their respective alkynes). This is probably an indication of competing reactions between 1, phenylacetylene and possibly the intermediate complexes. For instance, the oligomerization of phenylacetylene in the presence of transition metal catalysts is well documented. In an effort to observe these intermediates and minimize side reactions, 1 was reacted with only one equivalent of phenylacetylene, PhCCH. The green colour of the residue isolated from this reaction is indicative of unreacted starting material, 1. The $^{31}\text{P}^{(1\text{H})}$ NMR spectrum of this residue confirms the presence of 1 and the desired product 4. However, the resonance for complex 4 is broad at room temperature and partially obscures additional smaller peaks in the same region ($\delta_p -14.3$). Two of the additional peaks are a result of the decomposition of 1: complex 7 and the protonated ligand $[\text{P}_2\text{N}_2]\text{H}_2$. The identification of the other peaks, and possibly the intermediates in the formation of 4, was not further pursued.

The main difference between the two proposed reaction pathways is whether the first equivalent of PhCCH added to 1 ultimately generates the bridging alkynyl unit (Scheme 2.5) or the alkenylhydrazido unit (Scheme 2.6) of complex 4. Both steps in the first pathway, as presented in Scheme 2.5, require the formation and cleavage of N-H and C-H bonds. However, the second pathway requires only one step where C-H bonds are broken and formed (Scheme 2.6). If the first pathway is operative, evidence for a primary kinetic isotope effect is expected regardless of whether the first or second step is rate-determining. The second process will only show a primary kinetic isotope effect if the second step is rate-determining.

Although this system is not ideal for kinetic analysis, 4 is presumed to be the primary product resulting from the reaction between complex 1 and PhCCH. In an effort to observe a primary kinetic isotope effect, the depletion of 1 was monitored by $^{31}\text{P}^{(1\text{H})}$ NMR spectroscopy following the addition of PhCCH, and again with PhCCD. The disappearance of 1 is not significantly slower in the presence of PhCCD, as would be expected for a primary kinetic isotope effect. Namely, the results are identical within experimental error and indicate
a $k_{H}/k_{D}$ of 1.0. Consequently, the rate-determining step for the formation of complex 4 does not involve the formation or cleavage of C-H or N-H bonds.

Based on this information, the pathway presented in Scheme 2.5 is improbable. In turn, the pathway proposed in Scheme 2.6 is consistent with the experimental data where the first step, formation of the azazirconacyclobutene intermediate, would represent the rate-determining step. However, there is insufficient evidence to accurately determine the true nature of the intermediate or rate-determining step.

2.5 Reactivity of Complexes 8 and 9: Attempted Liberation of an Organonitrogen Product

As discussed previously, the motivation for preparing and studying dinitrogen complexes is so that new processes may ultimately be developed in which dinitrogen is used directly as the feedstock for the synthesis of nitrogenous products. The activation of N$_2$, or reduction of the nitrogen-nitrogen triple bond, by a transition metal complex is commonly viewed as the preliminary step toward achieving this goal. Subsequent steps would involve the incorporation of the activated dinitrogen ligand into other molecules, like organic substrates, to generate organonitrogen ligands. Under appropriate conditions, such a complex could potentially liberate the organonitrogen product, which would ideally be followed by the regeneration of the original complex to complete the nitrogen fixation cycle. However, the strong reducing conditions required to synthesize 1, coupled with the propensity for side reactions to occur, precludes the possibility of developing a catalytic process in which dinitrogen and organic molecules can be converted to organonitrogen products in a ‘one-pot’ reaction mixture. In particular, 1 likely cannot be regenerated by simply liberating the alkenylhydrazido moiety of complexes 4, 8 or 9 and introducing more N$_2$ gas. Even so, a stoichiometric reaction in which a dinitrogen feedstock is used to produce valuable N-containing compounds is still worthy of further investigation.

Complexes 8 and 9 were reacted with hydrogen and a proton source, respectively, to determine whether the alkenylhydrazido moiety could be released from each complex as an organonitrogen product. The reactivity of 4 was not studied due to the limited solubility of
this compound in organic solvents. Hydrogenation and scission of the N-N bond of the alkenylhydrazido moiety in complexes 8 or 9 is expected to result in a mixture of products including an enamine, imine, and ammonia.\(^{56}\) Alternatively, a hydrazone product\(^{57}\) would result if the hydrogenation did not promote N-N bond cleavage. A selection of the products anticipated from the release of the alkenylhydrazido moiety from complexes 8 or 9 is presented in Scheme 2.7.

\[
\begin{align*}
\text{Zr} & \quad \text{Zr} \\
\text{[P}_2\text{N}_2\text{]} & \quad \text{[P}_2\text{N}_2\text{]} \\
\text{H} & \quad \text{H} \\
\text{R} & \quad \text{R} \\
\text{C} & \quad \text{C} \\
\text{=} & \quad \text{=} \\
\text{C} & \quad \text{C} \\
\text{=} & \quad \text{=} \\
\text{H} & \quad \text{H} \\
\text{N} & \quad \text{N} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{E-enamine product} & \quad \text{aldimine product} \\
\end{align*}
\]

Scheme 2.7

The Z-enamine product could conceivably be formed by tautomerization of the imine, or aldimine, product. However, theoretical calculations indicate that the E-isomer for 2-aminostyrene (i.e., R = Ph) is sterically more favourable than the Z-enamine isomer.\(^{58}\) Moreover, the corresponding aldimine tautomer is lower in energy than either enamine isomer.\(^{58}\) Further, the hydrogenation of this aldimine could result in the formation of a primary amine.\(^{56}\) Similar results are expected for an enamine/imine tautomeric equilibrium where the R group is (p-methyl)phenyl or (p-tert-butyl)phenyl.

References begin on page 69
Unfortunately, none of the products presented in Scheme 2.7 were observed experimentally. Complex 8 remained unchanged even after extended exposure to 1 atmosphere of hydrogen gas. There is no evidence in the NMR spectra to suggest that 8 decomposed or gave the N-containing products proposed. The reaction of 9 with trimethylammonium chloride resulted in the decomposition of the complex. The $^{31}$P-$^1$H and $^1$H NMR spectra for the sample indicate the presence of only one species, [P$_2$N$_2$]H$_2$. These experimental conditions were probably unsuitable for the liberation of the desired products from the Zr complexes, 8 and 9.

## 2.6 Reactivity of ([P$_2$N$_2$]Zr)$_2$(μ-η$_2$⁻:η$_2$⁻-N$_2$) with Other Alkynes and Miscellaneous Compounds

Complex 1 was also reacted with other alkynes and unsaturated molecules to determine whether the addition of these organic substrates would also result in N-C bond formation.

The addition of two equivalents of (p-fluoro)phenylacetylene to 1 resulted in the formation of an orange product, which is believed to be analogous in structure to complexes 4, 8 and 9 (Equation 2.7). This assertion is based on the similarity between the $^1$H and $^{31}$P-$^1$H NMR spectra for ([P$_2$N$_2$]Zr)$_2$(μ-η$_2$⁻-N$_2$CH=CH(p-F-C$_6$H$_4$))(μ-C≡C(p-F-C$_6$H$_4$)), 10, and those of 4, 8 and 9. Namely, a doublet at δ 6.21 ($^2$J$_{HH}$ = 13.7 Hz) in the $^1$H NMR spectrum of 10 is characteristic of the trans-disposed hydrogen atom for the alkenylhydrazido moiety, RHC=CHN, observed in 4, 8 and 9. At room temperature, the doublet for the other hydrogen atom of the alkenylhyrazido moiety is hidden under the complicated aromatic region.
Further, the eight different silylmethyl resonances in the $^1$H NMR spectrum indicate that 10 is less symmetrical than 1. Some decomposition of 1 also occurred, as is evidenced by the presence of 7 and $[P_2N_2]H_2$ in the $^{31}$P{$^1$H} NMR spectrum of the product. However, a broad resonance at $\delta$ -14.5 in the same spectrum is assigned to the proposed complex, 10. Also, free (p-fluoro)phenylacetylene was not present in the product since the terminal hydrogen of the alkyne is not evident in the $^1$H NMR spectrum. Thus, the singlets in the $^{19}$F NMR spectrum, $\delta$ -43.2 and -34.1, may both be attributed to the two fluorine environments expected for complex 10. Further characterization of 10 was hindered by the inability to purify the product by recrystallization.

The reactivity of 1 with a selection of other terminal alkynes was also investigated. The addition of (trimethylsilyl)acetylene, 3,3-dimethyl-1-butyne, 3-methyl-1-butyne, and 1-pentyne each caused a transformation in complex 1, as observed by a colour change in the solution and later verified by NMR spectroscopy. Multiple products are evident in the $^{31}$P{$^1$H} NMR spectrum for each reaction. There are many overlapping peaks in all the $^1$H NMR spectra; however, resonances expected for an alkenyldiazido moiety are not apparent.

Complex 1 was also reacted with other unsaturated organic compounds. No reaction was observed with the addition of 1-phenyl-2-(trimethylsilyl)acetylene to 1. Exposure of 1 to propene (1 atm) produced a small quantity of white precipitate, likely propene oligomers, with no apparent change to the dinitrogen complex. In contrast, a colour change was immediate following the addition of hexafluoro-2-butyne (<1 atm) to 1; however, the isolated brown residues were composed of many products according to the NMR data. Similarly, the
reaction of 1 with allene resulted in the formation of an orange mixture, but attempts to separate the products by recrystallization were unsuccessful.

Although 1 is consumed by reactions with organic molecules, the role of the N₂ moiety in these reactions is unknown. Only terminal phenylacetylenes are known to form N-C bonds with bridging dinitrogen of complex 1.

### 2.7 Summary and Conclusions

In this chapter, recent advances in the chemistry of ([P₂N₂Zr]₂(µ-η²:η²-N₂), 1, were presented. The preparation of 1 was optimized to improve both its yield and purity. Complex 1 reacts with p-substituted phenylacetylenes to generate complexes that are analogous to 4. However, the N₂ moiety is not functionalized by the addition of other alkynes or unsaturated molecules to 1. The formation of a new N-C bond, as found in 4, 8, and 9, is an outcome observed only for the addition of terminal arylalkynes to 1.

Complexes 8 and 9 were isolated from the reaction of 1 with two equivalents of (p-methyl)phenylacetylene and (p-tert-butyl)phenylacetylene, respectively. Solution and solid state characterization of these complexes indicate that the N₂ moiety of 1 was transformed into a bridging alkenylhydrazido ligand. The fluxional behaviour observed by ³¹P{¹H} NMR spectroscopy for these complexes is attributed to the flexible nature of P₂N₂ and the asymmetry of the complex imposed by the bridging ligands.

Two possible reaction pathways were proposed for the formation of 4, 8 or 9 from 1. A crude kinetic analysis of the reaction of 1 with PhCCH or PhCCD suggests that the rate-determining step does not involve C-H cleavage or N-H bond formation. Although this data does not provide any conclusive information regarding the reaction mechanism, the formation of these alkenylhydrazido complexes by way of an azazirconacarbocyclobutene intermediate is feasible.

The electron-withdrawing capability of the p-substituent of phenylacetylene does not appear to influence the outcome of the reaction with 1. Namely, the reaction of 1 with (p-fluoro)phenylacetylene produced 10, which is believed to have a molecular structure that is similar to 4, 8 and 9 based on NMR spectroscopy.
2.8 Experimental

2.8.1 General Procedures

Unless otherwise specified, all procedures and manipulations were performed under an atmosphere of dry, oxygen-free dinitrogen or argon by means of standard Schlenk or glovebox techniques (Vacuum Atmospheres HE-553-2 glovebox equipped with a MO-40-2H purification system and a -40°C freezer). Argon and nitrogen were dried and deoxygenated by passing the gases through a column containing molecular sieves and MnO. Hexanes and toluene were purchased from Aldrich and dried by passage through a tower of alumina and degassed by passage through a tower of Q-5 catalyst under positive pressure of nitrogen. Anhydrous THF was pre-dried by refluxing over CaH₂ and distilled from sodium benzophenone ketyl under argon. Anhydrous diethyl ether was stored over molecular sieves and distilled from sodium benzophenone ketyl under argon prior to use. Deuterated toluene, THF and benzene were refluxed over sodium/potassium alloy under partial pressure, trap-to-trap distilled and freeze-pump-thaw degassed three times. Unless otherwise stated, d₆-benzene was the solvent used for all NMR samples. ¹H and ³¹P{¹H} NMR spectra were recorded on either a Bruker AMX-500 instrument operating at 500.1 MHz for ¹H spectra, a Bruker AV-300 instrument operating at 300.1 MHz for ¹H spectra or a Bruker AC-200 instrument operating at 200.1 MHz for ¹H spectra. ¹H NMR spectra were referenced to residual protons in the deuterated solvent: C₆D₅H (7.15 ppm) and C₇D₇H (2.09 ppm). ³¹P{¹H} NMR spectra were referenced to external P(OMe)₃ (141.0 ppm with respect to 85% H₃PO₄ at 0.0 ppm) or to a known impurity within the sample (−36.8 ppm singlet, [P₂N₂]H₂). ¹⁹F NMR spectra were referenced to external CF₃COOH (−74.8 ppm with respect to CFCI₃ at 0.0 ppm). All spectra were measured at room temperature, unless otherwise stated.

Microanalyses (C, H, N) were performed by Mr. P. Borda or Mr. M. Lakha of this department. Mass spectroscopy, low resolution EI, was performed by Mr. M. Lapawa of this department.

Caution: All reactions that resulted in a pressure of 1.5 atm or greater within a sealed vessel upon warming to room temperature were performed with great care and always manipulated behind a blast shield.
2.8.2 Materials

Potassium graphite, KC₈,⁶¹,⁶² and [P₂N₂]ZrCl₂⁶³ were prepared according to literature procedures. Hydrazine (neat) or 1M in THF was purchased from Aldrich. Neat hydrazine was dried and degassed according to literature procedures.⁶⁴ All terminal alkynes were purchased (Aldrich or GFS Chemicals), distilled and freeze-pump-thaw degassed three times prior to use and stored over molecular sieves in the dark. Hydrogen, (p-fluoro)phenylacetylene, allene, propene, and hexafluoro-2-butyne were used without further purification.

2.8.3 Attempted Procedures for the Synthesis of Complex 1 in High Yield and Purity

Reaction of [P₂N₂]ZrCl₂ with Hydrazine and ⁶BuLi

(i) THF (25 mL) and hydrazine (0.02 mL, 0.638 mmol) were added to a Schlenk flask under an Ar atmosphere. The solution was cooled to −78°C (IPA/CO₂ bath) and ⁶BuLi (1.6 M in hexanes, 1.6 mL, 2.56 mmol) was added dropwise. The stirred yellow solution was warmed to room temperature and darkened to an orange colour. This solution was cooled again to −78°C and a THF (35 mL) solution of [P₂N₂]ZrCl₂ (0.712 g, 1.02 mmol) was added via cannula. As this solution was warmed to room temperature, a colour change from green to yellow was observed. The THF was removed in vacuo, the yellow residues were extracted into toluene, and filtered through Celite. Toluene was also removed in vacuo, leaving a yellow residue.

³¹P{¹H} NMR (C₆D₆, 81 MHz): δ 0 to −20 (many singlets, unknown sources), −36.8 (s, [P₂N₂]H₂)

(ii) THF (50 mL) was added to a flask containing [P₂N₂]ZrCl₂ (0.350 g, 0.504 mmol) and cooled to −78°C under an Ar atmosphere. A 1 M solution of hydrazine in THF (0.25 mL, 0.25 mmol) was added, followed by the dropwise addition of ⁶BuLi (1.6 M in hexanes, 0.63 mL, 1.01 mmol). The stirred solution changed from clear orange to brown and then green-yellow, with no appearance of precipitate. The cold bath was removed after 20 minutes, and
the solution was allowed to warm to room temperature. The solvent was removed in vacuo, the green residues were extracted into hexanes and filtered through a scinttered-glass crucible.

$^{31}$P{$^1$H} NMR (C$_6$D$_6$, 81 MHz): δ 0 to -20 (many singlets, unknown sources), -36.8 (s, [P$_2$N$_2$H]$_2$), -37.7 (q, [P$_2$N$_2$]Li$_2$(THF))

Optimized Synthesis of ([P$_2$N$_2$]Zr)$_2$(μ-η$^2$:η$^2$-N$_2$), 1

A modified procedure, resulting in a better yield and greater purity of 1, was developed since the synthesis was first reported. A thick-walled flask fitted with a Kontes valve adaptor was charged with [P$_2$N$_2$]ZrCl$_2$ (2.070 g, 2.98 mmol) and KC$_8$ (0.877 g, 6.49 mmol). The mixture was stirred and degassed prior to the addition of THF* (40 mL) via a trap-to-trap transfer under static vacuum at -196°C. The flask was warmed to -78°C (IPA/CO$_2$ bath) while the mixture was stirred and supplied with a constant flow of N$_2$ (1 atm). Once the solvent had fully melted, the flask was sealed. The cold temperature was maintained for another 4-5 hours before the slurry was warmed to room temperature. The teal slurry was stirred for another 24 hours. The reaction mixture was filtered through Celite on a scinttered-glass crucible and the filtrate was evaporated to dryness. Further purification of the resulting powder, complex 1, was unnecessary. Yield 1.8 g, 95%.

*THF produced the best results. Cyclohexane and toluene were also tried.

$^1$H NMR (C$_6$D$_6$, 300 MHz): δ 0.08 (br s, 24H, SiCH$_3$), 0.38 (s, 24H, SiCH$_3$), 1.28 (m, 8H, ring CH$_2$), 1.55 (m, 8H, ring CH$_2$), 6.93 (br m, 8H, phenyl), 7.14 (m, 8H, phenyl), 8.05 (br m, 4H, phenyl)

$^{31}$P{$^1$H} NMR (C$_6$D$_6$, 121 MHz): δ -16.3 (s)

Decomposition of ([P$_2$N$_2$]Zr)$_2$(μ-η$^2$:η$^2$-N$_2$), 1, with the addition of H$_2$O

Distilled water was degassed by passing a stream of N$_2$(g) through the water as it boiled for approximately 1 hour. A toluene solution of 1 (0.100 g, 0.0784 mmol) was prepared and one equivalent of water (1.41 μL, 0.0784 mmol) was added via micro syringe. The teal solution was stirred for 5 days without any noticeable dissipation of colour. The
solvent was removed *in vacuo* and the green-blue residues collected. The ratio of the integrated area for the peaks of complex 1 (δ -16.3): complex 7 (δ -12.4): [P₂N₂]H₂ (δ -36.8) in the ³¹P{¹H} NMR spectrum (C₆D₆, 121 MHz) of the original sample was 10.0: 0.6: 0.2. After the addition of water the integrated area for each peak was determined in the same manner and found to be 10.0 (complex 1): 9.6 (complex 7): 5.2 ([P₂N₂]H₂). By considering the number of P atoms in each molecule, the relative amount of each compound may be determined. The relative amount of each compound in solution prior to the addition of water was 100 (complex 1): 6 (complex 7): 4 ([P₂N₂]H₂). After the addition of water, the relative amount was 100 (complex 1): 96 (complex 7): 104 ([P₂N₂]H₂). The increase in the amount of 7 and [P₂N₂]H₂ in the solution indicates that they are the predominant decomposition products of 1. Other singlets at δ -10 and -20 in the ³¹P{¹H} NMR spectrum of the reaction mixture are of unknown origin.

**Thermostability of Complex 1**

A toluene solution of complex 1 (0.100 g, 0.0784 mmol) was transferred to a flask fitted with a Kontes valve. The headspace was evacuated and the sample was heated to reflux temperature (~ 65°C) for a 24-hour period. No noticeable change in colour was observed and the NMR spectra for the sample indicate that no decomposition of 1 occurred.

**2.8.4 Synthesis and Characterization of Complexes 8 and 9**

**Synthesis and Characterization of ([P₂N₂]Zr)₂(u-η⁵:η²-N₂CH=CH(p-Me-C₆H₄))(μ-C≡C(p-Me-C₆H₄)), 8**

A 0.06 M solution of (p-methyl)phenylacetylene was quantitatively prepared in toluene. A slight excess of (p-methyl)phenylacetylene (0.06 M, 8.0 mL, 0.48 mmol) was added to a stirred solution of 1 (0.250 g, 0.196 mmol) in toluene (10 mL) at room temperature. The mixture was not stirred and a colour change from blue-green to orange was observed over the course of a week. The solution was concentrated to a brown oil and
hexanes (5 mL) were added. Orange crystalline platelets of 8 were deposited \textit{in situ} from the slow evaporation of the toluene/hexanes solution. Yield 133 mg, 45%.

Anal. Calcd. for C_{66}H_{100}N_{6}P_{4}Si_{8}Zr_{2}: C, 52.55; H, 6.68; N, 5.57. Found: C, 52.95; H, 6.87; N, 5.74. El-MS \textit{m/z}: 1509 \text{[M]}^{+}

\textbf{1H NMR (C\textsubscript{7}D\textsubscript{8}, 300 MHz, 300 K):} \delta -0.06 (s, 6H, SiCH\textsubscript{3}), 0.04 (br s, 6H, SiCH\textsubscript{3}), 0.09 (s, 3H, SiCH\textsubscript{3}), 0.13 (s, 3H, SiCH\textsubscript{3}), 0.23 (s, 6H, SiCH\textsubscript{3}), 0.26 to 0.27 (overlapping s, 6H, SiCH\textsubscript{3}), 0.34 (s, 6H, SiCH\textsubscript{3}), 0.39 to 0.41 (overlapping s, 12H, SiCH\textsubscript{3}), 0.74 to 1.77 (br m, 16H, ring CH\textsubscript{2}), 1.97 (s, 3H, PhCH\textsubscript{3}), 2.14 (s, 3H, PhCH\textsubscript{3}), 3.64 (d, 1H, \textit{J}_{\text{HH}} = 14.0 \text{ Hz}, NCHCH(p-Me-C\textsubscript{6}H\textsubscript{4})), 6.68 (d, 2H, 7.9 Hz, phenyl), 6.86 (d, 2H, 7.9 Hz, phenyl), 6.91 (d, 2H, 8.3 Hz, phenyl), 7.09 to 7.33 (br m, 16H, phenyl), 7.53 (d, 2H, 8.3 Hz, phenyl), 7.59 to 7.78 (br m, 5H, phenyl and NCHCH(p-Me-C\textsubscript{6}H\textsubscript{4})).

\textbf{1H NMR (C\textsubscript{7}D\textsubscript{8}, 300 MHz, 240 K):} \delta -0.18 (s, 3H, SiCH\textsubscript{3}), -0.02 (s, 6H, SiCH\textsubscript{3}), 0.10 (s, 3H, SiCH\textsubscript{3}), 0.17 (s, 3H, SiCH\textsubscript{3}), 0.26 (s, 3H, SiCH\textsubscript{3}), 0.32 (overlapping s, 12H, SiCH\textsubscript{3}), 0.36 (s, 3H, SiCH\textsubscript{3}), 0.39 (s, 3H, SiCH\textsubscript{3}), 0.45 (overlapping s, 6H, SiCH\textsubscript{3}), 0.58 (s, 3H, SiCH\textsubscript{3}), 0.73 (s, 3H, SiCH\textsubscript{3}), 0.81 to 1.64 (br m, 16H, ring CH\textsubscript{2}), 1.92 (s, 3H, PhCH\textsubscript{3}), 2.17 (s, 3H, PhCH\textsubscript{3}), 6.42 (d, 1H, \textit{J}_{\text{HH}} = 14.0 \text{ Hz}, NCHCH(p-Me-C\textsubscript{6}H\textsubscript{4})), 6.66 (d, 2H, 7.9 Hz, phenyl), 6.81 (d, 2H, 7.9 Hz, phenyl), 6.88 (br m, 2H, phenyl), 7.14 to 7.25 (br m, 10H, phenyl), 7.34 to 7.46 (br m, 6H, phenyl), 7.59 (d, 2H, 7.9 Hz, phenyl), 7.77 (d, 1H, \textit{J}_{\text{HH}} = 14.0 \text{ Hz}, NCHCH(p-Me-C\textsubscript{6}H\textsubscript{4})), 7.90 (m, 2H, phenyl), 8.37 (m, 2H, phenyl).

\textbf{31P\textsubscript{1H} NMR (C\textsubscript{7}D\textsubscript{8}, 121 MHz, 300 K):} \delta -14.4 \text{ (br s, } \Delta w_{1/2} \text{ (peak width at half height) = 14.9 Hz)}

\textbf{31P\textsubscript{1H} NMR (C\textsubscript{7}D\textsubscript{8}, 121 MHz, 240 K):} \delta -16.4 \text{ (d, } J_{\text{PP}} = 74.3 \text{ Hz)}, -16.0 \text{ (d, } J_{\text{PP}} = 66.8 \text{ Hz)}, -10.3 \text{ (d, } J_{\text{PP}} = 66.8 \text{ Hz)}, -9.8 \text{ (d, } J_{\text{PP}} = 74.3 \text{ Hz)}

\textbf{31P\textsubscript{1H} NMR (C\textsubscript{7}D\textsubscript{8}, 202 MHz, 350 K):} \delta -14.8 \text{ (br d, } J_{\text{PP}} = 68.7 \text{ Hz)}

References begin on page 69
Synthesis and Characterization of ([P₂N₂]Zr)₂(μ-η²:N₂CH=CH(p-²Bu-C₆H₄))(μ-C≡C(p-²Bu-C₆H₄)), 9

A slight excess of (p-tert-butyl)phenylacetylene (0.198 g, 1.25 mmol) was added to a stirred solution of 1 (0.500 g, 0.392 mmol) in toluene (10 mL) at room temperature. The mixture was left undisturbed and a colour change of blue/green to orange was observed over the course of one week. Slow evaporation of toluene yielded orange needle-like crystals of 9. Yield 200 mg, 40%.

Anal. Calcd. for C₇₂H₁₁₂N₆P₄Si₈Zr₂: C, 54.29; H, 7.09; N, 5.28. Found: C, 53.78; H, 7.18; N, 5.52. EI-MS m/z: 1592 [M⁺]

'H NMR (C₇D₈, 300 MHz, 299 K): δ -0.06 (s, 6H, SiCH₃), 0.04 (br s, 6H, SiCH₃), 0.23 to 0.40 (overlapping br s, 30H, SiCF₃), 0.66 (br s, 6H, SiCH₃), 0.89 (br m, 8H, ring CH₂), 1.09 (s, 9H, ³Bu), 1.23 (br m, 8H, ring CH₂), 1.26 (s, 9H, ³Bu), 6.35 (d, 1H, ³JHH = 13.9 Hz, NCHCH(p-²Bu-C₆H₄)), 6.78 (d, 2H, 8.5 Hz, phenyl), 6.92 to 7.31 (overlapping br m, 20H, phenyl), 7.37 (d, 2H, 8.5 Hz, phenyl), 7.59 (d, 2H, 8.5 Hz, phenyl), 7.61 to 7.79 (br m, 3H, phenyl and NCHCH(p-²Bu-C₆H₄))

'H NMR (C₇D₈, 300 MHz, 235 K): δ -0.13 (s, 3H, SiCH₃), -0.06 (s, 3H, SiCH₃), 0.00 (s, 3H, SiCH₃), 0.21 (s, 3H, SiCH₃), 0.23 (s, 3H, SiCH₃), 0.30 (s, 3H, SiCH₃), 0.35 (br s, 15H, SiCH₃), 0.47 (br s, 6H, SiCH₃), 0.54 (s, 3H, SiCH₃), 0.58 (s, 3H, SiCH₃), 0.72 (s, 3H, SiCH₃), 0.87 to 0.96 (overlapping multiplets, 8H, ring CH₂), 1.06 (s, 9H, ³Bu), 1.15 to 1.26 (overlapping m, 8H, ring CH₂), 1.30 (s, 9H, ³Bu), 6.46 (d, 1H, ³JHH = 13.9 Hz, NCHCH(p-²Bu-C₆H₄)), 6.82 (br d, 2H, phenyl), 6.90 to 7.45 (overlapping m, 20H, phenyl), 7.63 (d, 2H, 8.1 Hz, phenyl), 7.84 (d, 1H, ³JHH = 13.9 Hz, NCHCH(p-²Bu-C₆H₄)), 7.92 (m, 2H, phenyl), 8.38 (m, 2H, phenyl)

'³P{'H} NMR (C₇D₈, 121 MHz, 299 K): δ -14.3 (br s, Δω₁₁ (peak width at half height) = 14.3 Hz)

'³P{'H} NMR (C₇D₈, 121 MHz, 235 K): δ -15.5 (d, ²JPP = 74.1 Hz), -15.1 (d, ²JPP = 65.6 Hz), -10.8 (d, ²JPP = 65.6 Hz), -10.4 (d, ²JPP = 74.1 Hz)
2.8.5 Reactivity of Complexes 8 and 9

Unless otherwise stated, all NMR data in this section were recorded on a Bruker AV-300 instrument.

**Attempted Hydrogenation of ([P₂N₂]Zr)₂(μ-η²:η²-N₂CH=CH(p-Me-C₆H₄))(μ-C≡C(p-Me-C₆H₄)), 8**

Complex 8 (0.060 g, 0.040 mmol) was dissolved in d₈-toluene (~0.4 mL) and transferred to an NMR tube, which was then fitted with a Kontes valve adaptor. On a Schlenk line, the sample was treated with three freeze-pump-thaw cycles to remove the N₂ atmosphere. The room temperature sample was exposed to H₂ (1 atm) for approximately one minute prior to flame-sealing the NMR tube. No colour change was observed; the sample solution remained orange. The ¹H and ³¹P{¹H} NMR spectra of the sample at room temperature and low temperature are identical to the spectra reported for complex 8. After several months, low temperature NMR spectra were again obtained for the sample and indicate that no reaction took place.

**Reaction of ([P₂N₂]Zr)₂(μ-η²:η²-N₂CH=CH(p⁻⁴Bu-C₆H₄))(μ-C≡C(p⁻⁴Bu-C₆H₄)), 9, with Trimethylammonium Chloride, [(CH₃)₃NH]⁺Cl⁻**

Complex 9 (0.030 g, 0.019 mmol) was placed in a vial and dissolved in d₈-toluene. Trimethylammonium chloride (0.020 g, 0.2 mmol) was added to the solution and the vial was capped and shaken. The excess [(CH₃)₃NH]⁺Cl⁻ settled out of solution as a white powder. The pale orange solution was decanted and transferred to an NMR tube. Both the ¹H and ³¹P{¹H} NMR spectra of the sample suggest the presence of only one product, [P₂N₂]H₂.
2.8.6 Additional Reactions of \([\text{P}_2\text{N}_2\text{Zr}]_2(\mu-\eta^2:\eta^2-\text{N}_2), 1\), with Terminal Alkynes

Unless otherwise stated, NMR data reported in this section was recorded on a Bruker AV-300 instrument.

**Reaction of Complex 1 with One Equivalent of Phenylacetylene, PhC≡CH**

Phenylacetylene (0.410 g, 4.02 mmol) was diluted with toluene (50.00 mL total volume). A syringe was used to transfer 5.0 mL of this solution (0.0803 M) to a flask containing 1 (0.520 g, 0.408 mmol). Toluene (15 mL) was added to ensure that 1 was fully dissolved. The teal solution was stirred for several days and a slight colour change to forest green was observed. Green residues were isolated following the removal of toluene in vacuo. Peaks corresponding to complex 4 (br s, δ -14.3), complex 1 (s, δ -16.3), complex 7 (s, δ -12.4) and \([\text{P}_2\text{N}_2\text{H}_2]\) are present in the \(^{31}\text{P}^{1\text{H}}\) NMR (202.5 MHz) spectrum of the sample at room temperature. Additional peaks in the \(^{31}\text{P}^{1\text{H}}\) NMR spectrum are of unknown origin, but could be a result of intermediates and/or decomposition products. Further, the peak resulting from 4 is very broad at room temperature and is known to mask other resonances. The \(^1\text{H}\) NMR (500 MHz) spectrum is not informative due to the presence of many broad and overlapping peaks.

**Reaction of Complex 1 with (p-fluoro)phenylacetylene, \((p-\text{F-C}_6\text{H}_4)\text{C≡CH}: \text{Preparation of }([\text{P}_2\text{N}_2\text{Zr}]_2(\mu-\eta^2:\eta^2-\text{N}_2\text{C}=\text{CH}(p-\text{F-C}_6\text{H}_4))(\mu-\text{C}=\text{C}(p-\text{F-C}_6\text{H}_4)), 10)**

A sample of (p-fluoro)phenylacetylene (0.100 g, 0.832 mmol) was dissolved and diluted with toluene (50.00 mL). A 30.0 mL syringe was used to transfer 26.0 mL of the alkyne solution (0.0167 M, 0.434 mmol) to a toluene solution of 1 (0.273 g, 0.214 mmol). The teal colour of 1 dissipated over the course of 4 days, forming a dark brown solution. An orange precipitate was isolated following the removal of solvent in vacuo. Attempts to grow X-ray quality crystals were unsuccessful.

\(^1\text{H}\) NMR (\(\text{C}_4\text{D}_8\text{O}, 200\text{ MHz}\)): δ -0.33 (s, 3H, SiCH\(_3\)), -0.21 (s, 3H, SiCH\(_3\)), 0.05 (s, 6H, SiCH\(_3\)), 0.08 (s, 6H, SiCH\(_3\)), 0.11 (s, 6H, SiCH\(_3\)), 0.18 to 0.20 (overlapping s, 12H, SiCH\(_3\)),
0.24 (s, 6H, SiCH$_3$), 0.37 (s, 6H, SiCH$_3$), 0.89 (br m, 8H, ring CH$_2$), 1.29 (br m, 8H, ring CH$_2$), 6.21 (d, 1H, 13.7 Hz, NCHCH(p-F-C$_6$H$_4$)), 6.29 to 6.37 (m, 2H, phenyl), 6.66 (t, 2H, 8.79 Hz, phenyl), 7.01 to 7.16 (overlapping m, 6H, phenyl), 7.23 to 7.55 (br m, 16H, phenyl), 7.66 (br m, 3H, phenyl)

$^{31}$P{$_1^1$H} NMR (C$_4$D$_8$O, 81 MHz): $\delta$ -36.8 (s), -14.5 (br s), -12.5 (s, complex 7)

$^{19}$F NMR (C$_4$D$_8$O, 188 MHz): $\delta$ -43.2 (s), -34.1 (s)

Reaction of Complex 1 with (trimethylsilyl)acetylene, Me$_3$SiC=CH

A d$_6$-benzene solution of 1 (0.025 g, 0.020 mmol) was transferred to an NMR tube and 2-3 drops of (trimethylsilyl)acetylene (0.04 mL, 0.3 mmol) were added to the sample. The solution changed from teal green to emerald green over the course of several hours. The $^1$H NMR (200 MHz) spectrum for the sample consists of resonances that are typical for the P$_2$N$_2$ ligand. However, the characteristic doublets for the trans-disposed protons of the alkenylhydrazido moiety in complexes 4, 8, 9 or 10 are not apparent in the $^1$H NMR spectrum of this sample. The reaction was carried out on a larger scale and several attempts were made to isolate the product, corresponding to the broad singlet at $\delta$ -13.3 in the $^{31}$P{$_1^1$H} NMR spectrum, by fractional crystallization from a THF/hexanes solution. However, the desired fraction could not be isolated. The formation of a complex that is analogous to 4, 8 or 9 from the addition of (trimethylsilyl)acetylene to 1 could not be verified.

$^{31}$P{$_1^1$H} NMR (C$_6$D$_6$, 81 MHz): $\delta$ -36.8 (s, [P$_2$N$_2$]H$_2$), -16.3 (s, complex 1), -13.3 (br s), -12.5 (s, complex 7)

Reaction of Complex 1 with 3,3-dimethyl-1-butyne, (CH$_3$)$_3$CC=CH

A d$_6$-benzene solution of 1 (0.045 g, 0.035 mmol) was transferred to an NMR tube and 4 drops of 3,3-dimethyl-1-butyne (0.08 mL, 0.6 mmol) were added to the sample. The solution changed from teal green to emerald green over the course of several days. The $^{31}$P{$_1^1$H} NMR spectrum consists of several broad and sharp resonances, which includes a
signal corresponding to the decomposition product \([P_2N_2]H_2\) (\(\delta -36.8\)). The signal for 1 is absent from the spectrum.

**Reaction of Complex 1 with 3-methyl-1-butyne, \((CH_3)_2CHC≡CH\)**

Two drops of 3-methyl-1-butyne (0.04 mL, 0.4 mmol) were added to a d\(_6\)-benzene solution of 1 (0.025 g, 0.020 mmol) in an NMR tube. The colour of the teal solution changed over the course of one day to an orange-brown. Some alkyne had evaporated off before NMR spectra were obtained. The \(^1H\) (200 MHz) and \(^{31}P\{^1H\}\) (81 MHz) NMR spectra are complicated by many overlapping peaks. There is evidence for trace amounts of 1 and \([P_2N_2]H_2\), however none of the peaks in the \(^1H\) NMR spectrum suggest the presence of an alkenylhydrazido complex.

**Reaction of Complex 1 with 1-pentyne, \(CH_3(CH_2)_2C≡CH\)**

A few drops of 1-pentyne (3-4 drops, 0.06 mL, 0.6 mmol) were added to a d\(_6\)-benzene solution of 1 (0.025 g, 0.020 mmol) in an NMR tube. Within one hour a change from teal to a brown-green colour was observed. After 4 days the sample solution was orange-brown with a trace of green precipitate. The \(^{31}P\{^1H\}\) NMR spectrum indicates the presence of multiple products, including the decomposition products 7 (\(\delta -12.5\)) and \([P_2N_2]H_2\) (\(\delta -36.8\)). However, the peak for 1 (\(\delta -16.3\)) is absent from the spectrum. The \(^1H\) NMR spectrum is uninformative due to the many overlapping peaks.
2.8.7 Miscellaneous Reactions of \( ([P_2N_2]Zr)_2(\mu-\eta^2:\eta^2-N_2) \), 1

Unless otherwise stated, NMR data reported in this section was recorded on a Bruker AV-300 instrument.

Reaction of Complex 1 with Substituted Acetylenes

(i) A few drops of 1-phenyl-2-(trimethylsilyl)acetylene, PhC=CSiMe\(_3\), (1-2 drops, ~0.03 mL, 0.15 mmol) were added to a d\(_6\)-benzene solution of 1 (0.030 g, 0.024 mmol) in an NMR tube. The solution remained teal in colour over a period of days. The \(^{31}\text{P}\{^1\text{H}\} \) NMR (81 MHz) spectrum for the sample indicates no reaction took place.

(ii) A toluene solution of 1 (0.506 g, 0.397 mmol) was transferred to a flask fitted with a Kontes Teflon valve. The sample was degassed by three freeze-pump-thaw cycles prior to the addition of hexafluoro-2-butyne, CF\(_3\)C=CCF\(_3\), (<1 atm) at room temperature. Almost immediately, a colour change from teal to yellow occurred at the surface of the solution. Over a period of 5-10 minutes, the sample went from dark green-yellow to a dark brown solution with a large amount of brown precipitate. The flask was sealed and the contents were stirred for one day. A brown precipitate (0.70 g) was isolated from the brown filtrate and washed with hexanes. Attempts to grow crystals of the brown product were unsuccessful. The \(^1\text{H} \) NMR spectrum of the brown powder consists of many overlapping peaks.

\(^{19}\text{F}\{^1\text{H}\} \) NMR (C\(_4\)D\(_8\)O, 282 MHz): \( \delta \) -133.4 (s), -132.2 (s)

\(^{31}\text{P}\{^1\text{H}\} \) NMR (C\(_4\)D\(_8\)O, 121 MHz): \( \delta \) -36.8 (s, smallest resonance, \([P_2N_2]H_2\)), -15.2 (s, largest resonance, unknown), -12.9 (s, unknown)

Reaction of Complex 1 with other Unsaturated Molecules: Allene and Propene

(i) A degassed toluene solution of 1 (0.0784 g, 0.0614 mmol) was stirred for a period of 30-40 minutes while exposed to allene, H\(_2\)C=C=CH\(_2\), (<1 atm). The resulting emerald green solution was stirred overnight and the solvent was removed \textit{in vacuo}. The \(^{31}\text{P}\{^1\text{H}\} \) NMR spectrum indicates that 1 was consumed by the reaction and the resulting pale yellow
residues consisted of a mixture of products, where 7 and [P₂N₂]H₂ predominate. The ¹H NMR spectrum consists of many overlapping peaks.

(ii) A d₆-benzene solution of 1 (0.030 g, 0.024 mmol) was transferred to a sealable NMR tube fitted with a Kontes valve adaptor. The solution was degassed by three freeze-pump-thaw cycles and exposed to propene, H₂C=CHCH₃, (1 atm) for 2-3 minutes. The NMR tube was flame-sealed and the contents were mixed by continuously inverting the tube over several days (motorized rotation). A small amount of precipitate formed in the teal solution. The ³¹P{¹H} NMR spectrum of the sample indicates the presence of a mixture that consists of 1, 7 and [P₂N₂]H₂.

2.8.8 Isotopic Labeling Experiment: Reaction of Complex 1 with PhC≡CH or PhC≡CD

A detailed experimental procedure, raw data and graphical plots for this experiment are provided in Appendix 2.
2.9 References


References begin on page 69
Chapter 2: Formation of C-N Bonds from Molecular Nitrogen and Arylalkynes


References begin on page 69
Chapter 2: Formation of C-N Bonds from Molecular Nitrogen and Arylalkynes


3.1 Introduction

The successful preparation of dinitrogen complexes from elemental nitrogen relies largely on the chosen set of ancillary ligands, the metal centre and the reducing agent. Even so, dinitrogen complexes may not necessarily result from these reactions. A good case in point involves zirconium derivatives with various cyclopentadienyl-based ancillary ligands. The simplest zirconocene dichloride, CpaZrCl₂ (Cp = η⁵-C₅H₅), has been used in a variety of catalytic and stoichiometric processes.¹ ² Under reducing conditions, various modes of decomposition have been documented that involve C-H activation of the Cp ring and formation of dinuclear species.³ However, the use of pentamethylcyclopentadienyl ligands has allowed for a more controlled reduction and the isolation of a dinitrogen complex (Equation 3.1).⁴
The complex, (Cp^*2ZrN_2)2(μ-N_2) where Cp^* = η^5-C_5Me_5, has one terminal dinitrogen group for each zirconium centre, as well as another dinitrogen moiety bridging the two metals in an end-on fashion. Under reduced pressure, all three dinitrogen molecules are released, reversibly. As a source of Zr(II), this complex is highly reactive and has been studied extensively (Scheme 3.1). Reaction of the complex with HCl at room temperature produces hydrazine and releases two equivalents of dinitrogen. Analysis of the products resulting from the reaction of (Cp^*2Zr^{14}N_2)2(μ-^{15}N_2) with HCl has shown that both the bridging and terminal N_2 are the source of dinitrogen in the produced hydrazine. A proposed intermediate for this reaction is a symmetrical species, such as Cp^*2Zr(N_2H)_2, where a terminal N_2 and the bridging N_2 would become equivalent. Reaction with two additional equivalents of HCl would then release one equivalent each of N_2H_4 and N_2.
Chapter 3: Synthesis and Reactivity of ([NPN]ZrY)\(_2\)(\(\mu\cdot\eta^1\cdot\eta^2\)-\(\mu\)-\(\eta^2\)-N\(_2\)), where \(Y = \) THF, Pyridine, Benzonitrile

Treatment of (Cp*\(_2\)ZrN\(_2\))\(_2\)(\(\mu\)-N\(_2\)) with H\(_2\) under ambient conditions displaces all three equivalents of N\(_2\) to form Cp*\(_2\)ZrH\(_2\). However, the reactivity of (Cp*\(_2\)ZrN\(_2\))\(_2\)(\(\mu\)-N\(_2\)) with CO\(_6\) or PH\(_3\)\(_9\) at low temperatures is unique in that the original bridging dinitrogen is not displaced. These modified versions of the original N\(_2\) complex are of limited utility since they are thermally labile. At room temperature, the addition of CO results in the formation of Cp*\(_2\)Zr(CO)\(_2\). Above 0\(^\circ\)C, the N\(_2\) complex formed from the addition of PH\(_3\) to (Cp*\(_2\)ZrN\(_2\))\(_2\)(\(\mu\)-N\(_2\)) undergoes a structural rearrangement involving P-H activation that also includes the evolution of N\(_2\).

Recent work has shown that a minor change in Cp*\(_2\)ZrCl\(_2\) (Equation 3.1) from (pentamethyl)cyclopentadienyl to (tetramethyl)cyclopentadienyl ligands has a dramatic effect on the structure and reactivity of the resulting dinitrogen complex (Scheme 3.2). The modified ligand is less sterically hindered; however, this may not be the source of the reactivity difference. Reduction of the modified Zr-dichloride complex, (\(\eta^5\)-C\(_5\)Me\(_4\)H)\(_2\)ZrCl\(_2\), with sodium amalgam under an N\(_2\) atmosphere produces a complex with a side-on coordinated N\(_2\), which bridges two Zr centres. In addition to the difference in hapticity of the bridging N\(_2\) unit in each complex, the N-N bond length of \{(\(\eta^5\)-C\(_5\)Me\(_4\)H)\(_2\)Zr\}\(_2\)(\(\mu\)-\(\eta^2\)-\(\mu\)-\(\eta^2\)-N\(_2\)) is larger than that of the original N\(_2\) complex, (Cp*\(_2\)ZrN\(_2\))\(_2\)(\(\mu\)-N\(_2\)) (1.377(3)\(\AA\) vs. 1.182(5)\(\AA\), respectively). The most drastic difference between the two complexes is evident in their reactivity with H\(_2\). When exposed to one atmosphere of H\(_2\) at ambient temperature, \{(\(\eta^5\)-C\(_5\)Me\(_4\)H)\(_2\)Zr\}\(_2\)(\(\mu\)-\(\eta^2\)-\(\mu\)-\(\eta^2\)-N\(_2\)) reacts to form a dinuclear zirconocene hydrazido complex, \{(\(\eta^5\)-C\(_5\)Me\(_4\)H)\(_2\)ZrH\}\(_2\)(\(\mu\)-N\(_2\))\(_2\). Scission of the N-N bond can be observed in situ by heating a solution of the hydrazido complex to form \{(\(\eta^5\)-C\(_5\)Me\(_4\)H)\(_2\)Zr\}\(_2\)(\(\mu\)-N\(_2\))\(_2\) and free H\(_2\). Treating this complex with anhydrous HCl completes the fixation of nitrogen by regenerating (\(\eta^5\)-C\(_5\)Me\(_4\)H)\(_2\)ZrCl\(_2\) and releasing the desired product, NH\(_4\)Cl. Alternatively, heating the zirconocene hydrazido complex under a constant pressure of H\(_2\) also leads to nitrogen fixation, as evidenced by the formation of ammonia (10-15% yield) and a Zr hydride complex, (\(\eta^5\)-C\(_5\)Me\(_4\)H)\(_2\)ZrH\(_2\). The complete fixation of molecular N\(_2\) to ammonia by way of a well-defined zirconium dinitrogen complex and molecular H\(_2\) is extraordinary.
Research in the Fryzuk group has focused on the use of mixed donor amidophosphine ligands rather than cyclopentadienyl ligands for the preparation of zirconium dinitrogen complexes. Reduction of Zr complexes of the general formula ZrCl$_2$X[N(SiMe$_2$CH$_2$PP)$_2$], where X = Cl, O-2,6-Me$_2$C$_6$H$_3$ and Cp, under an N$_2$ atmosphere affords dinitrogen complexes with different geometries and N$_2$ bonding modes (Scheme 3.3).$^{13-15}$

References begin on page 109
Chapter 3: Synthesis and Reactivity of ([NPN]ZrY)_2(μ-η²:η²-N₂), where Y = THF, Pyridine, Benzonitrile

\[
2 \text{ZrCl}_2X[N(SiMe_2CH_2PPr')_2] + 4 \text{Na/Hg}
\]

**Scheme 3.3**

Complex A in Scheme 3.3 has longest N-N bond length, 1.548(7) Å, for a dinitrogen molecule reported to date. Attempts to use different adducts in the Zr(IV) precursor did not always yield a dinitrogen complex upon reduction. The aryloxide complex, C, has the same side-on binding mode for the N₂ ligand as A, which suggests that the replacement of chloride ligands with aryloxide does not significantly affect the frontier orbitals required in the binding of N₂. However, C adopts a ‘hinged’ geometry about the bridging N₂ moiety, unlike the planar configuration of A. In contrast, the dinitrogen complex with a Cp adduct, B,
exemplifies the unpredictable influence ancillary ligands have on the coordination mode of dinitrogen.\(^{14}\) None of these complexes form N-H bonds when exposed to hydrogen.\(^{16}\)

A major disadvantage encountered with the PNP ligand set shown in Scheme 3.3 is the dissociation of the phosphine arms from early transition metals, which may be responsible for the formation of intractable PNP complexes.\(^{17}\) A macrocyclic ligand, P\(_2\)N\(_2\), was developed to alleviate this problem by including an additional disilylamido unit to help anchor the phosphine donors to the metal (Section 1.5, Scheme 1.5).\(^{18}\) The success of this ancillary ligand with zirconium for nitrogen activation and functionalization is evidenced by the synthesis and reactivity of complex 1, discussed in Chapter 2. However, efforts to prepare a Ta dinitrogen complex with the P\(_2\)N\(_2\) ligand set have not been successful.\(^{19,20}\)

A new ligand with only three donors was prepared to promote reactivity at the metal by reducing the coordinative saturation (Section 1.5).\(^{21}\) The NPN ligand is the acyclic variation of P\(_2\)N\(_2\) where one of the phosphine donors has been removed (Scheme 1.7).\(^{22}\)

A natural extension of the NPN tantalum chemistry is the investigation of this ligand with other early transition metals. The preparation and reactivity of zirconium dinitrogen complexes containing the NPN ligand is the focus of this chapter. In addition to NPN, these complexes have a neutral donor on each Zr centre, including THF, pyridine and benzonitrile, that may be replaced with another donor without displacing the coordinated N\(_2\) unit. The ability to easily substitute this donor ligand provided a means for exploring the effect of ligand changes on the reactivity of the bound dinitrogen unit.
3.2 Synthesis of [NPN]ZrCl$_2$(THF), 11, and ([NPN]ZrTHF)$_2$(μ-η$^2$:η$^2$-N$_2$), 12

The preparation of [NPN]ZrCl$_2$(THF) is a straightforward metathesis reaction. A yellow slurry is formed when toluene is added to a mixture of [NPN]Li$_2$(THF)$_2$ and ZrCl$_4$(THF)$_2$, which are both white powders. Heating the slurry at reflux temperature overnight and under reduced pressure forms a milky white slurry from which 11 can be isolated in high yield.

One singlet resonance is observed in the $^{31}$P{'H} NMR spectrum at $\delta$ 1.67. The $^1$H NMR spectrum of 11 provides more information regarding the symmetry of the complex in solution. The presence of only two singlets for the SiMe$_2$ groups of the NPN ligand suggests the complex has C$_s$ symmetry, where a mirror plane bisects the angle between the Zr metal and the amido groups of the ligand. One molecule of THF is coordinated to the metal based on the integration of broad resonances observed at $\delta$ 3.35 and $\delta$ 0.87. Resonances due to the protons of free THF are observed at $\delta$ 3.57 and $\delta$ 1.40 in C$_6$D$_6$.

The procedure (Equation 3.2) for preparing a dinitrogen complex from [NPN]ZrCl$_2$(THF) is nearly identical to that followed for the synthesis of ([P$_2$N$_2$]Zr)$_2$(μ-η$^2$:η$^2$-N$_2$), 1. The THF solvent is added to a mixture of [NPN]ZrCl$_2$(THF) and KC$_8$ by a trap-to-trap distillation at $-196^\circ$C prior to the introduction of a dinitrogen atmosphere. Unlike the synthesis of 1, no immediate color change is observed as the frozen mixture is warmed under an N$_2$ atmosphere and the THF begins to melt ($\sim -109^\circ$C). Even at $-78^\circ$C, the slurry appears brown and unchanged. By slowly warming the brown slurry to room temperature, and ensuring vigorous stirring throughout, a dark purple slurry is formed. The dinitrogen complex 12 may be isolated from this slurry in good yield (87%) and in high purity. Varying the N$_2$ pressure of the reaction (i.e., 1.5 or 4 atm) does not noticeably affect either the yield or purity. Impurities were usually only formed when the reaction mixture was not vigorously stirred and gave the resultant product a maroon colour. Attempts to isolate these impurities were unsuccessful.
Complex 12 can only be prepared in high yield if THF is used as the solvent for the reaction. Only trace amounts of 12 were observed by $^{31}$P{${}^1$H} NMR spectroscopy when the reduction of 11 was carried out under a dinitrogen atmosphere in either toluene or ether. The reduction of 11 under various conditions will be discussed in Section 3.6.

One singlet resonance at $\delta$ -5.57 is observed in the $^{31}$P{${}^1$H} NMR spectrum for 12. Integration of the signals in the $^1$H NMR spectrum is consistent with a structure containing a one-to-one ratio of NPN ligand and coordinated THF. The presence of only two singlets for the silylmethyl groups of NPN suggests that the complex is highly symmetrical ($C_{2h}$ or $C_{2v}$). A broad singlet at $\delta$ 3.21 is indicative of coordinated THF; the other peak expected for THF is hidden under the large SiMe$_2$ resonance at $\delta$ 0.55. All other peaks in the $^1$H NMR spectrum are typical of resonances observed for coordinated NPN ligand. The parent peak for the molecular ion [M$^+$] of 12 was not observed by mass spectrometry, however a fragment at $m/z$ 1080 is consistent with the presence of the fragment, [NPN]$_2$Zr$_2$(N$_2$). The mass spectrum and elemental analysis collectively support the dimeric composition of 12.

The molecular structure of 12 in the solid state was determined by single crystal X-ray diffraction and provides further information regarding the coordination mode of N$_2$ within the complex (Figure 3.1).$^{24}$ Selected bond lengths and angles of 12 are listed in Table 3.1. The dinitrogen unit adopts a side-on coordination mode and bridges the two zirconium centres such that all four atoms lie in the same plane.
Figure 3.1. ORTEP representation (ellipsoid probability 50%) of the molecular structure of ([NPN]ZrTHF)$_2$(μ-η$^2$-N$_2$), 12, as determined by single crystal X-ray diffraction. Hydrogen atoms and silylmethyl groups are omitted for clarity and only ipso carbons of the NPN ligand phenyl rings are shown. Crystals of 12 were grown by Dr. P. Yu.

The long N-N bond length of 1.503(3)Å suggests that the original triple bond of N$_2$ has been reduced to a single bond in 12. Complex 12 has an inversion centre in the middle of the N-N bond. As a result, the THF and NPN ligands coordinated to one zirconium centre are on the opposite side of their respective counterparts on the other zirconium centre. Each zirconium may be considered pseudo-trigonal bipyramidal in geometry, with THF and phosphine in the axial positions and the dinitrogen unit and amides in the equatorial positions. The dinitrogen ligand lies in a plane of symmetry that includes the O-Zr-P axis, while the amido groups of the NPN ligand are perpendicular to this plane. Table 3.2 lists N-N bond distances for Zr complexes with a planar Zr$_2$N$_2$ core that is similar to 12.

References begin on page 109
**Table 3.1.** Selected Bond Lengths and Angles in \([(\text{NPN})\text{ZrTHF})_2(\mu-\eta^2:\eta^2-\text{N}_2)]\), 12

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atom</th>
<th>Distance (Å)</th>
<th>Atom</th>
<th>Atom</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(3)'</td>
<td>N(3)</td>
<td>1.503(3)</td>
<td>Zr(1)</td>
<td>N(2)</td>
<td>2.228(2)</td>
</tr>
<tr>
<td>Zr(1)</td>
<td>N(3)</td>
<td>2.026(2)</td>
<td>Zr(1)</td>
<td>O(1)</td>
<td>2.305(1)</td>
</tr>
<tr>
<td>Zr(1)</td>
<td>N(3)'</td>
<td>2.069(2)</td>
<td>Zr(1)</td>
<td>P(1)</td>
<td>2.6685(5)</td>
</tr>
<tr>
<td>Zr(1)</td>
<td>N(1)</td>
<td>2.175(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atom</th>
<th>Atom</th>
<th>Angle (°)</th>
<th>Atom</th>
<th>Atom</th>
<th>Atom</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(1)</td>
<td>Zr(1)</td>
<td>O(1)</td>
<td>149.24(4)</td>
<td>N(1)</td>
<td>Zr(1)</td>
<td>N(2)</td>
<td>116.84(6)</td>
</tr>
<tr>
<td>P(1)</td>
<td>Zr(1)</td>
<td>N(2)</td>
<td>77.15(5)</td>
<td>N(1)</td>
<td>Zr(1)</td>
<td>N(3)</td>
<td>114.07(6)</td>
</tr>
<tr>
<td>P(1)</td>
<td>Zr(1)</td>
<td>N(1)</td>
<td>76.62(5)</td>
<td>N(2)</td>
<td>Zr(1)</td>
<td>N(3)</td>
<td>116.77(6)</td>
</tr>
<tr>
<td>P(1)</td>
<td>Zr(1)</td>
<td>N(3)</td>
<td>80.73(5)</td>
<td>O(1)</td>
<td>Zr(1)</td>
<td>N(1)</td>
<td>89.88(6)</td>
</tr>
<tr>
<td>O(1)</td>
<td>Zr(1)</td>
<td>N(2)</td>
<td>84.90(5)</td>
<td>O(1)</td>
<td>Zr(1)</td>
<td>N(3)'</td>
<td>87.08(5)</td>
</tr>
</tbody>
</table>

A cis-configuration of NPN ligands about the Zr-Zr axis for 12 is also feasible. However, on the basis of NMR data there is no definitive evidence to support the presence of this geometric isomer. Only the trans-isomer of 12 was characterized in the solid state.

**Table 3.2.** Comparison of N\(_2\) Bond Lengths for Zr Complexes with a Planar Zr\(_2\)N\(_2\) Core and a Side-On Bridged N\(_2\) Unit

<table>
<thead>
<tr>
<th>Complex</th>
<th>N-N (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>([(\text{NPN})\text{ZrTHF})_2(\text{N}_2)])</td>
<td>1.503(3)</td>
<td>24</td>
</tr>
<tr>
<td>([(\text{PNP})\text{ZrCl})_2(\text{N}_2)])</td>
<td>1.548(7)</td>
<td>13</td>
</tr>
<tr>
<td>([(\text{P}_2\text{N}_2]\text{Zr})_2(\text{N}_2)])</td>
<td>1.43(1)</td>
<td>25</td>
</tr>
<tr>
<td>([(\eta^5-C_3\text{Me}_4\text{H})_2\text{Zr})_2(\text{N}_2)])</td>
<td>1.377(3)</td>
<td>11</td>
</tr>
<tr>
<td>((\text{rac-BpZr})_2(\text{N}_2)])</td>
<td>1.241(3)</td>
<td>26</td>
</tr>
</tbody>
</table>

References begin on page 109
3.3 Adduct Exchange: Replacement of THF in ([NPN]ZrTHF)$_2$(μ-η$^2$-N$_2$), 12, with Pyridine and Benzonitrile

Although the PNP zirconium dinitrogen complexes described in Scheme 3.3 are similar in composition, each possesses a different donor ligand (i.e., Cl, Cp, O-2,6-Me$_2$C$_6$H$_3$). Addition of an aryloxide to complex A was expected to allow for direct substitution of the chloride donor atoms; however, reaction of A with various aryloxides or alkoxides results in either no reaction or decomposition of the parent complex.$^{15}$ As a result, the only route to these particular complexes (A-C) requires modification of the starting material prior to reduction under dinitrogen. The ability to easily prepare a series of Zr dinitrogen complexes with different neutral donor ligands would be ideal for investigating the affect these particular ligands have on the reactivity of coordinated dinitrogen. Unlike the PNP zirconium dinitrogen complexes, the THF donor ligands in 12 can be directly substituted to form new dinitrogen complexes.

(i) Synthesis and Characterization of ([NPN]Zrpy)$_2$(μ-η$^2$-N$_2$), 13

Complex 13 is prepared by the addition of pyridine, either a stoichiometric amount or an excess, to a purple toluene solution of 12. An instantaneous colour change of the solution to dark green is observed. Complex 13 is isolated as a green powder in good yield by removing the solvent in vacuo. The purity of the product is dependent on the quality of the original material, 12.

Characterization of 13 both in solution and in the solid state indicates that it is a dinitrogen complex with a pyridine molecule coordinated to each Zr centre; it is analogous to complex 12, which has two coordinated THF molecules. The $^1$H NMR spectrum of 13 appears similar to that of 12, except for the absence of the broad THF resonances and the presence of new aromatic resonances corresponding to coordinated pyridine. The ratio of the o-H or m-H pyridine resonances to the SiMe$_2$ resonances is consistent with the presence of one pyridine molecule for each NPN ligand. Similar to 12, a singlet at δ = -6.55 is observed in the $^{31}$P{$^1$H} NMR spectrum of 13. The parent peak for the molecular ion [M$^+$] of 13 is observed at m/z 1235 by mass spectrometry.
Chapter 3: Synthesis and Reactivity of ([NPN]ZrY)$_2$(μ-$\eta^2$-$\eta^2$-N$_2$), where Y = THF, Pyridine, Benzonitrile

The molecular structure of 13 was confirmed by single crystal X-ray diffraction (Figure 3.2). The orientation of the NPN and pyridine ligands with respect to the side-on coordinated dinitrogen in 13 is analogous to that in 12. The similarity between the complexes also extends to the molecule’s symmetry and the geometry at each Zr atom.

![Figure 3.2. ORTEP representation (ellipsoid probability 50%) of the molecular structure of ([NPN]Zrpy)$_2$(μ-$\eta^2$-$\eta^2$-N$_2$), 13, as determined by single crystal X-ray diffraction. Hydrogen atoms and silylmethyl groups are omitted for clarity and only ipso carbons of the NPN ligand phenyl rings are shown.](image)

In the solid state, complex 13 also belongs to the C$_{2h}$ point group and possesses an inversion centre located in the middle of the N-N bond. The bond lengths and angles of 13 are very similar to those of 12 and a selected list is presented in Table 3.3. The angles
between the coordinating atoms with respect to zirconium suggest a pseudo-trigonal bipyramidal geometry surrounds each metal centre. When considering only half the molecule, an axis is defined by N3-Zr1-P1 where the two coordinating amido groups and one N of dinitrogen encircle Zr. The equatorial groups are spaced ~120° from each other and ~90° from the axis.

Table 3.3. Selected Bond Lengths and Angles in ([NPN]ZrY)\(_2\)(µ-\(\eta^2\).\(\eta^2\)-\(\text{N}_2\)), 13

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atom</th>
<th>Distance (Å)</th>
<th>Atom</th>
<th>Atom</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(4)(\prime)</td>
<td>N(4)</td>
<td>1.503(2)</td>
<td>Zr(1)</td>
<td>N(2)</td>
<td>2.1871(13)</td>
</tr>
<tr>
<td>Zr(1)</td>
<td>N(4)</td>
<td>2.0453(14)</td>
<td>Zr(1)</td>
<td>N(3)</td>
<td>2.4114(14)</td>
</tr>
<tr>
<td>Zr(1)</td>
<td>N(4)(\prime)</td>
<td>2.0819(13)</td>
<td>Zr(1)</td>
<td>P(1)</td>
<td>2.6938(5)</td>
</tr>
<tr>
<td>Zr(1)</td>
<td>N(1)</td>
<td>2.2309(13)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atom</th>
<th>Atom</th>
<th>Angle (°)</th>
<th>Atom</th>
<th>Atom</th>
<th>Atom</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(3)</td>
<td>Zr(1)</td>
<td>P(1)</td>
<td>149.15(4)</td>
<td>N(1)</td>
<td>Zr(1)</td>
<td>N(2)</td>
<td>116.84(5)</td>
</tr>
<tr>
<td>N(1)</td>
<td>Zr(1)</td>
<td>P(1)</td>
<td>77.94(4)</td>
<td>N(2)</td>
<td>Zr(1)</td>
<td>N(4)</td>
<td>115.21(5)</td>
</tr>
<tr>
<td>N(2)</td>
<td>Zr(1)</td>
<td>P(1)</td>
<td>75.87(4)</td>
<td>N(1)</td>
<td>Zr(1)</td>
<td>N(4)</td>
<td>116.84(5)</td>
</tr>
<tr>
<td>N(4)</td>
<td>Zr(1)</td>
<td>P(1)</td>
<td>82.55(4)</td>
<td>N(2)</td>
<td>Zr(1)</td>
<td>N(3)</td>
<td>90.41(5)</td>
</tr>
<tr>
<td>N(1)</td>
<td>Zr(1)</td>
<td>N(3)</td>
<td>84.21(5)</td>
<td>N(3)</td>
<td>Zr(1)</td>
<td>N(4)(\prime)</td>
<td>85.75(5)</td>
</tr>
</tbody>
</table>

(ii) Synthesis and Characterization of ([NPN]Zr(PhCN))\(_2\)(µ-N\(_2\)), 14

The addition of two equivalents of benzonitrile to a solution of 12 is believed to result in the formation of complex 14. The reaction is observed as an instantaneous colour change from a purple to a red solution. Brown residues may then be isolated upon removal of solvent; however, attempts to grow crystals of the product were unsuccessful. In the absence of crystallographic data, the composition of 14 is believed to be analogous to that of 12 and 13 based on the similarities observed between all three complexes in their NMR and mass spectra.

Three fragments observed in the mass spectrum are consistent with the composition assigned to 14. A parent ion at m/z 1284 indicates that the complex is dimeric, where two
benzonitrile molecules have been incorporated into the structure and two THF molecules have been removed from the original complex, 12. Other fragment peaks for this product correspond to a mixed-adduct complex, [NPN]ZrTHF(PhCN)N₂ (m/z 1255), and an adduct free complex, [NPN]ZrN₂ (m/z 1080). A fragment at m/z 1080 and another corresponding to [NPN]ZrTHF(py)N₂ (m/z 1231) are also observed in the mass spectrum for 13. Based on this fragmentation pattern, benzonitrile likely acts as a donor ligand, which replaces THF, and does not react with N₂ in 12.

Only one major singlet is observed in the ³¹P{¹H} NMR spectrum at δ -8.34, indicating that the phosphorus of each NPN ligand is in an identical chemical environment. However, the ¹H NMR spectrum suggests 14 is not as symmetrical in solution as complexes 12 and 13. The silylmethyl region for 14 is more complicated with eight overlapping singlets, in contrast to only two SiMe₂ singlets for each of complexes 12 and 13. The absence of a broad singlet in the region of ~3.5 ppm indicates that all of the starting material, 12, was consumed and any residual THF was removed from the reaction mixture. The aromatic region is difficult to interpret due to many overlapping resonances. Without further experiments, the structure of 14 remains speculative; particularly the coordination mode of the N₂ ligand.

3.4 Evidence for the Formation of a Mixed-Adduct Intermediate ([NPN]ZrTHF)(μ-η²:η²-N₂)(pyZr[NPN]), 15

In Section 3.3i, the preparation and isolation of 13 from 12 was presented. The reverse of this reaction can also be observed in situ by ³¹P and ¹H NMR spectroscopy. The addition of THF to 13 does regenerate 12 to some degree. However, the removal of solvent only results in a mixture of purple colored residues in which 12 is a major component, but cannot be further isolated. Even with the addition of an excess amount of THF, and significant amounts of THF still present in the isolated residues, complex 12 is not quantitatively reformed from 13. The reversibility of this reaction suggests that a solution containing both complexes, 12 and 13, is in equilibrium. A rudimentary view of this equilibrium is presented in Equation 3.3 and includes only these complexes and the donor ligands, THF and pyridine.
With the removal of solvent in vacuo, THF and pyridine are also removed from the reaction; however, THF is more volatile than pyridine and, as a result, is removed more quickly. In response to the loss of THF, the equilibrium is expected to shift towards the production of 13. Although Equation 3.3 is consistent with experimental observations, the existence of intermediates and the role they may play in the equilibrium is not taken into consideration.

The procedure for synthesizing 13 precludes the detection of any possible "intermediate" complexes by NMR spectroscopy. In particular, the NMR spectra obtained for 13 was only that of very pure samples. It was not until the two complexes were analyzed together in solution that clear evidence for an additional product emerged.

Known quantities of each complex, 12 and 13, were dissolved in d6-benzene and analyzed by $^1$H and $^{31}$P{${^1}$H} NMR spectroscopy. The reason for this experiment was to determine whether this solution would change in composition without the addition of external donor ligands (THF or pyridine) to shift the equilibrium. The ratio of the complexes in solution can be determined from the integration of comparable resonances in each spectrum. Namely, the integration of the o-H resonance from P-phenyl of the NPN ligand can be used to determine the amount of one complex in relation to the other. However, additional resonances were observed in the spectra that could not be assigned to either 12 or 13. Closer examination suggested that the additional peaks were consistent with those expected for another complex: the mixed adduct, ([NPN]ZrTHF)(μ-η^2:η^2-N_2)(pyZr[NPN]), 15.
The $^1$H and $^{31}$P{$^1$H} NMR spectra for this mixed solution is presented in Figure 3.3. The letters denote the type of proton that would produce a given resonance and the subscripted numbers indicate the corresponding complex. In most regions of the $^1$H NMR spectrum, the complexes are indistinguishable due to overlap of peaks. However, $o$-H pyridine (A), $o$-H P-phenyl (B) and THF (C) protons give rise to resonances that are distinctive for the three complexes. The additional peaks ($A_{15}$, $B_{15}$, $C_{15}$) in the spectrum are similar in chemical shift and multiplicity to those expected for 12 ($B_{12}$ and $C_{12}$) and 13 ($A_{13}$ and $B_{13}$) in the same region. The peaks labeled $A_{15}$ and $C_{15}$ are not indicative of free pyridine and THF, respectively. Rather, the additional peaks suggest that a new complex with both THF and pyridine donor ligands is present in solution.
Chapter 3: Synthesis and Reactivity of ([NPN]ZrY)$_2$(μ-η$^2$-N$_2$), where Y = THF, Pyridine, Benzonitrile

The proposed composition of this new complex, 15, is partially based on integration data that shows the relationship between these three peaks. Table 3.4 lists these values. Namely, the relative integration ratio of A$_{15}$:B$_{15}$:C$_{15}$ was found to be 2:4:4. This is consistent for a complex containing one pyridine ligand (2 o-H for each pyridine), two NPN ligands (2 o-H for each P-phenyl) and one THF ligand (4 H per THF). To verify this approach, the integration values for peaks corresponding to 12 and 13 were also determined and found to

**Figure 3.3.** $^{31}$P{$^1$H} (121 MHz) and $^1$H NMR (300 MHz) spectra of a solution containing approximately equimolar amounts of 12 and 13.

The proposed composition of this new complex, 15, is partially based on integration data that shows the relationship between these three peaks. Table 3.4 lists these values. Namely, the relative integration ratio of A$_{15}$:B$_{15}$:C$_{15}$ was found to be 2:4:4. This is consistent for a complex containing one pyridine ligand (2 o-H for each pyridine), two NPN ligands (2 o-H for each P-phenyl) and one THF ligand (4 H per THF). To verify this approach, the integration values for peaks corresponding to 12 and 13 were also determined and found to
have relative ratios that are in agreement with the composition of those complexes. The ratio of \( \text{B}_{12}:\text{C}_{12} \) is 4:8, which is consistent with a 1:1 ratio of NPN ligand to THF for \( \text{12} \). Likewise, the ratio of \( \text{A}_{13}:\text{B}_{13} \) is 4:4, which is consistent with one pyridine ligand for each NPN ligand in \( \text{13} \).

### Table 3.4. Relative Integration Values for a Solution Containing Complexes 12, 13 and 15

<table>
<thead>
<tr>
<th>Complex</th>
<th>Peak label in Figure 3.3</th>
<th>Resonance, ( \delta_H )</th>
<th>Protons/1 equiv. of complex</th>
<th>Integration value(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>( \text{B}_{12} )</td>
<td>7.98</td>
<td>4H, o-H P-phenyl</td>
<td>70</td>
</tr>
<tr>
<td>12</td>
<td>( \text{C}_{12} )</td>
<td>3.22</td>
<td>8H, 2,5-H THF</td>
<td>133</td>
</tr>
<tr>
<td>13</td>
<td>( \text{A}_{13} )</td>
<td>8.72</td>
<td>4H, o-H pyridine</td>
<td>40</td>
</tr>
<tr>
<td>13</td>
<td>( \text{B}_{13} )</td>
<td>8.27</td>
<td>4H, o-H P-phenyl</td>
<td>42</td>
</tr>
<tr>
<td>15</td>
<td>( \text{A}_{15} )</td>
<td>8.60</td>
<td>2H, o-H pyridine</td>
<td>47</td>
</tr>
<tr>
<td>15</td>
<td>( \text{B}_{15} )</td>
<td>8.14</td>
<td>4H, o-H P-phenyl</td>
<td>101</td>
</tr>
<tr>
<td>15</td>
<td>( \text{C}_{15} )</td>
<td>3.33</td>
<td>4H, 2,5-H THF</td>
<td>104</td>
</tr>
</tbody>
</table>

\(^a\)Integration values were referenced to the complex of lowest concentration in solution, which was found to be \( \text{13} \). The resonance due to o-H pyridine for \( \text{13} \) was set to a convenient value of 40 (assuming one equivalent of \( \text{13} \) is present, which would give an integrated value of 4 for this particular resonance). Resonances corresponding to analogous protons, but observed in two different complexes, were integrated over the same ppm-range (e.g., the resonance for THF in \( \text{12} \) and in \( \text{15} \) were each integrated over a total range of 0.13 ppm).

The integration data from the \(^1\text{H} \) NMR spectrum can also be used to estimate the relative amount of each complex in solution. The parameters used to integrate each peak for a particular type of resonance were the same and the resulting values are all relative to \( \text{A}_{13} \). An equimolar solution of \( \text{12} \) and \( \text{13} \) would be expected to have a 1:1 ratio of o-H P-phenyl protons (\( \text{B}_{12} \) and \( \text{B}_{13} \)) since both complexes possess two NPN ligands. However, the value for \( \text{B}_{12} \) is almost double that of \( \text{B}_{13} \), which is the first indication of an equilibrium shift occurring in solution that disfavours \( \text{13} \). If the proposed composition of \( \text{15} \) is correct, \( \text{B}_{15} \) can be
directly compared to \( B_{12} \) and \( B_{13} \) since all three complexes contain two NPN ligands and therefore the same number of \( o-H \) P-phenyl protons (B). Based on these values, the relative amounts of each complex in solution is 101 (\( B_{15} \)): 70 (\( B_{12} \)): 42 (\( B_{13} \)). Similar comparisons made between \( A_{13} \) and \( A_{15} \) (or \( C_{12} \) and \( C_{15} \)) yield similar results: the predominant species in solution is \( 15 \).

The \(^{31}\text{P}\{^1\text{H}\} \) NMR spectrum of the mixture (Figure 3.3) consists of two singlets with what appear to be shoulder peaks. These shoulder peaks are from the two different \(^{31}\text{P}\)-environments in \( 15 \) and overlap slightly with those for \( 12 \) and \( 13 \). Additional evidence for \( 15 \) can be seen in the mass spectrum for a slightly impure sample of \( 13 \). The parent ion for \( 13 \) is observed at 1235 m/z and a fragment at 1231 m/z is also apparent in the spectrum, which corresponds to \([M^+]\) for \( 15 \). No further attempts were made to isolate \( 15 \). The geometry of \( 15 \) is presumed to be similar to that of complexes \( 12 \) and \( 13 \); the donor ligands, THF and py, likely adopt a \textit{trans}-conformation to each other with respect to the centre of the molecule.

![Scheme 3.4](image)

The discovery of complex \( 15 \) adds a new facet to the equilibrium between \( 12 \) and \( 13 \), as originally presented in Equation 3.3. Scheme 3.4 depicts an equilibrium where \( 15 \) acts as an intermediate for the reversible conversion of \( 12 \) to \( 13 \). The NMR experiment revealed that THF and pyridine ligands of \( 12 \) and \( 13 \), respectively, are labile in solution; furthermore, an external source for THF or pyridine is not necessary for the formation of \( 15 \). In agreement
with previous observations, the removal of excess THF (or the addition of pyridine) drives
the reaction toward the formation of 15 and 13. Removal of all the THF in solution then
ensures that 13 can be isolated. Addition of THF to 13 results in the formation of 15 and 12;
however, the higher boiling point of pyridine, compared to THF, prevents it from being
completely removed from the solution. As a result, the regeneration of 12 from 13 should
produce a mixture of all three complexes. Examination of the NMR for that experiment
confirmed the presence of 15, in addition to 13.

3.5 Reactivity of Complexes 12 and 13

In Chapter 2, the reactivity of the N₂ moiety in complex 1 with arylalkynes was
presented. Previous work with 1 has shown that the N₂ ligand in this complex can react with
H₂ or "BuSiH₃ to form new N-H or N-Si bonds, respectively.25,27 The Zr dinitrogen
complexes 12 and 13 differ from 1 in that they possess a smaller amidophosphine ligand
(NPN vs. P₂N₂) and have labile donor ligands (THF and pyridine) that dissociate in solution.
The reactivity of 12 and, to a lesser extent, that of 13 was investigated to see if these changes
would promote the functionalization of dinitrogen.

Exposing a solution of 12 to hydrogen gas (4 atm) did not result in any visible
reaction over several weeks. The solution remained purple and multinuclear NMR spectra of
the residues confirmed that no reaction had taken place. Complex 13 was prepared in situ
and exposed to similar conditions. A slight change in colour from dark green to olive green
was observed after a few days with the concomitant formation of a cream coloured
precipitate. However, a green precipitate was isolated from the reaction mixture, which was
determined to be 13 by NMR spectroscopy. The green filtrate contained many products of
which only 13 and [NPN]H₂ could be identified by ³¹P{¹H} and ¹H NMR spectroscopy.
Further isolation of these products was not attempted.

Complex 12 was also reacted with (p-methyl)phenylacetylene in an attempt to
generate an NPN analogue of complex 8 (Chapter 2). A colour change was observed
immediately upon addition of the alkyne. The NMR data confirms that all of the starting
complex, 12, was consumed in the formation of several products. Repeating the reaction with
Chapter 3: Synthesis and Reactivity of \((\text{NPN}\text{Zr}Y)_{2}(\mu-\eta^{2}:\eta^{2}-\text{N}_{2})\), where \(Y = \text{THF, Pyridine, Benzonitrile}\)

one equivalent of alkyne resulted in the formation of the same products and residual 12, which had not reacted. Attempts made to isolate these products by crystallization were unsuccessful.

Similar observations were made when 12 was reacted with allene and borane-THF. A dark red solution formed within minutes of exposing 12 to either reagent; however, the numerous resulting products could not be isolated. Complex 12 also reacts with each of acetonitrile, phenylsilane, and \(n\)-butylsilane to form a brown solution. In all cases, the products were intractable.

In contrast, 12 did not undergo any transformation when exposed to triethylamine or ethylene. However, the accumulation of white precipitate in the latter reaction suggests that 12 facilitated the oligomerization or polymerization of ethylene. The dinitrogen complex was fully recovered from both reactions.

Although 12 and 13 undergo transformations when exposed to certain reagents, the reactivity of the \(\text{N}_{2}\) moiety in these complexes is uncertain.

3.6 Reduction of \([\text{NPN}]\text{ZrCl}_{2}(\text{THF})\), 11, under Various Conditions

The reduction of \([\text{NPN}]\text{ZrCl}_{2}(\text{THF})\), 11, with KC\(_8\) was explored in various solvents and under different atmospheres (Ar, H\(_2\) or \(\text{in vacuo}\)). The objective of these experiments was to determine whether other Zr dinitrogen complexes, in addition to 12, would form as a result of the reduction process.

When THF is used as a solvent for the reduction of 11, complex 12 is the major product. However, additional resonances are occasionally present in the \(^{31}\text{P}\{\text{\(^{1}\text{H}\)}\}\) NMR spectrum of the resulting crude reaction mixture. When the reaction was repeated under an Ar atmosphere, these particular signals are much larger. Given that these products can form even in the absence of \(\text{N}_{2}\), they are likely not a result of the activation of \(\text{N}_{2}\). This indicates that when the reduction of 11 under \(\text{N}_{2}\) is performed in THF only one dinitrogen complex, 12, is produced.

Different solvents were employed in the reduction of 11 to see if this would facilitate the formation of other dinitrogen complexes. When toluene was used, several products
resulted, including a trace amount of 12. The major products formed in this reaction were also produced when the reaction was carried out under an Ar atmosphere. These results suggest that no new N\textsubscript{2} containing products had formed. In particular, there was no evidence for the formation of an adduct free complex, such as ([NPN]Zr\textsubscript{2}(N\textsubscript{2}). Similar results were obtained when diethyl ether was used as the solvent. Namely, the presence of a trace amount of 12 is evident as a small singlet in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, along with a few of the same resonances that were observed in the spectrum obtained for the toluene reduction reactions. Using pyridine, or a 1:1 mixture of pyridine and THF, as the solvent in the reduction of 11 under an N\textsubscript{2} atmosphere did not result in the formation of 12, 13 or even 15. The products that formed, however, were also present in the reaction mixture resulting from the reduction of 11 in pyridine under static vacuum (based on $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy). Pyridine, or a mixture of pyridine and THF, is clearly not an effective solvent for the formation of a dinitrogen complex under these reducing conditions.

These experiments suggest that 12 is the only dinitrogen-containing product formed by the reduction of 11 in any solvent under a dinitrogen atmosphere. Further, an excess of THF is necessary to produce 12 in high yield. This is apparent when only a quantitative amount of THF, from 11, is available in the reaction mixture. In such a case, only a small amount of 12 is formed.

### 3.7 Summary and Conclusions

In this chapter, the chemistry of the NPN ligand with Zr for the activation of N\textsubscript{2} was presented. Complex 11, [NPN]ZrCl\textsubscript{2}(THF), can be reduced under N\textsubscript{2} to form a dinitrogen complex, 12, in which the N\textsubscript{2} moiety is bound between the two Zr centres in a side-on fashion.

The conditions for preparing 12, ([NPN]ZrTHF)\textsubscript{2}(\mu-\eta^{2}::\eta^{2}-N\textsubscript{2}), have been optimized. The yield of 12 increases significantly when THF is the solvent used during the reduction of 11. The selective formation of 12 is not dependent on the pressure of N\textsubscript{2} in the reaction vessel during the reduction. Rather, the introduction of N\textsubscript{2} to a very cold solution of 11 and the reducing agent, KC\textsubscript{8}, ensures the resulting high purity of 12.
In solution, the THF donor ligands of 12 are labile and dissociate from the complex. This characteristic has allowed for the isolation of 13, ([NPN]Zrpy)2(μ-η2:η2-N2), following the addition of pyridine to 12. Similarly, the pyridine ligands of 13 are also labile and 12 can be regenerated, to some degree, with the addition of THF. The dissociative nature of these donor ligands is not apparent on the NMR timescale. Namely, the 1H NMR spectra of 12 and 13 suggest that these ligands remain coordinated to Zr in their respective complexes in solution. However, NMR spectra of a solution containing a mixture of 12 and 13 have shown that a third complex, 15, acts as an intermediate in this conversion. Spectroscopic evidence suggests that both 12 and 13 can be converted to 15, ([NPN]ZrTHF)(μ-η2:η2-N2)(pyZr[NPN]). In a closed system, 15 is the favoured species in solution, which is a result of an equilibrium involving all three complexes. However, the removal of solvent from a solution containing an excess of pyridine shifts the equilibrium such that 13 can be prepared quantitatively. The addition of benzonitrile to 12 is also believed to result in the replacement of THF donor ligands to produce ([NPN]Zr[PhCN])2(μ-N2), 14. Further experiments are necessary to definitively determine the structure of 14.

The long bond length for N2 in 12 and 13 (1.503(3)Å and 1.503(2)Å, respectively) implies that dinitrogen has been activated and may be susceptible to further reactivity. Although complexes 12 and 13 are consumed in some reactions, there is no clear evidence to support the functionalization of the N2 ligand. Without the ability to isolate these products, the reactivity of bound N2 in these complexes remains speculative. The reactivity of 12 (or 13) is drastically different than that observed for 1 and serves to demonstrate the critical role that the ligands play in the functionalization of coordinated N2.
Chapter 3: Synthesis and Reactivity of ([NPN]ZrY)_2(μ-η^1:η^1-N_2), where Y = THF, Pyridine, Benzonitrile

3.8 Experimental

3.8.1 General Procedures

Unless otherwise stated, solvents used in KC_8 reduction reactions were degassed by three freeze-pump-thaw cycles immediately prior to use and all other general procedures are the same as those found in Section 2.8.1.

3.8.2 Materials

Anhydrous pyridine was dried by refluxing over CaH_2, then decanted into another flask and distilled under a dinitrogen atmosphere. The phenylacetylene compound, (p-methyl)phenylacetylene, was distilled, degassed and stored over molecular sieves in the dark. Benzonitrile and acetonitrile were distilled and degassed prior to use. The borane(THF) 1.0M solution and triethylamine were used without further purification. Ethylene, allene and hydrogen gases were purchased (Praxair or Matheson) and used without further purification. Phenylsilane and n-butylsilane had been previously synthesized by a colleague using literature methods. Potassium graphite, KC_8, ZrCl_4(THF)_2, and [NPN]Li_2(THF)_2 were prepared according to reported literature methods.

3.8.3 Synthesis and Characterization of Complexes 11, 12, 13 and 14

Synthesis and Characterization of [NPN]ZrCl_2(THF), 11

Complex 11 was first isolated by Dr. Peihua Yu, of this research group. The procedure, reported here, has been significantly optimized from the original.

A sample of [NPN]Li_2(THF)_2 (3.435 g, 5.795 mmol) was transferred to a thick-walled flask, fitted with a Kontes valve. Toluene (50 mL) was added and the slurry was stirred until the white powder fully dissolved. A sample of ZrCl_4(THF)_2 (2.290 g, 6.071 mmol) was added to the toluene solution. Alternatively, the two powders could be mixed together prior
to adding toluene. The headspace was evacuated and the pale-yellow/orange slurry was heated to ~60°C and stirred for a minimum of 24 hours. The flask was allowed to cool and the cream coloured slurry was filtered through a scinted-glass crucible containing Celite. The resulting clear, pale yellow solution was concentrated by removing much of the solvent in vacuo. With the addition of hexanes (~15mL), a white powder precipitated out of the solution. The creamy-yellow powder, 11, was collected immediately and dried on a scinted-glass crucible by vacuum filtration. The product was isolated without the need for further purification. Yield 2.6 g, 68%. More product was recovered from the yellow filtrate by completely removing the solvent in vacuo and washing the residues repeatedly with hexanes.

\(^1\)H NMR (C\(_6\)D\(_6\), 300 MHz): \(\delta -0.11 \) (s, 6H, SiCH\(_3\)), 0.25 (s, 6H, SiCH\(_3\)), 0.87 (m, 4H, 3,4-H THF), 1.44 (m, 2H, CH\(_2\)), 1.48 (m, 2H, CH\(_2\)), 3.35 (m, 4H, 2,5-H THF), 6.84 (m, 2H, phenyl), 7.11 (m, 5H, phenyl), 7.22 (m, 2H, phenyl), 7.59 (m, 4H, phenyl), 8.28 (m, 2H, o-H P-phenyl)

\(^31\)P(\(^1\)H) NMR (C\(_6\)D\(_6\), 121 MHz): \(\delta 1.67 \) (s)

Synthesis and Characterization of ([NPN]ZrTHF)\(_2\)(μ-η\(^2\):η\(^2\)-N\(_2\)), 12

Complex 12 was first synthesized by Dr. Peihua Yu of this research group. The procedure, reported here, has been slightly modified from the original.

A thick-walled flask fitted with a Kontes valve was charged with [NPN]ZrCl\(_2\)(THF), 11, (1.050 g, 1.570 mmol) and KC\(_8\) (0.437 g, 3.23 mmol) under an inert atmosphere. The reaction flask was then connected through a vacuum-transfer tube to another flask, also fitted with a Kontes valve, which contained degassed THF (~75 mL). The contents of the reaction flask were placed under vacuum and stirred for 5-10 minutes. Degassed THF was added to the reaction flask by a trap-to-trap transfer under static vacuum at -196°C. After transferring all of the solvent the liquid nitrogen bath was removed and the reaction flask was warmed to -78°C (IPA/CO\(_2\) bath) under a constant flow of N\(_2\) (1 atm), while the contents were gently stirred. Once the solvent had completely melted, the flask was closed to N\(_2\) and the resulting brown slurry was stirred vigorously. The cold temperature was maintained for another 4-5
hours before the slurry was warmed to room temperature and a colour change from brown to
dark purple was observed. The dark purple slurry was stirred for another 24-48 hours. The
reaction mixture was quickly filtered through Celite on a scinttered-glass crucible and the
solvent was removed in vacuo. A dark purple powder, 12, was collected from the residues.
Yield 0.84 g, 87%.

A mixture of products resulted from the reduction of 11 if the slurry was not stirred
vigorously while warming to room temperature. A maroon coloured product and additional
peaks in the $^{31}P\{^1H\}$ NMR spectrum indicates the presence of these impurities. The desired
complex may be isolated, if necessary, by dissolving the crude solids in hexanes and allowing
12 to precipitate out of the slowly evaporating solution over several weeks.

Anal. Calcd. for C$_{56}$H$_{78}$N$_6$O$_2$P$_2$Si$_4$Zr$_2$: C, 54.95; H, 6.42; N, 6.87. Found: C, 54.66; H, 6.47;
N, 6.65

EI-MS $m/z$: 1080 [([NPN]$_2$Zr$_2$N$_2$)$_+]$

$^1H$ NMR (C$_6$D$_6$, 300 MHz): $\delta$ 0.15 (s, 12H, SiCH$_3$), 0.55 (br s, 20H, SiCH$_3$ and 3,4-H
THF), 1.44 (m, 4H, CH$_2$), 1.66 (m, 4H, CH$_2$), 3.21 (br m, 8H, 2,5-H THF), 6.75 (m, 4H, m-H
P-phenyl), 6.98 (m, 10H, phenyl), 7.13 (m, 12H, phenyl), 7.98 (m, 4H, o-H P-phenyl)

$^{31}P\{^1H\}$ NMR (C$_6$D$_6$, 121 MHz): $\delta$ −5.57 (s)

Synthesis and Characterization of ([NPN]Zrpy)$_2$(µ-η$^2$·η$^2$-N$_2$), 13: Reaction of 12 with
Pyridine

A 0.041 M solution of pyridine was prepared by transferring neat pyridine (0.162 g,
2.05 mmol) into a 50.00 mL volumetric flask and filling the flask to volume with toluene. A
sample of ([NPN]ZrTHF)$_2$(µ-η$^2$·η$^2$-N$_2$), 12, (0.105 g, 0.0860 mmol) was transferred to an
Erlenmeyer flask and dissolved in a minimal amount of toluene (~15 mL). A sample of the
pyridine solution (4.60 mL, 0.189 mmol, 2.2 equivalents) was added to the dark purple
solution of 12 by syringe. An instantaneous colour change to dark green was observed. The
green solution was swirled and the solvent was removed immediately in vacuo. A green
powder, 13, was collected from the residues. Alternatively, adding a large excess of neat
pyridine produced the same results. Yield 0.10 g, 94%. Crystals suitable for X-ray diffraction
were grown from the slow evaporation of a concentrated toluene solution of 13. The NMR spectra of the green powder and of the crystals are identical. Attempts to obtain a satisfactory elemental analysis were unsuccessful.

Anal. Calcd. for C_{58}H_{72}N_8P_2Si_4Zr_2: C, 56.27; H, 5.86; N, 9.05. Found: C, 57.44; H, 6.22; N, 7.71. EI-MS m/z: 1235 [M^+], 1231 [([NPN]_2Zr_2THFpyN_2)^+], 1080 [([NPN]_2Zr_2N_2)^+]

\( ^1H \) NMR (C_6D_6, 300 MHz): δ 0.09 (s, 12H, SiCH_3), 0.61 (s, 12H, SiCH_3), 1.48 (m, 4H, CH_2), 1.82 (m, 4H, CH_2), 5.94 (m, 4H, \( m \)-H pyridine), 6.51 (m, 6H, \( m \)-H P-phenyl and \( p \)-H pyridine), 6.87 (m, 10H, phenyl), 6.98 to 7.14 (m, 12H, phenyl), 8.25 (m, 4H, \( o \)-H P-phenyl), 8.70 (m, 4H, \( o \)-H pyridine)

\( ^31P\{^1H\} \) NMR (C_6D_6, 121 MHz): δ −6.55 (s)

Synthesis and Characterization of ([NPN]Zr(PhCN))_2(\( \mu \)-N_2), 14: Reaction of 12 with Benzonitrile, PhCN

A toluene solution of benzonitrile (0.0595 M, 2.88 mL, 0.174 mmol) was transferred by syringe to an Erlenmeyer flask containing a solution of 12 (0.105 g, 0.0858 mmol) in toluene. A colour change from dark purple to a dark red-brown solution was observed immediately. After 2 days the solution was orange-brown in colour and was allowed to stand for another week. Toluene was removed in vacuo and NMR spectra of the residues were obtained. Attempts to grow crystals of the product, formed in situ, from toluene were unsuccessful. Crude yield 0.085 g, 77% (for the predicted product 14, ([NPN]Zr[PhCN])_2(\( \mu \)-N_2)).

EI-MS m/z: 1284 [M^+], 1255 [([NPN]_2Zr_2THF(PhCN)N_2)^+], 1183 [([NPN]_2Zr_2(PhCN)N_2)^+], 1080 [([NPN]_2Zr_2N_2)^+]

\( ^1H \) NMR (C_6D_6, 300 MHz): δ −0.17 (s, 3H, SiCH_3), −0.10 (s, 3H, SiCH_3), −0.04 (s, 3H, SiCH_3), 0.09 (s, 3H, SiCH_3), 0.18 (s, 3H, SiCH_3), 0.22 (s, 3H, SiCH_3), 0.27 (s, 6H, SiCH_3), 0.86 (m, 4H, CH_2), 1.24 (m, 4H, CH_2), 6.58 to 7.38 (overlapping m, 32H, phenyl), 7.60 (m, 4H, phenyl), 8.06 (m, 2H, \( o \)-H phenyl), 8.93 (m, 2H, \( o \)-H phenyl)

\( ^31P\{^1H\} \) NMR (C_6D_6, 121 MHz): δ −8.34 (s)

(i) Addition of Excess THF to ([NPN]Zrpy)$_2$(μ-η$^2$:η$^2$-N$_2$), 13, for the Regeneration of ([NPN]ZrTHF)$_2$(μ-η$^2$:η$^2$-N$_2$), 12

A dark purple solution was formed when a sample of solid, green 13 (0.0300 g, 0.0242 mmol) was dissolved in THF (10 mL). The solvent was immediately removed in vacuo and the purple residues were dissolved in d$_6$-benzene for NMR analysis. The $^1$H NMR spectrum of the purple residue is complicated by many overlapping broad resonances. However, a large resonance at 3.58 ppm indicates that a large excess of free THF was still present in the sample. There are two major resonances in the $^{31}$P{$^1$H} NMR spectrum: the largest is due to the presence of 12 and the other resonance is assigned to 13 (which is approximately half the size, by integration, of 12). Resonances that are nearly coincident with those for 12 and 13 are believed to belong to the intermediate, 15, and are observed as shoulder peaks and presumed to be singlets.

$^{31}$P{$^1$H} NMR (C$_6$D$_6$, 121 MHz): δ −22.45 (s, unknown), −11.98 (s, unknown), −6.59 (s, 15), −6.55 (s, 13), −5.61 (s, 15), −5.57 (s, 12), −0.84 (s, unknown)

(ii) Dissociation of Pyridine and THF in a Solution Containing a Mixture of ([NPN]ZrTHF)$_2$(μ-η$^2$:N$_2$), 12, and ([NPN]Zrpy)$_2$(μ-η$^2$:N$_2$), 13

A d$_6$-benzene solution of 13 (0.0136 g, 0.0110 mmol in 0.060 mL C$_6$D$_6$) was transferred to a vial containing 12 (0.0166 g, 0.0136 mmol). The resulting dark purple-blue solution was mixed well to ensure all of 12 had dissolved prior to transferring the solution to an NMR tube. The $^{31}$P{$^1$H} and $^1$H NMR spectra confirm the presence of all three of the complexes, 12, 13 and 15, in the sample. Resonances in the $^{31}$P{$^1$H} NMR spectrum that are nearly coincident with those for 12 and 13 are believed to belong to the intermediate, 15, and are presumed to be singlets. A comparison of various peaks in the $^1$H NMR spectrum
sugests that a larger amount of 15 was present in the sample than either 12 or 13. For relative integrals of the relevant signals, refer to Table 3.4.

**1H NMR (C₆D₆, 300 MHz):**
- δ 0.09 (s, SiCH₃ of 13), 0.15 (s, SiCH₃ of 12), 0.55 (s, SiCH₃ and 3,4-H THF of 12), 0.56 (s, SiCH₃ of 15), 0.61 (s, SiCH₃ of 13), 1.45 (br m, CH₂ of 12, 13 and 15), 1.74 (br m, CH₂ of 12, 13 and 15), 3.22 (br m, 2,5-H THF of 12), 3.33 (br m, 2,5-H THF of 15), 5.90 (br m, pyridine and P-phenyl of 13 and 15), 6.51 (br m, pyridine and P-phenyl of 13 and 15), 6.76 (br m, phenyl of 12), 6.81 to 7.23 (overlapping m, phenyl of 12, 13 and 15), 7.98 (m, o-H P-phenyl of 12), 8.14 (overlapping m, o-H P-phenyl of 15), 8.27 (m, o-H P-phenyl of 13), 8.60 (m, o-H pyridine of 15), 8.72 (m, o-H pyridine of 13)

**31P{1H} NMR (C₆D₆, 121 MHz):**
- δ -6.59 (s, 15), -6.55 (s, 13), -5.61 (s, 15), -5.57 (s, 12)

### 3.8.5 Reactivity of Complexes ([NPN]ZrTHF)₂(μ-η²:η²-N₂), 12, and ([NPN]Zrpy)₂(μ-η²:η²-N₂), 13

All NMR data reported in this section were recorded on a Bruker AV-300 instrument operating at 300.1 MHz for ¹H NMR spectra and 121 MHz for ³¹P{¹H} NMR spectra.

#### Attempted Hydrogenation of 12 and 13

(i) Complex 12 (0.360 g, 0.294 mmol) was dissolved in toluene (25 mL) and transferred to a thick-walled flask fitted with a Kontes valve. The dark purple solution was degassed by three freeze-pump-thaw cycles. The flask was immersed in a liquid nitrogen bath (-196°C) and H₂ (1 atm) was introduced to the sample. The flask was closed, and slowly warmed to room temperature behind a blast-shield. The purple solution was stirred over a period of 3-4 weeks and no visible colour change was observed. After venting the pressure within the flask (~4 atm H₂), the solvent was removed and the purple residues were isolated. The ³¹P{¹H} and ¹H NMR spectra of the residues are identical to those of 12, indicating that no reaction took place.
(ii) A solution of 13 (with a small amount of 12) was prepared *in situ* by dissolving 12 (0.0991 g, 0.0810 mmol) in hexanes (10 mL) and adding an excess of pyridine (0.0249 g, 0.315 mmol). The dark green solution was transferred to a thick-walled flask equipped with a Kontes valve. The solution was degassed by three freeze-pump-thaw cycles prior to introducing $\text{H}_2$ (1 atm) into the flask, which was immersed in a liquid nitrogen bath ($-196^\circ\text{C}$). The flask was closed, and slowly warmed to room temperature behind a blast-shield. After 5 days of stirring, the solution appeared olive green and a cream coloured precipitate was observed. The pressure ($\sim$4 atm $\text{H}_2$) within the flask was vented and the solution was exposed to a dinitrogen atmosphere. A green precipitate was collected on a scinttered-glass crucible and solvent was removed from the green filtrate, leaving green residues. The hexane-insoluble, green precipitate dissolved easily in a $d_6$-benzene/$d_8$-toluene mixture. The green-filtrate residues dissolved in $d_6$-benzene. The $^{31}\text{P}\{^1\text{H}\}$ and $^1\text{H}$ NMR spectra of the green precipitate are identical to those of ([NPN]Zrpy)$_2$(μ-$\eta^2$:$\eta^2$-N$_2$), 13. The $^{31}\text{P}\{^1\text{H}\}$ and $^1\text{H}$ NMR spectra of the green residues from the filtrate indicate the presence of many products. However, the largest resonances in the $^{31}\text{P}\{^1\text{H}\}$ NMR may be assigned to [NPN]H$_2$ and 13.

**NMR Scale Reactions of ([NPN]ZrTHF)$_2$(μ-$\eta^2$:$\eta^2$-N$_2$), 12, with Acetonitrile (CH$_3$CN), Phenylsilane (PhSiH$_3$), and n-Butylsilane ($^n$BuSiH$_3$), Triethylamine (NEt$_3$), Ethylene (CH$_2$CH$_2$)**

The addition of a liquid to 12 was carried out using the following procedure: An excess of nitrile/silane/amine (3 drops, 0.06 mL) was added to a vial containing a solution of 12 (0.030 g, 0.025 mmol) in $d_6$-benzene (0.5 mL). In each case, for the addition of CH$_3$CN, PhSiH$_3$, and $^n$BuSiH$_3$, a colour change from purple to varying shades of brown was observed. The $^{31}\text{P}\{^1\text{H}\}$ and $^1\text{H}$ NMR spectra of these samples indicate that 12 was consumed and several unknown products were formed. The sample containing NEt$_3$ did not change colour and the $^{31}\text{P}\{^1\text{H}\}$ and $^1\text{H}$ NMR spectra confirm that 12 was unchanged.

For the reaction of 12 with ethylene, a $d_6$-benzene solution of 12 (0.030 g, 0.025 mmol) was transferred to a sealable NMR tube fitted with a Kontes valve adaptor. The sample was degassed by three freeze-pump-thaw cycles prior to the addition of ethylene.
(1 atm) at room temperature. The NMR tube was sealed and the contents were mixed by continuously inverting the tube over 2 days (motorized rotation). The solution remained purple, however, a white precipitate accumulated in the tube over a period of weeks. The $^{31}$P{$^1$H} spectrum confirms that 12 was unchanged. The white precipitate is presumed to be polyethylene and was not further characterized.

**Reaction of ([NPN]ZrTHF)$_2$(μ-η$^2$:η$^2$-N$_2$), 12, with (p-methyl)phenylacetylene**

An aliquot of a p-methylphenylacetylene solution (0.0613 M in toluene, 0.80 mL, 0.049 mmol) was transferred by syringe to a flask containing a sample of 12 (0.030 g, 0.025 mmol) dissolved in toluene (10 mL). A colour change from purple to wine-red was observed within minutes of the addition. After stirring for 3 days, the solution was dark red-orange. Toluene was removed in vacuo. The $^{31}$P{$^1$H} and $^1$H NMR spectra of the residues indicate the presence of several products and the absence of 12. The reaction was repeated with one equivalent of alkyne and the same resonances, in addition to 12, are seen in the $^{31}$P{$^1$H} NMR spectrum of these residues. Attempts to separate products by crystallization were unsuccessful.

**Reaction of ([NPN]ZrTHF)$_2$(μ-η$^2$:η$^2$-N$_2$), 12, with Allene (CH$_2$CCH$_2$)**

A toluene (30 mL) solution of 12 (0.246 g, 0.201 mmol) in a flask fitted with a Kontes valve was degassed by three freeze-pump-thaw cycles. The flask was placed in an ice water bath while allene (<1 atm) was introduced to the solution. The solution was stirred under a flow of allene for 30-40 minutes. The purple solution changed to a dark red colour within 10 minutes of exposure to allene. The flask was sealed and stirred overnight before removing the solvent in vacuo. The $^{31}$P{$^1$H} and $^1$H NMR spectra of the maroon residues reveal that 12 is absent from a mixture of multitudinous products.
Chapter 3: Synthesis and Reactivity of ([NPN]ZrY)$_2$(μ-η$_2^2$:η$_2^2$-N$_2$), where Y = THF, Pyridine, Benzonitrile

Reaction of ([NPN]ZrTHF)$_2$(μ-η$_2^2$:η$_2^2$-N$_2$), 12, with Borane-THF, (BH$_3$-THF)

A sample of BH$_3$(THF) (1.0 M, 0.30 mL, 0.30 mmol) was transferred by syringe to a flask containing a toluene (10 mL) solution of 12 (0.0988 g, 0.0807 mmol). The purple solution became a dark maroon within minutes and dark orange after 24 hours. Toluene was removed in vacuo. The $^1$H NMR spectrum of the residues is difficult to interpret due to many overlapping broad resonances.

$^{31}$P{$^1$H} NMR (C$_6$D$_6$, 81 MHz): δ -4.83 (s, unknown), -3.12 (s, unknown), 9.03 (br s, largest by integration, unknown)

Reaction of ([NPN]ZrTHF)$_2$(μ-η$_2^2$:η$_2^2$-N$_2$), 12, with H$_2$O

Distilled water was degassed by passing a stream of N$_2$(g) through the water, for approximately 1 hour, as it was boiled. Water (3.0 μL, 0.17 mmol) was then transferred by syringe to a toluene (15 mL) solution of 12 (0.108 g, 0.0882 mmol). An immediate colour change to yellow was observed. The solvent was removed in vacuo and the residues were extracted into d$_6$-benzene. Resonances in the $^1$H NMR spectrum correspond to those expected for [NPN]H$_2$.

$^{31}$P{$^1$H} NMR (C$_6$D$_6$, 121 MHz): δ -36.80 (s, [NPN]H$_2$), -16.46 (s, unknown)
3.8.6 Reduction of \([\text{NPN}]\text{ZrCl}_2(\text{THF}), 11,\) under Different Conditions

The procedure outlined in 3.8.3 for the synthesis of \([(\text{NPN})\text{ZrTHF}_2(\mu-\eta^2\cdot\text{N}_2)], 12,\) was used with minor changes noted for the following reductions. The details of the reduction reaction, in different solvents and in the presence or absence of \(\text{N}_2,\) are given below.

Reduction of \([\text{NPN}]\text{ZrCl}_2(\text{THF}), 11,\) with \(\text{KC}_8\) under an Atmosphere of \(\text{N}_2\) with Various Solvents:

(i) Reduction in Toluene: Toluene (50 mL) was degassed by one freeze-pump-thaw cycle and added by vacuum transfer to a thick-walled flask containing \([\text{NPN}]\text{ZrCl}_2(\text{THF})\) (0.532 g, 0.795 mmol) and \(\text{KC}_8\) (0.215 g, 1.59 mmol). The frozen reaction mixture (−196°C) was exposed to \(\text{N}_2\) (1 atm), and then sealed after 5-10 minutes. The mixture was warmed to room temperature and stirred for an additional 12-36 hours. The pressure (~4 atm) within the flask was vented and the dark brown-yellow slurry was filtered through Celite. The solvent was removed \textit{in vacuo}. The \(^{31}\text{P}\{\text{^1H}\}\) NMR spectrum of the brown residues indicate the presence of many products. The \(^1\text{H}\) NMR spectrum of the sample is complicated by the presence of many overlapping and indistinguishable resonances.

\(^{31}\text{P}\{\text{^1H}\}\) NMR (\(\text{C}_6\text{D}_6, 121 \text{ MHz}\)): (largest and/or known resonances only) \(\delta -11.46\) (d, \(J_{PP} = 34 \text{ Hz}, \text{unknown})\), \(-7.10\) (d, \(J_{PP} = 34 \text{ Hz}, \text{unknown})\), \(-5.80\) (s, unknown), \(-5.56\) (s, likely a small amount of \([(\text{NPN})\text{ZrTHF}_2(\mu-\eta^2\cdot\text{N}_2)], 12,\)), 0.02 (s, unknown)

(ii) Reduction in Ether: Degassed diethyl ether (40 mL) was added by vacuum transfer to a thick-walled flask containing \([\text{NPN}]\text{ZrCl}_2(\text{THF})\) (0.265 g, 0.395 mmol) and \(\text{KC}_8\) (0.112 g, 0.829 mmol). The reaction was carried out as (i) above. After 36 hours, the solvent was removed \textit{in vacuo}. The dark green-brown residues were extracted into toluene and filtered through Celite. Toluene was removed \textit{in vacuo}. The \(^{31}\text{P}\{\text{^1H}\}\) and \(^1\text{H}\) NMR spectra of the residues indicate the presence of many products.
Chapter 3: Synthesis and Reactivity of \((\text{[NPN]ZrY})_2(\mu-\eta^2:-N_2)\), where \(Y = \text{THF, Pyridine, Benzonitrile}\)

\(^{31}\text{P}{^1\text{H}}} \text{NMR} \ (\text{C}_6\text{D}_6, \ 121 \text{ MHz}): \text{ (largest and/or known resonances only) } \delta -21.01 \text{ (s, unknown), } -20.70 \text{ (s, unknown), } -5.80 \text{ (s, unknown), } -5.56 \text{ (s, likely a trace amount of (}[\text{NPN}]\text{ZrTHF})_2(\mu-\eta^2-N_2), 12), -0.01 \text{ (s, unknown), 2.80 (s, unknown)}

(iii) Reduction in Pyridine: Pyridine (40 mL) was degassed by one freeze-pump-thaw cycle and added by vacuum transfer to a thick-walled flask containing \([\text{NPN}]\text{ZrCl}_2(\text{THF}) \) (0.270 g, 0.404 mmol) and \(\text{KC}_8 \) (0.115 g, 0.849 mmol). The frozen reaction mixture \((-196^\circ\text{C})\) was flushed with \(\text{N}_2 \) (1 atm), and transferred to an IPA/\(\text{CO}_2\) bath \((-78^\circ\text{C})\) before sealing the flask. The frozen mixture was warmed to room temperature and stirred for 12 hours. Pyridine was removed \text{in vacuo} and the resulting purple-red residues were extracted into toluene and filtered through Celite. Toluene was removed \text{in vacuo}. The \(^{31}\text{P}{^1\text{H}}} \text{ and } {^1\text{H}} \text{ NMR spectra of the residues indicate the presence of several products.}

\(^{31}\text{P}{^1\text{H}}} \text{NMR} \ (\text{C}_6\text{D}_6, \ 121 \text{ MHz}): \text{ (largest and known resonances only) } \delta -36.80 \text{ (s, likely [NPN]H}_2\text{), } -11.41 \text{ (m, unknown), 3.90 (s, unknown)}

(iv) Reduction in Pyridine/THF: A degassed mixture of pyridine (12 mL) and THF (12 mL) was added by vacuum transfer to a thick-walled flask containing \([\text{NPN}]\text{ZrCl}_2(\text{THF}) \) (0.226 g, 0.338 mmol) and \(\text{KC}_8 \) (0.100 g, 0.740 mmol). The frozen reaction mixture \((-196^\circ\text{C})\) was flushed with \(\text{N}_2 \) (1 atm) while warmed to \(-78^\circ\text{C}\). The flask was sealed and the orange-brown mixture was stirred vigorously overnight. The solvents were removed \text{in vacuo}. The maroon-purple residues were extracted into toluene and filtered through Celite. Toluene was removed \text{in vacuo}. The \(^{31}\text{P}{^1\text{H}}} \text{ and } {^1\text{H}} \text{ NMR spectra of the residues indicate the presence of several products.}

\(^{31}\text{P}{^1\text{H}}} \text{NMR} \ (\text{C}_6\text{D}_6, \ 121 \text{ MHz}): \text{ (largest and known resonances only) } \delta -36.80 \text{ (s, likely [NPN]H}_2\text{), } -11.41 \text{ (m, unknown), 3.92 (s, unknown)}

References begin on page 109
Reduction of \([\text{NPN}]\text{ZrCl}_2(\text{THF}),\) 11, with KC\(_\text{8}\) under an atmosphere of Ar, H\(_2\) or under Static Vacuum:

(v) Reduction under Ar, in THF: A thick-walled flask containing \([\text{NPN}]\text{ZrCl}_2(\text{THF})\) (0.310 g, 0.463 mmol) and KC\(_\text{8}\) (0.128 g, 0.947 mmol) was flushed with argon by three evacuate-refill cycles, and cooled in an IPA/CO\(_2\) bath (−70°C). THF (30 mL) was degassed and then added by cannula to the flask. The resultant dark brown slurry was warmed to room temperature under Ar. The flask was closed and the contents were stirred overnight. THF was removed in vacuo, and the brown-green residues were extracted into toluene and filtered through Celite. Toluene was removed in vacuo. The \(\text{^31P}^\{^1\text{H}\}\) and \(^1\text{H}\) NMR spectra of the residues indicate the presence of several products.

\(\text{^31P}^\{^1\text{H}\}\ NMR\ (\text{C}_6\text{D}_6,\ 121\ \text{MHz}):\) (largest resonances only) \(\delta -11.95\) (s, unknown), \(-5.80\) (s, unknown), \(0.02\) (s, unknown)

(vi) Reduction under Ar, in Toluene: A thick-walled flask containing \([\text{NPN}]\text{ZrCl}_2(\text{THF})\) (0.305 g, 0.456 mmol) and KC\(_\text{8}\) (0.124 g, 0.918 mmol) was flushed with Ar by three evacuate-refill cycles, and cooled in an IPA/CO\(_2\) bath (−70°C). Degassed toluene (35 mL) was added by cannula to the flask. The resultant dark brown slurry was warmed to room temperature under Ar. The flask was closed and the contents were stirred overnight. The brown-green slurry was filtered through Celite and toluene was removed in vacuo. The \(\text{^31P}^\{^1\text{H}\}\) and \(^1\text{H}\) NMR spectra of the residues indicate the presence of several products.

\(\text{^31P}^\{^1\text{H}\}\ NMR\ (\text{C}_6\text{D}_6,\ 121\ \text{MHz}):\) (largest resonances only) \(\delta -11.45\) (d, \(J_{PP} = 35\) Hz, unknown), \(-7.09\) (d, \(J_{PP} = 35\) Hz, unknown), \(-5.80\) (s, unknown), \(0.02\) (s, unknown)

(vii) Reduction under H\(_2\), in THF: THF (25 mL) was degassed and added by vacuum transfer to a thick-walled flask containing \([\text{NPN}]\text{ZrCl}_2(\text{THF})\) (0.263 g, 0.393 mmol) and KC\(_\text{8}\) (0.115 g, 0.848 mmol). While still immersed in a liquid N\(_2\) bath (−196°C), the flask was opened to H\(_2\) (1 atm) and flushed for 5 minutes. The flask was sealed and allowed to warm to room temperature. The slurry was stirred overnight. The pressure was vented (~4 atm) and
THF was removed *in vacuo*. The residues were extracted into toluene and filtered through Celite. Glassy brown residues were isolated following the removal of toluene. The $^{31}\text{P}\{^1\text{H}\}$ and $^1\text{H}$ NMR spectra of the residues indicate the presence of many indistinguishable products.

**(viii) Reduction under Static Vacuum, in Pyridine**: pyridine (25 mL) was degassed and then added by vacuum transfer to a thick-walled flask containing $[\text{NPN}]\text{ZrCl}_2(\text{THF})$ (0.250 g, 0.374 mmol) and $\text{KC}_8$ (0.108 g, 0.796 mmol). The flask was sealed, without introducing $\text{N}_2$ or Ar, and allowed to warm to room temperature. The slurry was stirred overnight and pyridine was then removed *in vacuo*. The residues were extracted into toluene and filtered through Celite. The $^{31}\text{P}\{^1\text{H}\}$ and $^1\text{H}$ NMR spectra of the residues indicate the presence of several products.

$^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{C}_6\text{D}_6$, 81 MHz): (largest and known resonances only) $\delta$ -36.80 (s, $[\text{NPN}]\text{H}_2$), -11.41 (m, unknown), 3.92 (s, unknown)
Chapter 3: Synthesis and Reactivity of ([NPN]ZrY)$_2$(μ-η$^2$:η$^2$-N$_2$), where Y = THF, Pyridine, Benzonitrile

3.9 References

Chapter 3: Synthesis and Reactivity of ([NPN]ZrY)$_2$(μ-η$^2$-N$_2$), where Y = THF, Pyridine, Benzonitrile


References begin on page 109
Chapter 4

Chapter 4: Amidophosphine Complexes of Titanium for the Activation of N₂

4.1 Introduction

Titanium compounds are particularly suitable for the fixation of molecular nitrogen.¹,² Early research in this area established that TiCl₄, when treated with a reducing agent, could fix N₂ at room temperature; however, a Ti dinitrogen complex itself was not directly observed or isolated from these systems.³ Rather, a product of nitrogen fixation, ammonia, results from the hydrolysis or acidification of these reaction mixtures. Similarly, a Ti nitride complex is formed by the reduction of TiCl₃(THF)₃ under a dinitrogen atmosphere (Equation 4.1).⁴ One equivalent of NH₃ is produced from this complex following hydrolysis. In both cases, cleavage of the N-N bond is achieved at room temperature and an ill-defined nitrogen-containing titanium complex is formed.

\[
\text{TiCl}_3(\text{THF})_3 + 2.5 \text{ Mg} \quad \xrightarrow{1 \text{ atm } N_2} \quad [\text{TiNg}_2\text{Cl}_2(\text{THF})] + 0.5 \text{ MgCl}_2(\text{THF})_2 \quad [4.1]
\]

References begin on pg 146
A minor modification to these titanium-based systems led to the development of a new method for incorporating nitrogen into organic compounds under mild conditions. In general, the 'one-pot' reaction requires the preparation of N-containing Ti complexes \textit{in situ}, and these compounds then serve as the nitrogen source for the formation of organonitrogen products in subsequent steps. The reduction of TiCl₄ or Ti(O'Pr)₄ with Li, in the presence of Me₃SiCl, under N₂ generates several nitrogen-containing compounds (Scheme 4.1). The structures of such complexes are not known; however, the black product is believed to be a mixture consisting of N(SiMe₃)₃, X₂Ti-N(SiMe₃)₂ and XTi=N(SiMe₃), where X is either Cl or O'Pr depending on the starting material. Under the appropriate conditions, benzamide and N-heterocyclic compounds can be isolated in good yield using this procedure. A particularly fascinating aspect of these reactions is that these N-heterocyclic compounds can be derived from N₂ that has been fixed from \textit{dry air}. However, the yield for the product in dry air is always lower than that of reactions carried out under N₂. For example, the yield for the indole derivative shown in Scheme 4.1 is 56% when the reduction reaction is carried out in dry air as opposed to 86% when pure N₂ is used.

\[
\begin{align*}
\text{TiX}_4 + \text{Li} + \text{Me}_3\text{SiCl} & \xrightarrow{\text{N}_2} \text{X}_2\text{Ti}-\text{N(SiMe}_3\text{)}_2 \text{N(SiMe}_3\text{)}_3 \\
\text{1. 10\% HCl} & \rightarrow \text{1. Benzamide} \\
\text{2. K}_2\text{CO}_3 & \rightarrow \text{2. X = Cl} \\
\text{3. PhCOCI} & \rightarrow \text{3. X = O'Pr} \\
\text{CsF, THF} & \rightarrow \text{88\% (Air)} \\
\text{80\% (Air)} & \rightarrow \text{90\% (N}_2\text{)} \\
\text{91\% (N}_2\text{)} & \rightarrow \text{56\% (Air)} \\
\text{86\% (N}_2\text{)} & \\
\text{X = Cl} & \\
\text{Schematic 4.1} & \\
\text{References begin on pg 146}
\end{align*}
\]
The first dinitrogen compounds of titanium to be isolated were derived from pentamethylcyclopentadienyl\textsuperscript{10-12} and cyclopentadienyl\textsuperscript{13-15} precursors. The Ti(II) complex \(\eta^5-C_5Me_5\)\(\text{Ti}\) coordinates \(N_2\) at room temperature without the need for an external reducing agent (Scheme 4.2). However, \(N_2\) coordination is reversible: \(N_2\) is released under vacuum at room temperature. As a result, low temperatures are required to isolate the complexes. An \(N-N\) distance of 1.16 Å was determined for \([\eta^5-C_5Me_5]_2\text{Ti}(\mu-\eta^1:\eta^1-N_2)\),\textsuperscript{11} which suggests that the bonding is similar to that of free \(N_2\) (1.09 Å). At lower temperatures, the formation of \([\eta^5-C_5Me_5]_2\text{TiN}_2\)\(\text{Ti}\)\(\mu-\eta^1:\eta^1-N_2\) is supported by spectroscopic evidence\textsuperscript{12} and this complex is believed to have the same structure as the Zr analogue\textsuperscript{16} discussed in Chapter 3 (Scheme 3.1). The reversible coordination of \(N_2\) is also observed for the Ti(III) complex \([\eta^5-C_5H_5]_2\text{Ti}(\rho-\text{Me-C}_6\text{H}_4)\)\(\text{Ti}\)\(\mu-\eta^1:\eta^1-N_2\), which also has a bridging end-on \(N_2\) unit with a similar \(N-N\) bond length (1.162(12) Å)\textsuperscript{14,15}

\[
2(\eta^5-C_5\text{Me}_5)\text{Ti} \xrightleftharpoons[0^\circ\text{C}]{N_2} [\eta^5-C_5\text{Me}_5]_2\text{Ti}(\mu-\eta^1:\eta^1-N_2) \xrightleftharpoons[-80^\circ\text{C}]{N_2} [\eta^5-C_5\text{Me}_5]_2\text{TiN}_2\text{Ti}(\mu-\eta^1:\eta^1-N_2)
\]

\[
2(\eta^5-C_5\text{H}_5)\text{Ti}(\rho-\text{Me-C}_6\text{H}_4) \xrightarrow[-20^\circ\text{C}]{N_2} [\eta^5-C_5\text{H}_5]_2\text{Ti}(\rho-\text{Me-C}_6\text{H}_4)\text{Ti}(\mu-\eta^1:\eta^1-N_2)
\]

**Scheme 4.2**

The short \(N-N\) bond distance, together with the lability of the \(N_2\) ligand, suggests that the coordinated \(N_2\) unit is weakly activated in titanium complexes with cyclopentadienyl-type ligands. Several other titanocene dinitrogen complexes are known to exhibit the same behaviour: the reversible coordination of \(N_2\)\textsuperscript{17-19}

A list of \(N-N\) and \(Ti-N\) bond lengths of end-on bridging titanium dinitrogen complexes is given in Table 4.1. In titanium dinitrogen complexes containing ligands with nitrogen donors, the \(Ti-N\) bond distance of the \(Ti(\mu-N_2)\text{Ti}\) unit is shorter and the \(N-N\) bond
distance is longer than in the related titanocene dinitrogen complexes.\textsuperscript{20-24} Within the same complex, this Ti-N bond length is significantly shorter than that for Ti-N_{ligand}, the bond distance for Ti and the nitrogen donor of the ligand. These features suggest that there is electron delocalization across the Ti(\textmu-N_2)Ti unit and partial double bond character in the (\textmu-N_2) bridge.\textsuperscript{25,26} Also, the N_2 in these complexes is not released under vacuum.

Table 4.1. Bond Lengths and Angles for Ti Complexes with an End-On Bridging N_2 Unit

<table>
<thead>
<tr>
<th>Complex</th>
<th>N-N (\text{\AA})</th>
<th>Ti-N (\text{\AA})</th>
<th>Ti-N_{ligand} (\text{\AA})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>([PNP]TiCl)_2(N_2)</td>
<td>1.275(7)</td>
<td>1.775(4)</td>
<td>2.035(5)</td>
<td>20</td>
</tr>
<tr>
<td>{[(Me_3Si)_2N]TiCl(TMEDA)}_2(N_2)</td>
<td>1.289(9)</td>
<td>1.762(5)</td>
<td>2.352(6), 2.351(6), 2.023(5)</td>
<td>21</td>
</tr>
<tr>
<td>([iPrNON]Ti(PMe_3)_2(N_2)</td>
<td>1.264(8)</td>
<td>1.811(4)</td>
<td>2.068(4), 2.123(4)</td>
<td>23</td>
</tr>
<tr>
<td>{[(Me_2N)C(NiPr)_2]_2Ti}_2(N_2)</td>
<td>1.28(1)</td>
<td>1.723(8), 1.744(8)</td>
<td>2.109(5), 2.141(4), 2.114(5), 2.138(4)</td>
<td>24</td>
</tr>
<tr>
<td>((\eta^5-C_5H_5)_2Ti(PMe_3))_2(N_2)</td>
<td>1.191(8)</td>
<td>1.920(6), 1.921(5)</td>
<td>---</td>
<td>17</td>
</tr>
<tr>
<td>((\eta^5-C_5Me_4H)_2Ti)_2(N_2)</td>
<td>1.170(4)</td>
<td>1.987(3)</td>
<td>---</td>
<td>18</td>
</tr>
</tbody>
</table>

The end-on coordination mode for dinitrogen is the most common mode for titanium complexes; however, examples of side-on coordination are known (Figure 4.1).\textsuperscript{21,27} In these complexes, the N-N bond distances are slightly longer than the end-on bond distances listed in Table 4.1.
Chapter 4: Amidophosphine Complexes of Titanium for the Activation of $N_2$

**Figure 4.1.** Titanium complexes with a) a side-on/end-on $N_2$ unit bridging three Ti atoms\(^{27}\) and b) two Ti atoms bridged by two side-on $N_2$ units.\(^{21}\)

The titanium analogue of ([PNP]ZrCl)$_2$(μ-$\eta^2$-$\eta^2$-$N_2$) (complex A, Scheme 3.3) has also been prepared in the Fryzuk group.\(^{20}\) The Ti complex has some notable differences from its Zr counterpart: the $N_2$ unit is end-on coordinated to Ti, the N-N distance is shorter (1.275(7) Å vs. 1.548(7) Å) and there is no inversion centre in the complex (Equation 4.2).

\[
2 \text{TiCl}_3[N(\text{SiMe}_2\text{CH}_2\text{PPr}^\text{i}^2)_2] \xrightarrow{\text{xs Mg}} \text{[4.2]}
\]
In the previous two chapters, the preparation and reactivity of dinitrogen zirconium complexes with either the P$_2$N$_2$ or NPN ligand were presented: ([P$_2$N$_2$]Z)$_2$(μ-η$^2$:η$^2$-N$_2$), 1, ([NPN]ZrTHF)$_2$(μ-η$^2$:η$^2$-N$_2$), 12 and ([NPN]Zrp)$_2$(μ-η$^2$:η$^2$-N$_2$), 13. Each of these complexes has a side-on bound dinitrogen unit that is elongated. The formation of N-H, N-Si and N-C bonds is only observed for reactions of 1 with the appropriate substrate. Prior to preparing the titanium analogues of 1 and 12, the resulting complexes were expected to have the common end-on coordination mode for the bridging N$_2$ unit. Although this is true for the Ti congener of 1, the reduction of Ti[NPN] precursors under N$_2$ gave unusual results. The focus of this chapter is the preparation of these Ti analogues.

4.2 Titanium and the P$_2$N$_2$ Ligand

Prior to this work, other members of the Fryzuk group had also successfully prepared [P$_2$N$_2$]TiCl$_2$, 16, and attempted its reduction under N$_2$ (see Section 4.8.3). The resulting dinitrogen product was characterized by NMR spectroscopy, but the structure was unknown. Herein, revised procedures for the preparation and reduction of 16, as well as the solid state structure of the dinitrogen-containing product are reported. The synthesis of the P$_2$N$_2$ ligand was presented in Chapter 1 (Scheme 1.5).

(i) Synthesis and Characterization of [P$_2$N$_2$]TiCl$_2$, 16

Complex 16, [P$_2$N$_2$]TiCl$_2$, is prepared by the reaction of [P$_2$N$_2$]Li$_2$(dioxane) with either TiCl$_4$ or TiCl$_4$(THF)$_2$ (Equation 4.3). A dark red slurry results from the addition of toluene to a yellow mixture of TiCl$_4$(THF)$_2$ and [P$_2$N$_2$]Li$_2$(dioxane) or by the dropwise addition of TiCl$_4$ to a toluene solution of [P$_2$N$_2$]Li$_2$(dioxane). Heating the slurry to reflux does not noticeably improve the yield or purity of the desired product, 16. Minor impurities such as [P$_2$N$_2$]H$_2$ may be removed, without a significant decrease in the yield of 16, by washing the resultant brick red powder with a toluene/hexanes solution.
Chapter 4: Amidophosphine Complexes of Titanium for the Activation of \( \text{N}_2 \)

\[
\text{[P}_2\text{N}_2\text{]}\text{Li}_2(\text{dioxane}) + \text{TiCl}_4 \quad \text{or} \quad \text{[P}_2\text{N}_2\text{]}\text{Li}_2(\text{dioxane}) + \text{TiCl}_4(\text{THF})_2
\]

The two phosphorus nuclei of 16 are equivalent and are observed as a singlet at \( \delta 0.8 \) in the \( ^{31}\text{P}\{^1\text{H}\} \) NMR spectrum. The \( ^1\text{H} \) NMR spectrum further suggests that 16 has \( C_{2v} \) symmetry in solution. The chemical shifts and coupling patterns for 16 are similar to those observed for \([\text{P}_2\text{N}_2]\text{ZrCl}_2\). Two singlets at \( \delta 0.36 \) and \( \delta 0.40 \) account for the silylmethyl groups. A multiplet observed at \( \delta 7.88 \) is indicative of the o-H atoms of the phosphine phenyl rings, which is comparable to that observed for \([\text{P}_2\text{N}_2]\text{ZrCl}_2\) at \( \delta 7.84 \). All other resonances are typical for the \( \text{P}_2\text{N}_2 \) ligand. The elemental analysis also supports the proposed composition of 16.

(ii) Synthesis and Characterization of \([\text{P}_2\text{N}_2]\text{Ti}_2(\mu-\eta^1:\eta^1-\text{N}_2), 17\)

The reduction of \([\text{P}_2\text{N}_2]\text{TiCl}_2\), 16, with KC\(_8\) under an atmosphere of dinitrogen produces \([\text{P}_2\text{N}_2]\text{Ti}_2(\mu-\eta^1:\eta^1-\text{N}_2), 17\). The procedure for the preparation of 17 is like those described for 1, \([\text{P}_2\text{N}_2]\text{Zr}_2(\mu-\eta^2:\eta^2-\text{N}_2)\), and 12, \([\text{NPN}]\text{ZrTHF}_2(\mu-\eta^2:\eta^2-\text{N}_2)\), with one minor exception: a trap-to-trap transfer of THF at \(-196^\circ\text{C}\) is not required to ensure the resulting high purity of 17. The addition of THF by cannula to a cooled \((-78^\circ\text{C})\) 1-to-2 mixture of \([\text{P}_2\text{N}_2]\text{TiCl}_2\) and KC\(_8\) under 1 atm \( \text{N}_2 \) results in a red slurry. As the solution warms to room temperature, a colour change to yellow-brown is observed. Complex 17 is isolated as a brown powder from this mixture in moderate yield, 69%, and high purity. The only impurity observed by \( ^{31}\text{P}\{^1\text{H}\} \) and \( ^1\text{H} \) NMR spectroscopy is \([\text{P}_2\text{N}_2]_2\text{H}_2\). Since \([\text{P}_2\text{N}_2]_2\text{H}_2\) is more soluble in toluene/hexanes than 17, it is simply removed by washing the brown powder with a mixture of those solvents.

References begin on pg 146
One singlet is observed at $\delta = -4.8$ in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 17. The relative integration ratio between peaks in the $^1\text{H}$ NMR spectrum for 17 are the same as those observed for 16; however, the chemical shifts are different. Singlets are observed at $\delta = 0.14$ and $\delta = 0.23$ for the SiMe$_2$ protons and the o-H P-phenyl protons are characterized by a multiplet at $\delta = 8.16$. The fragment observed at m/z 1188 in the EI-mass spectrum is consistent with a complex possessing one equivalent of N$_2$ and two equivalents of the [P$_2$N$_2$]Ti fragment. However, elemental analysis of a pure sample of 17 gave results that are consistent for ([P$_2$N$_2$]Ti)$_2$(N) on two separate attempts. The inability to obtain a satisfactory analysis is presumed to be caused by the formation and incomplete combustion of Ti nitrides during the analysis procedure, which would interfere with the accuracy of the results.

The molecular structure of 17 was determined by single crystal X-ray diffraction. Complex 17 crystallizes as two independent molecules in the asymmetric unit. The two molecules have very similar structural parameters, thus the bond lengths and angles for only one of the two molecules is reported herein. An ORTEP representation of the molecular structure of 17 is shown in Figure 4.2. Table 4.2 is a list of selected bond lengths and angles for 17.

The coordination geometry at Ti is distorted square pyramidal, with one N of the bridging N$_2$ unit at the apex for each Ti[P$_2$N$_2$]. Alternatively, the geometry about Ti may be considered pseudo-trigonal bipyramidal, with the phosphines in the axial positions and the amides and one N of N$_2$ in the equatorial positions. The lower half of the molecule is rotated 90° relative to the top, such that N atoms of one P$_2$N$_2$ ligand nearly eclipse the P atoms of the other ligand when the molecule is viewed along the Ti-Ti axis; the donor atoms adopt a configuration that approximates D$_{2d}$ symmetry in the solid state.

The N$_2$ unit bridges the Ti centres in an end-on fashion with a bond length of 1.255(7) Å (or 1.245(7) Å for the second molecule in the asymmetric unit), which is similar to that found for PhN=NPh$^{31,32}$ as well as N-N bond lengths reported for other Ti complexes (Table 4.1). This differs from the Zr analogue, 1, where the N$_2$ is side-on coordinated, with an elongated bond length of 1.43(1) Å.$^{28}$

References begin on pg 146
Figure 4.2. ORTEP representation (ellipsoid probability 50%) of the molecular structure of ([P$_2$N$_2$]Ti)$_2$(μ-η$^1$:η$^1$-N$_2$), 17, as determined by single crystal X-ray diffraction. Hydrogen atoms and silylmethyl groups are omitted for clarity and only ipso carbons of the P$_2$N$_2$ ligand phenyl rings are shown.

The Ti-N3-N3' angle is virtually linear (177.7(3)$^\circ$) and the Ti1-N3 bond distance (1.783(4) Å) is considerably shorter than the Ti-N$_{ligand}$ distances of 2.049(4) Å and 2.076(4) Å. These structural features and the diamagnetism of 17 suggest that the two titanium centres are formally Ti(IV), where the bridging N$_2$ unit is a hydrazido ligand, (N$_2$)$_2$~, with partial double bond character.$^{23,24}$

Titanium is situated deeper within the cavity of the P$_2$N$_2$ ligand compared to Zr in complex 1. This is supported by the relatively short Ti-P and Ti-N$_{ligand}$ bond distances in 17 when compared to the Zr-P and Zr-N$_{ligand}$ distances of 2.734(2) Å and 2.023(4) Å, respectively, in complex 1. Also, the P1-Ti-P2 and N1-Ti-N2 angles in 17 (154.58(6)$^\circ$ and
119.46(15)°, respectively) are larger than comparable angles in 1, where P-Zr-P is 140.90(7)° and N-Zr-N is 108.4(2)°.

Table 4.2. Selected Bond Lengths and Angles in \([\text{P}_2\text{N}_2\text{Ti}_2(\mu-\eta^1:\eta^1-\text{N}_2)]\), 17

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atom</th>
<th>Distance (Å)</th>
<th>Atom</th>
<th>Atom</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(3)</td>
<td>N(3)'</td>
<td>1.255(7)</td>
<td>Ti(1)</td>
<td>N(3)</td>
<td>1.783(4)</td>
</tr>
<tr>
<td>N(6)</td>
<td>N(6)'</td>
<td>1.245(7)</td>
<td>Ti(1)</td>
<td>N(2)</td>
<td>2.049(4)</td>
</tr>
<tr>
<td>Ti(1)</td>
<td>P(1)</td>
<td>2.5669(13)</td>
<td>Ti(1)</td>
<td>N(1)</td>
<td>2.076(4)</td>
</tr>
<tr>
<td>Ti(1)</td>
<td>P(2)</td>
<td>2.5552(13)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Italicized values are those for the second molecule of 17 within the asymmetric unit.33

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atom</th>
<th>Atom</th>
<th>Angle (°)</th>
<th>Atom</th>
<th>Atom</th>
<th>Atom</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(1)</td>
<td>N(3)</td>
<td>N(3)'</td>
<td>177.7(4)</td>
<td>Ti(2)</td>
<td>N(6)</td>
<td>N(6)'</td>
<td>179.0(4)</td>
</tr>
<tr>
<td>P(2)</td>
<td>Ti(1)</td>
<td>P(1)</td>
<td>154.58(6)</td>
<td>P(1)</td>
<td>Ti(1)</td>
<td>N(2)</td>
<td>87.19(11)</td>
</tr>
<tr>
<td>N(1)</td>
<td>Ti(1)</td>
<td>N(2)</td>
<td>119.46(15)</td>
<td>P(1)</td>
<td>Ti(1)</td>
<td>N(2)</td>
<td>79.30(11)</td>
</tr>
<tr>
<td>P(2)</td>
<td>Ti(1)</td>
<td>N(3)</td>
<td>100.17(11)</td>
<td>P(1)</td>
<td>Ti(1)</td>
<td>N(1)</td>
<td>123.60(15)</td>
</tr>
<tr>
<td>P(2)</td>
<td>Ti(1)</td>
<td>N(2)</td>
<td>80.75(11)</td>
<td>N(1)</td>
<td>Ti(1)</td>
<td>N(3)</td>
<td>116.91(17)</td>
</tr>
<tr>
<td>P(2)</td>
<td>Ti(1)</td>
<td>N(1)</td>
<td>87.25(11)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(iii) Reactivity of \([\text{P}_2\text{N}_2\text{Ti}_2(\mu-\eta^1:\eta^1-\text{N}_2)]\), 17

In Chapter 2, the reactivity of \(([\text{P}_2\text{N}_2\text{Zr}_2(\mu-\eta^2:\eta^2-\text{N}_2)]\), 1, with phenylacetylene derivatives and the isolation of complexes with new N-C bonds was presented. The N₂ unit in 1 is also known to be reactive toward H₂ and "BuSiH₃.28 Attempts were made to reproduce these results with 12, ([NPN]ZrTHF)₂(μ-η²:η²-N₂), but the products of these reactions could
not be isolated (Chapter 3). Consequently, the reactivity of 17 with H₂ and (p-methyl)phenylacetylene was also investigated. In both cases, no discernible reaction had taken place: the solution of 17 remained brown in colour and the ³¹P{¹H} and ¹H NMR spectra of each reaction indicate that no transformation had taken place. However, an increase in the amount of [P₂N₂]H₂ in the reaction with (p-Me-C₆H₄)C=CH suggests that some decomposition of 17 occurred, which was probably a result of traces of moisture in the sample. Complex 17 was also found to be thermally robust; a toluene solution of 17 was heated to 65°C under reduced pressure for 24 hours and the NMR spectra suggest that no decomposition had occurred. Further investigations into the reactivity of 17 were not explored.

(iv) Reduction of [P₂N₂]TiCl₂, 16, under Nitrogen-Free Conditions

In contrast to the preparation of 1, ([P₂N₂]Zr)(μ-η²:η²-N₂), complex 17 is the only product resulting from the reduction of 16 under N₂. In particular, the titanium analogue of 5, ([P₂N₂]Zr)₂, is not observed in the NMR spectra of 17. In this work, the preparation of 17 was always carried out in THF solvent, which would exclude the formation of a titanium analogue of 6, [P₂N₂]Zr(η⁶-C₇H₈).

Complex 16 was reduced in either toluene or THF under argon and the resulting brown-green residues were worked-up under N₂. The ¹H NMR spectrum of each reduction product is uninformative due to many overlapping peaks. For the reaction carried out in toluene, several products are apparent in the ³¹P{¹H} spectrum, including [P₂N₂]H₂. A pair of doublets at δ 20.2 and δ 32.1 (Jₚₚ = 98 Hz) resemble the resonances observed in the ³¹P{¹H} NMR spectrum of ([P₂N₂]Zr)₂, 5, (δ 3.1 and 12.4, Jₚₚ = 99 Hz).³⁴ One of the other singlets in the spectrum could be due to [P₂N₂]Ti(η⁶-C₇H₈); however, there is insufficient evidence to support the existence of this complex. When the reduction was carried out in THF, this pair of doublets is notably absent in the ³¹P{¹H} spectrum of the residues. These findings are inconclusive and the inability to separate the products means that the existence of ([P₂N₂]Ti)₂ remains speculative.

References begin on pg 146
Surprisingly, the dinitrogen complex 17 was also a product in the reduction reactions carried out under argon. Trace amounts of N₂ may have been present in the degassed solvent or in the argon supply. Alternatively, the reduced Ti species could have reacted with N₂ during the work-up to form 17. In any case, the presence of 17 in a reaction mixture where efforts were made to exclude dinitrogen suggests that the reduced Ti species, which is generated in situ, has an affinity for N₂. In an attempt to avoid potential sources of N₂, the reduction of 16 was repeated in toluene under static vacuum and the work-up was conducted under Ar. In this case, the product was maroon. The ³¹P{¹H} NMR spectrum suggests that 16 and [P₂N₂]H₂ were the major products of the reduction. The broad and overlapping resonances observed in the ¹H NMR spectrum are unusual for a mixture containing primarily 16 and [P₂N₂]H₂ and may indicate the presence of paramagnetic impurities.

4.3 Titanium and the NPN Ligand

In previous chapters, the preparation of the ligand precursor, [NPN]Li₂(THF)₂, (Section 1.5, Scheme 1.7) and the reactivity of zirconium complexes with the NPN ligand were presented (Chapter 3). Accordingly, the chemistry of titanium with the NPN ligand set was also explored.

(i) Synthesis and Characterization of [NPN]TiCl₂, 18

Complex 18, [NPN]TiCl₂, is prepared by the reaction of TiCl₄(THF)₂ with [NPN]Li₂(THF)₂ in toluene. If the resulting red-orange slurry is heated to reflux or the solution is stirred for more than 24 hours, a mixture of products is obtained. Thus, the best results were achieved when the reaction was stirred for only one hour at room temperature prior to work-up. Any impurities can be removed by washing the resulting dark orange residue with toluene and hexanes to give pure 18 in the form of a pale orange powder.

One singlet at δ 3.7 is observed in the ³¹P{¹H} NMR spectrum. The resonances in the ¹H NMR spectrum are consistent with coordinated NPN in a complex belonging to the C₃ point group; two singlets are observed for the silylmethyl groups. The spectrum is similar to that of 11, [NPN]ZrCl₂(THF), with one notable exception: there are no resonances due to
THF in the spectrum of 18. The elemental analysis and mass spectrum are consistent with the NMR data and support the composition of 18 as an adduct-free complex, [NPN]TiCl₂.

The molecular structure of 18 was confirmed by single crystal X-ray diffraction (Figure 4.3). A selected list of bond lengths and angles is given in Table 4.3. The geometry about Ti is distorted trigonal bipyramidal, where the axis is defined by Cl1-Ti-P1 (176.08(5)°) and the two N donors and Cl2 occupy the equatorial positions. The Ti-N bond lengths are slightly shorter than those expected for diamido ligands (see the third entry in Table 4.1), but the Ti-P and Ti-Cl bond lengths are typical (e.g., Ti-Cl is 2.33 Å and the average Ti-P distance is 2.16 Å in ([PNP]TiCl₂(μ-η¹:η¹-N₂)).

![Figure 4.3. ORTEP representation (ellipsoid probability 50%) of the molecular structure of [NPN]TiCl₂, 18, as determined by single crystal X-ray diffraction. Hydrogen atoms and silylmethyl groups are omitted for clarity.](image-url)
Table 4.3. Selected Bond Lengths and Angles in [NPN]TiCl₂, 18

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atom</th>
<th>Distance (Å)</th>
<th>Atom</th>
<th>Atom</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(1)</td>
<td>Cl(1)</td>
<td>2.2937(12)</td>
<td>Ti(1)</td>
<td>N(1)</td>
<td>1.914(3)</td>
</tr>
<tr>
<td>Ti(1)</td>
<td>Cl(2)</td>
<td>2.2874(12)</td>
<td>Ti(1)</td>
<td>N(2)</td>
<td>1.936(4)</td>
</tr>
<tr>
<td>Ti(1)</td>
<td>P(1)</td>
<td>2.6084(12)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atom</th>
<th>Atom</th>
<th>Angle (°)</th>
<th>Atom</th>
<th>Atom</th>
<th>Atom</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(1)</td>
<td>Ti(1)</td>
<td>P(1)</td>
<td>176.08(5)</td>
<td>N(2)</td>
<td>Ti(1)</td>
<td>Cl(2)</td>
<td>119.42(11)</td>
</tr>
<tr>
<td>N(1)</td>
<td>Ti(1)</td>
<td>N(2)</td>
<td>116.45(14)</td>
<td>N(2)</td>
<td>Ti(1)</td>
<td>Cl(1)</td>
<td>100.45(12)</td>
</tr>
<tr>
<td>N(1)</td>
<td>Ti(1)</td>
<td>Cl(2)</td>
<td>117.58(11)</td>
<td>N(2)</td>
<td>Ti(1)</td>
<td>P(1)</td>
<td>75.85(11)</td>
</tr>
<tr>
<td>N(1)</td>
<td>Ti(1)</td>
<td>P(1)</td>
<td>80.64(10)</td>
<td>Cl(2)</td>
<td>Ti(1)</td>
<td>P(1)</td>
<td>87.80(4)</td>
</tr>
<tr>
<td>N(1)</td>
<td>Ti(1)</td>
<td>Cl(1)</td>
<td>100.11(11)</td>
<td>Cl(2)</td>
<td>Ti(1)</td>
<td>Cl(1)</td>
<td>95.21(5)</td>
</tr>
</tbody>
</table>

(ii) Synthesis and Characterization of [NPN]TiCl(THF), 19

Complex 19, [NPN]TiCl(THF), is isolated as a flakey gray-blue solid from the reaction of TiCl₃(THF)₃ with a toluene solution of [NPN]Li₂(THF)₂ at room temperature (Equation 4.4).

\[
\begin{align*}
\text{Ph} & \quad \text{Me}_2 & \quad \text{Si} \\
\text{N} & \quad \text{i} & \quad \text{Li} \\
\text{Me}_2 & \quad \text{Si} & \quad \text{Ph} \\
\text{Ph} & \quad \text{P} & \quad \text{Li} \\
\text{S} & \quad \text{THF} & \quad \text{TiCl}_3(\text{THF})_3 \\
\text{toluene} & \quad (- \text{LiCl}) & \quad \text{[4.4]} \\
\rightarrow & & \\
\text{Me}_2 & \quad \text{Si} & \quad \text{N} \\
\text{Ph} & \quad \text{P} & \quad \text{Cl} \\
\text{Me}_2 & \quad \text{Si} & \quad \text{Ph} \\
\text{Ph} & \quad \text{N} & \quad \text{Ti} \\
19 & & 
\end{align*}
\]

The \(^{31}\text{P}\{^1\text{H}\} \text{ and } ^1\text{H} \text{ NMR spectra of the blue product show broadened resonances, which suggests that the product is paramagnetic. The elemental analysis for 19 is consistent with a complex with one NPN, one chloride and one THF ligand for each Ti centre. The fragment with the largest mass in the mass spectrum is observed at 590 m/z, which supports a}}
monometallic composition, [NPN]TiCl(THF), for 19. The isotope pattern for this fragment, m/z 590, is in agreement with the simulated pattern for the ([M$^+$] + H) fragment of 19. Other fragments in the mass spectrum are consistent with the loss of Cl (554 m/z) and THF (517 m/z) from the parent ion. Given the above results, the titanium atom in 19 is formally Ti(III). Further characterization of this complex was not pursued.


Complex 18, [NPN]TiCl$_2$, was reduced under N$_2$ with two equivalents of KC$_8$ to give complex 20, using the optimized procedures developed for the preparation of ([P$_2$N$_2$]Zr)$_2$(μ-η$_2$:η$_2$-N$_2$)$_2$, 1, and ([NPN]ZrTHF)$_2$(μ-η$_2$:η$_2$-N$_2$)$_2$, 12 in high yield and purity. In general, THF is added to the reactants by vacuum transfer, the reaction mixture is frozen, and N$_2$ is introduced as the mixture thaws. In this case, the resulting cold slurry is dark brown/olive green and no appreciable colour change occurs as the mixture is warmed to room temperature and stirred overnight. After filtration and the evaporation of solvent, a dark green/brown powder can be isolated. A toluene (or d$_6$-benzene) solution of the powder changes from olive green to emerald green over time. The rate of this change was not monitored, but it occurred over a period of days to weeks depending on the concentration of the solution, where a concentrated solution changed faster than a dilute solution. Forest green crystals of 20 were isolated from one of these toluene solutions for analysis by single crystal X-ray diffraction.

Complex 20 was initially thought to be a dinitrogen complex and, as such, the singlet observed at δ 39.9 in the $^{31}$P{$^1$H} NMR spectrum is unusual and considerably downfield compared to the starting dichloride 18 (δ 3.7) or the Ti dinitrogen complex 17 (δ -4.8). The $^1$H NMR spectrum of 20 is similar to that of 18, [NPN]TiCl$_2$, with one subtle difference: there are no resonances in the region of the spectrum typical for o-H P-phenyl hydrogen atoms of NPN. The resonance for this type of hydrogen atom is observed at δ 8.28, δ 7.98,
and $\delta$ 7.84 for complexes 11, 12 and 18, respectively. The reason for these unusual results was clarified once the molecular structure of 20 was determined by X-ray crystallography (Section 4.4 ii).

The parent peak for the molecular ion [M$^+$] of 20 is observed at m/z 992 by mass spectrometry, which suggests that 20 is composed of one equivalent of N$_2$ and two equivalents of the [NPN]Ti unit. The elemental analysis is also consistent with this molecular formula, ([NPN]Ti)$_2$(N$_2$).

The reduction of 19, [NPN]TiCl(THF), with one equivalent of KC$_8$ under dinitrogen also produced a brown/olive green powder. The $^{31}$P{$^1$H} NMR spectrum of the residue indicates that the product is a mixture that includes 20. Given the large quantity of impurities resulting from this procedure, the reduction of 18, [NPN]TiCl$_2$, is the preferred procedure for the preparation and isolation of complex 20.


An ORTEP depiction of the molecular structure of 20 is shown in Figure 4.4 with selected bond lengths and angles listed in Table 4.4. The structure is consistent with the molecular formula determined by mass spectrometry. However, there is no intact dinitrogen unit within the complex, and the phosphine donor of the NPN ligand is no longer coordinated to the Ti centre. Instead, nitrogen atoms have inserted between the phosphorus and titanium centres to form phosphinimide units that bridge the two Ti centres. Each bridging diamido phosphinimide ligand, [N(PN)N], in 20 is a trianion and, as a result, each titanium centre is formally Ti(III). The short Ti-Ti distance of 2.6710(6) Å could be an effect of the constrained geometry imposed by the bridging ligands; however, the diamagnetism of 20 also supports the possibility of a Ti-Ti single bond.

The nitrogen atoms, N5 and N6, in the phosphinimide fragments are presumed to originate from the reduction of one equivalent of dinitrogen. The N5-N6 separation of 2.94 Å is too large to be considered an N-N single bond and suggests that molecular nitrogen was cleaved in the formation of 20.
Figure 4.4. ORTEP representation (ellipsoid probability 50%) of the molecular structure of ([N(PN)N]Ti)_2, 20, as determined by single crystal X-ray diffraction. Hydrogen atoms and silylmethyl groups are omitted for clarity.

Table 4.4. Selected Bond Lengths and Angles in ([N(PN)N]Ti)_2, 20

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atom</th>
<th>Distance (Å)</th>
<th>Atom</th>
<th>Atom</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(2)</td>
<td>Ti(1)</td>
<td>2.6710(6)</td>
<td>P(1)</td>
<td>N(5)</td>
<td>1.591(2)</td>
</tr>
<tr>
<td>Ti(2)</td>
<td>N(6)</td>
<td>1.993(2)</td>
<td>Ti(1)</td>
<td>N(6)</td>
<td>1.980(2)</td>
</tr>
<tr>
<td>Ti(2)</td>
<td>N(5)</td>
<td>1.978(2)</td>
<td>Ti(1)</td>
<td>N(5)</td>
<td>1.997(2)</td>
</tr>
<tr>
<td>Ti(2)</td>
<td>N(4)</td>
<td>2.046(2)</td>
<td>Ti(1)</td>
<td>N(1)</td>
<td>2.042(2)</td>
</tr>
<tr>
<td>Ti(2)</td>
<td>N(3)</td>
<td>1.992(2)</td>
<td>Ti(1)</td>
<td>N(2)</td>
<td>2.008(2)</td>
</tr>
<tr>
<td>P(2)</td>
<td>N(6)</td>
<td>1.590(2)</td>
<td>N(5)</td>
<td>N(6)</td>
<td>2.942</td>
</tr>
</tbody>
</table>

References begin on pg 146
The P-N and Ti-N bond lengths for the phosphinimide unit are within the range of values reported for phosphinimide ligands coordinated to titanium.\textsuperscript{38,41,42} An example of a titanium complex with bridging phosphinimide ligands is shown in Figure 4.5.\textsuperscript{38} The bridging phosphinimide units in [\(\eta^5\)-C\(_5\)H\(_5\)]TiCl\(_2\)(\(\mu\)-N=PPr\(_3\))\(_2\) are almost equally shared between the two titanium centres; only a slight difference is observed between the Ti-N bond lengths and between P-N-Ti bond angles within the complex. In contrast, the bond angles in 20 for the bridging phosphinimide to each Ti centre are unequal. For example, P2-N6-Ti and P2-N6-Ti2 are 158.18(13)° and 112.83(11)°, respectively. The large P-N-Ti angles in 20, 158.18(13)° and 161.56(14)°, are similar to those reported for complexes with a chelating bis-phosphinimide ligand.\textsuperscript{43} It should also be noted that the singlet observed at \(\delta\) 39.9 in the \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum of 20 is not unusual for phosphinimide complexes.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atom</th>
<th>Atom</th>
<th>Angle (°)</th>
<th>Atom</th>
<th>Atom</th>
<th>Atom</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(2)</td>
<td>N(6)</td>
<td>Ti(1)</td>
<td>84.50(8)</td>
<td>P(2)</td>
<td>N(6)</td>
<td>Ti(1)</td>
<td>158.18(13)</td>
</tr>
<tr>
<td>Ti(2)</td>
<td>N(5)</td>
<td>Ti(1)</td>
<td>84.43(8)</td>
<td>P(2)</td>
<td>N(6)</td>
<td>Ti(2)</td>
<td>112.83(11)</td>
</tr>
<tr>
<td>N(6)</td>
<td>Ti(2)</td>
<td>N(5)</td>
<td>95.61(8)</td>
<td>P(1)</td>
<td>N(6)</td>
<td>Ti(1)</td>
<td>112.30(12)</td>
</tr>
<tr>
<td>N(6)</td>
<td>Ti(1)</td>
<td>N(5)</td>
<td>95.43(9)</td>
<td>P(1)</td>
<td>N(5)</td>
<td>Ti(2)</td>
<td>161.56(14)</td>
</tr>
<tr>
<td>N(6)</td>
<td>Ti(1)</td>
<td>N(2)</td>
<td>119.97(9)</td>
<td>N(5)</td>
<td>Ti(2)</td>
<td>N(3)</td>
<td>118.14(9)</td>
</tr>
<tr>
<td>N(6)</td>
<td>Ti(1)</td>
<td>N(1)</td>
<td>115.96(9)</td>
<td>N(5)</td>
<td>Ti(2)</td>
<td>N(4)</td>
<td>119.93(9)</td>
</tr>
<tr>
<td>N(2)</td>
<td>Ti(1)</td>
<td>N(1)</td>
<td>118.41(9)</td>
<td>N(4)</td>
<td>Ti(2)</td>
<td>N(3)</td>
<td>115.83(9)</td>
</tr>
</tbody>
</table>

**Interatomic Distances, Å**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-N</td>
<td>1.617(2), 1.612(2)</td>
</tr>
<tr>
<td>Ti-N</td>
<td>2.013(2), 2.024(2), 2.011(2), 2.017(2)</td>
</tr>
</tbody>
</table>

\[139.53(12)°\] \[137.27(13)°\]

\(^{31}\text{P}\{^1\text{H}\}\) NMR

\(\delta\) 36.7 (R = Me)

\(\delta\) 57.6 (R = \(^1\text{Pr}\))

**Figure 4.5.** A titanium complex with two bridging phosphinimide ligands. Bond lengths and angles for the R = \(^1\text{Pr}\) derivative are listed.\textsuperscript{38}
(iii) Identification of the Nitrogen-Source within ([N(PN)N]Ti)_2, 20

The origin of the additional nitrogen atoms in 20 (N5 and N6 in the molecular structure) was clarified by the reduction of 18, [NPN]TiCl₂, with KC₈ under ^1⁵N₂. Because of the low pressure of the ^1⁵N₂ source, the reaction is not as clean and a mixture of materials is obtained. However, a doublet at δ 39.9, ^1PN = 22 Hz, in the ^3¹P{¹H} NMR spectrum is evidence for ^1⁵N₂-20, ([N(P¹⁵N)N]Ti)₂ (Equation 4.5). A parent ion at 994 m/z is in agreement with the molecular composition expected for the ^1⁵N₂-congener of 20. Although a solution of the product was saturated, the concentration of ^1⁵N₂-20 in the sample was low and this hindered attempts to obtain an ^1⁵N NMR spectrum. Nevertheless, these results clearly indicate that the nitrogen atom in the phosphinimide units of 20 originated from molecular nitrogen.

4.5 Evidence for an Intermediate Titanium Dinitrogen Complex, ([NPN]Ti)₂(µ-N₂), 21

In section 4.4, the isolation and characterization of 20 from the reduction of [NPN]TiCl₂, 18, under N₂ in THF was discussed. However, besides 20, other species are detected during this transformation. A colour change from olive green to an emerald green is observed concurrently with the growth of the singlet at δ 39.9 and the disappearance of a singlet at δ 5.6 in the ^3¹P{¹H} NMR spectrum of the reduction product. Other singlets, including a signal due to [NPN]H₂, are also present in the ^3¹P{¹H} NMR spectrum of the
crude reduction product, but the relative intensities of these resonances does not appear to change. This suggests that the resonance at δ 5.6 results from an intermediate, referred to herein as complex 21, which is likely associated with the formation of 20.

Usually, the olive green product is a mixture of 20 and 21 in varying amounts, as evidenced by $^{31}$P{^1H} NMR spectroscopy. On a few rare and fortuitous occasions, an olive green product was isolated in which the peak associated with complex 20 was absent from the $^{31}$P{^1H} NMR spectrum and the singlet at δ 5.6 of 21 was the predominant peak. After three weeks, a toluene solution of 21 became emerald green, the singlet at δ 5.6 disappeared from the $^{31}$P{^1H} NMR spectrum and 20 was the major product with the exception of some minor impurities, such as [NPN]H₂.

The resonances in the $^1$H NMR spectrum of 21 are slightly different than those of 20. Two singlets for the silylmethyl groups at δ 0.11 and 0.31 suggest that 21 is symmetrical but the chemical shifts of these peaks are different than the corresponding resonances in 20 (δ 0.13 and 0.44). A broad multiplet at δ 3.66 suggests the presence of coordinated THF, which has a relative ratio of 2:1 when compared to the o-H P-phenyl resonance at δ 8.22. This indicates a 1:1 ratio of NPN and THF ligands for each titanium centre in 21. These are the most notable differences between the two complexes: for 20 the resonances due to the o-H P-phenyl hydrogens are hidden under other resonances in the aromatic region and there are no THF resonances in the $^1$H NMR spectrum.

The fragment with the largest molecular weight in the mass spectrum of 21 is at m/z 992, which is identical to that found in the mass spectrum of 20. If this fragment is the molecular ion [M⁺] of 21, then the two complexes are isomers. However, the presence of coordinated THF in the $^1$H NMR spectrum implies that 21 may be the titanium analogue of 12, ([NPN]ZrTHF)₂(μ-η²:η²-N₂). This apparent discrepancy can be resolved by noting that the molecular ion of 12 was also missing in its mass spectrum; instead, a fragment consistent with [NPN]₂Zr₂N₂ was observed (Section 3.2).

The similarity between the $^1$H NMR spectrum of 21 and that of 12 (and the upfield singlet at δ 5.6 in $^{31}$P{^1H} spectrum of 21) supports the likelihood that 21 is a dinitrogen complex. It should also be noted that when 18 was reduced under N₂ in toluene solvent,
neither 21 nor 20 were observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. This is analogous to the preparation of 12, where the reduction must be carried out in THF; the coordinated THF found in the precursor 11, [NPN]ZrCl$_2$(THF), is insufficient to ensure a high yield of 12 (Section 3.6). However, the titanium dichloride precursor 18, [NPN]TiCl$_2$, does not have coordinated THF; thus, the THF in 21 must originate from the solvent. In a closed system containing a mixture of 20 and 21, two overlapping multiplets are observed for the 2,5-H atoms of THF: coordinated THF at $\delta$ 3.66 and free THF at $\delta$ 3.57. Based on this information, the molecular formula for 21 is probably ([NPN]Ti)$_2$(THF)$_2$N$_2$; however, the coordination mode of the N$_2$ ligand is unknown. A pure sample of 21 could not be isolated for the purposes of obtaining an elemental analysis.

When 19, [NPN]TiCl(THF), was reduced with KC$_8$ under N$_2$, both complex 20 and 21 were formed. The reduction of either 18 or 19 produces a mixture containing 20 and 21, which suggests that the formation of both complexes proceeds through a common intermediate. Moreover, when 18, [NPN]TiCl$_2$, was reduced with KC$_8$ in the absence of dinitrogen (i.e., under static vacuum), neither 20 nor 21 were observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR and $^1\text{H}$ NMR spectra of the product. However, the reduction of 18 under $^{15}$N$_2$ produced a trace amount of 21 (presumed to be $^{15}$N$_2$-21) based on the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. These results provide additional evidence to support the existence of an intermediate dinitrogen complex, 21, which undergoes a transformation in which the N-N bond of dinitrogen is cleaved and 20 is formed (Scheme 4.3).
4.6 Proposed Mechanism for the Formation of \([\text{[N(PN)N]}\text{Ti}]_2\), 20, from \([\text{[NPN]}\text{Ti}]_2(\mu-\text{N}_2)\), 21

The formation of a phosphinimide ligand from molecular nitrogen is an unusual transformation; six electrons are needed to cleave the N≡N bond and the phosphine donor of the original starting material is oxidized from P(III) to P(V). Conceptually, the formation of 21 is initiated by the reduction of 18 or 19 to a transient Ti(II) intermediate, which is ultimately oxidized to Ti(III). As a result, the titanium centres give 2 electrons toward the cleavage of dinitrogen. The other 4 electrons are provided by the oxidation of the two phosphine donors.
One possible mechanism for this transformation is shown in Scheme 4.4. The first step involves the reduction of dinitrogen by two Ti(II) intermediates and the formation of 21. Although the structure of 21 is unknown, dinitrogen is depicted as a side-on coordinated hydrazido ligand, \((N_2)^+\), and THF donors have been omitted to simplify this illustration. Complex 21 undergoes a rearrangement where each phosphine attacks one nitrogen of the \(N_2\) unit; this promotes the cleavage of the N-N single bond and titanium is reduced from Ti(IV) in 21 to Ti(III) in 20. There is scant precedent in the literature for the reaction of coordinated dinitrogen with nucleophiles\(^{44,45}\) and phosphine attack on a coordinated \(N_2\) unit is undocumented. For this reason, an alternative mechanism can be proposed.

Scheme 4.4
Chapter 4: Amidophosphine Complexes of Titanium for the Activation of $N_2$

The second proposed mechanism for the conversion of 21 to 20 is inspired by two known processes: 1) the formation of metal nitrides from dinitrogen$^{46-53}$ and 2) nucleophilic attack on metal nitrides as observed in nitride coupling reactions$^{54,55}$ along with phosphinimide formation from Os(VI) nitride complexes.$^{56-58}$ For example, the reduction of a vanadium(III) dimer under $N_2$ produces a bridging dinitrido vanadium(V) complex (Equation 4.6)$^{51}$ The oxidation of the intermediate V(II) complex to V(V) is presumed to give the requisite six electrons needed to cleave the N≡N bond. An example of nucleophilic attack on a nitride is shown in Equation 4.7; an Os(IV) phosphinimide results from the reaction of an Os(VI) nitride with triphenylphosphine.$^{58}$

A second proposed mechanism for the formation of 20 is shown in Scheme 4.5. In step A, complex 21 is reduced by two electrons to give a dianionic bridging dinitride species. The nitrides are attacked by the ligand phosphines to generate a transitory Ti(II) species with bridging phosphinimide ligands (step B). The release of two electrons and the formation of a Ti-Ti bond produces 20 (step C). Overall, the transformation is electrocatalytic as the two
electrons required to cleave the N-N bond, and form the two bridging nitrides, are released. The cycle could be initiated by KC₈ or by a reduced Ti species formed in situ.

Scheme 4.5
4.7 Summary and Conclusions

In this chapter, the activation of dinitrogen by P2N2 and NPN complexes of titanium was presented. The dinitrogen complex 17, ([P2N2]Ti)2(µ-η₁:η₁-N2), was isolated from the reaction of [P2N2]TiCl2, 16, with KC8 under N2. Compared to the zirconium analogue 1, ([P2N2]Zr)2(µ-η²:η²-N2), the N2 unit in complex 17 has a smaller N-N bond distance of 1.25 Å and bridges the two metal centres in an end-on fashion. Complex 17 does not react with hydrogen or (p-methyl)phenylacetylene. Titanium is smaller than zirconium and, as such, the reactivity of N2 or Ti in 17 may be prevented by steric congestion imposed by the relatively large P2N2 ligand.

The use of the NPN ligand system affords titanium complexes with a less saturated coordination sphere around Ti than the P2N2 ligand. The reduction of 18, [NPN]TiCl2, or 19, [NPN]TiCl(THF), with the appropriate amount of KC8 (2 and 1 equivalents, respectively) under dinitrogen was expected to give a complex analogous to 12, ([NPN]ZrTHF)2(µ-η²:η²-N2). However, the reaction results in a much different outcome. Over time, the olive green reduction mixture changes to emerald green with the simultaneous conversion of an intermediate, 21, and growth of the final product, 20, as evidenced by multinuclear NMR spectroscopy. Complex 20, ([N(PN)N]Ti)2, can be isolated from the emerald green mixture in good yield and high purity. Solution and solid state characterization of 20 indicate that the complex consists of two Ti(III) centres bridged by the phosphinimide unit of a diamidophosphinimide ligand. Formally, the original phosphine donors in 18 have been oxidized from P(III) to P(V) in forming the phosphinimide. The origin of these nitrogen atoms, which are inserted between Ti and P to form the phosphinimide, was resolved by the reduction of 18 with 15N2. Complex 15N2-20 was observed by 31P{1H} NMR spectroscopy and mass spectrometry. The transformation of molecular nitrogen into a phosphinimide is likely an involved process requiring multiple steps. For instance, molecular nitrogen is probably coordinated to give a transitory dinuclear Ti dinitrogen complex, where the coordinated N2 unit is functionalized to give a new N-P bond with concomitant cleavage of the N-N bond.

Complex 21 is believed to be an intermediate dinitrogen complex in this transformation. The parent ion in the mass spectrum of 20 and the largest fragment in the
mass spectrum of 21 are the same and consistent with a molecule with the formula ([NPN]Ti)\(_2\)(N\(_2\)). Initially, 21 was thought to be a structural isomer of 20. However, resonances for coordinated THF in the \(^1\)H NMR spectrum of 21 suggests the formula ([NPN]Ti\(\eta^2\):\(\eta^2\)-THF)\(_2\)(\(\mu\)-N\(_2\)), which is analogous to 12, ([NPN]Zr\(\eta\)-THF)\(_2\)(\(\mu\)-N\(_2\)). The absence of the parent ion in the mass spectrum of 21 is not unexpected. Also, complex 21 is not formed unless the reduction of 18 is carried out under N\(_2\) and in THF, which is consistent with a dinitrogen complex with coordinated THF. Complex 21 is directly associated with the formation of 20 and, as such, the incorporation of molecular nitrogen into 21 is inferred even though the coordination mode of the N\(_2\) unit is unknown.

There is no definitive experimental evidence to support either of the two proposed mechanisms for the transformation of 21 into 20. The first mechanism suggests that the conversion is initiated by nucleophilic attack by the ligand phosphine on the coordinated N\(_2\) unit, which would then promote N-N bond cleavage; a reshuffle of the electrons then gives the final product 20 (Scheme 4.4). Although this mechanism is simple, there is no precedent in the literature for the first critical step. The second mechanism is modeled after known reactions in the literature, where the N-N bond of coordinated N\(_2\) can be cleaved to form bridging nitrides (Equation 4.6) and phosphine attack on a nitride is known to result in the formation of a phosphinimide (Equation 4.7). In order to facilitate the cleavage of the N-N bond, two electrons are needed in addition to the four electrons that are provided by the reduced titanium species. Only a catalytic amount of electrons is required to initiate the first step, which could possibly originate from KC\(_8\) or a reduced Ti species \(\text{formed in situ}\) (Scheme 4.5). Based on literature precedent, the second mechanism seems more plausible than the first mechanism.

The functionalization of molecular nitrogen by metal complexes with the NPN or P\(_2\)N\(_2\) ligand set is documented in the literature. For example, the formation of new N-H\(^{28}\), N-Si\(^{28,53}\), N-C\(^{29}\) and N-B\(^{59}\) bonds are a result of reactions involving the coordinated dinitrogen in Zr and Ta complexes. Complex 20 is also the product of a unique transformation involving molecular nitrogen: the formation of an N-P bond from N\(_2\).
Chapter 4: Amidophosphine Complexes of Titanium for the Activation of $N_2$

4.8 Experimental

4.8.1 General Procedures

Unless otherwise stated, all general procedures are the same as those found in section 2.8.1.

4.8.2 Materials

A glass 1 L ampoule containing 1 atm $^{15}N_2$ was obtained from Cambridge Isotopes and fitted with a Kontes-valve adaptor. Neat TiCl$_4$ was distilled and degassed by three freeze-pump-thaw cycles prior to use. TiCl$_4$(THF)$_2$,$^{60}$ TiCl$_3$(THF)$_3$,$^{60}$ [P$_2$N$_2$]Li$_2$(dioxane),$^{61}$ [NPN]Li$_2$(THF)$_2$,$^{62}$ and KC$_8$,$^{63,64}$ were prepared according to reported literature methods. Hydrogen was used without further purification and ($p$-methyl)phenylacetylene was distilled, freeze-pump-thaw degassed three times and then stored in the dark prior to use.

4.8.3 Synthesis and Characterization of Complexes 16 and 17

Synthesis and Characterization of [P$_2$N$_2$]TiCl$_2$, 16

Complex 16 was first synthesized by Dr. Jason Love of this research group. The procedure has been slightly modified from the original. It should be noted that within the scope of this thesis any reference to complex 16 refers only to syn-[P$_2$N$_2$]TiCl$_2$. Synthesis of anti-[P$_2$N$_2$]TiCl$_2$ has been reported elsewhere.$^{65}$

(i) Neat TiCl$_4$ (1.5 g, 0.867 mL, 7.91 mmol) was added dropwise to a clear colourless solution of [P$_2$N$_2$]Li$_2$(dioxane) (5.03 g, 7.92 mmol) in toluene (40 mL). The flask, fitted with a Kontes valve, was sealed under an atmosphere of dinitrogen and the resulting opaque red solution was stirred overnight. The red slurry was filtered through a scintereed-glass crucible containing Celite and the red filtrate was evaporated to dryness. A brick red powder of 16
was isolated and washed with a 1:1 toluene/hexanes solution to remove minor amounts of [P₂N₂]H₂. Purified yield 3.94 g, 76%.

(ii) A flask fitted with a Kontes valve was charged with [P₂N₂]Li₂(dioxane) (1.37 g, 2.16 mmol) and TiCl₄(THF)₂ powder (0.720 g, 2.16 mmol). Toluene (50 mL) was added to the yellow mixture. The headspace of the flask was evacuated and the dark red slurry was heated to reflux (~75°C) for 1.5 hours and stirred overnight at 50°C. Upon cooling, the slurry was filtered through Celite, toluene was removed in vacuo, and a brick red residue of 16 was isolated. Yield 0.98 g, 70%.

Anal. Calcd. for C₂₄H₄₂Cl₂N₂P₂Si₄Ti: C, 44.23; H, 6.50; N, 4.30. Found: C, 44.27; H, 6.56; N, 4.21

¹H NMR (C₆D₆, 300 MHz): δ 0.36 (s, 12H, SiCH₃), 0.40 (s, 12H, SiCH₃), 1.34 (br m, 4H, CH₂), 1.55 (br m, 4H, CH₂), 6.94 to 7.15 (overlapping multiplets, 6H, phenyl), 7.88 (m, 4H, o-H P-phenyl)

³¹P{¹H} NMR (C₆D₆, 121 MHz): δ 0.8 (s)

Synthesis and Characterization of ([P₂N₂]Ti)₂(µ-η¹⁻¹:η¹⁻N₂), 17

A thick-walled glass flask fitted with a Kontes valve was charged with a mixture of [P₂N₂]TiCl₂ (1.02 g, 1.57 mmol) and KC₈ (0.45 g, 3.33 mmol). The mixture was stirred, cooled to −78°C and exposed to a constant flow of N₂ gas (1 atm). The mixture was stirred vigorously as THF (40 mL) was added via cannula. After stirring for 10-15 minutes, the flask was sealed and the resulting red-brown slurry was kept cold for an additional 1-2 hours. The slurry slowly changed to yellow-brown as the reaction mixture warmed to room temperature and was stirred over night. The mixture was filtered through Celite to remove graphite. Toluene was removed in vacuo and a brown-green residue, 17, was isolated. Slow evaporation of a concentrated brown toluene solution of 17 produced crystals suitable for single crystal X-ray diffraction. Yield 0.64g, 69%.

Chapter 4: Amidophosphine Complexes of Titanium for the Activation of \( N_2 \)

\(^1\)H NMR (C\(_6\)D\(_6\), 300 MHz): \( \delta \) 0.14 (s, 24H, SiCH\(_3\)), 0.23 (s, 24H, SiCH\(_3\)), 1.23 (br m, 16H, CH\(_2\)), 6.89 to 7.27 (overlapping m, 12H, phenyl), 8.16 (br m, 8H, o-H phenyl)

\(^{31}\)P\(^1\)H NMR (C\(_6\)D\(_6\), 121 MHz): \( \delta \) −4.8 (s)

4.8.4 Reactivity of ([P\(_2\)N\(_2\)]Ti)_2(\(\mu\)-\(\eta^1\):\(\eta^1\)-N\(_2\)), 17

Reaction of ([P\(_2\)N\(_2\)]Ti)_2(\(\mu\)-\(\eta^1\):\(\eta^1\)-N\(_2\)), 17, with (p-methyl)phenylacetylene, (p-Me-C\(_6\)H\(_5\))C=CH

A d\(_6\)-benzene solution of 17 (0.033 g, 0.0277 mmol) was transferred to an NMR tube and 2 drops of (p-methyl)phenylacetylene (~0.04 mL, 0.3 mmol) were added to the sample. No colour change was observed; the solution remained brown for several days. The \(^1\)H NMR spectrum indicates that the sample is composed of a mixture of 17, [P\(_2\)N\(_2\)]H\(_2\), and (p-Me-C\(_6\)H\(_5\))C=CH.

\(^{31}\)P\(^1\)H NMR (C\(_6\)D\(_6\), 121 MHz): \( \delta \) −36.8 (s, [P\(_2\)N\(_2\)]H\(_2\)), −4.8 (s, complex 17)

Attempted Hydrogenation of ([P\(_2\)N\(_2\)]Ti)_2(\(\mu\)-\(\eta^1\):\(\eta^1\)-N\(_2\)), 17

A diethyl ether solution of 17 (0.100 g, 0.0841 mmol) was transferred to a flask fitted with a Kontes valve and degassed by three freeze-pump-thaw cycles. Hydrogen gas was introduced to the mixture at −196°C. The flask was sealed, warmed to room temperature and stirred for 48 hours. The solvent was removed in vacuo and brown residues were collected. The \(^{31}\)P\(^1\)H and \(^1\)H NMR spectra of the residues indicate no reaction took place.

Thermostability of ([P\(_2\)N\(_2\)]Ti)_2(\(\mu\)-\(\eta^1\):\(\eta^1\)-N\(_2\)), 17

A toluene solution of 17 (0.071 g, 0.060 mmol) was transferred to a flask fitted with a Kontes valve. The headspace was evacuated and the sample was heated to reflux (~65°C) for 24 hours. The solution remained brown and NMR spectra of the sample indicate that no decomposition of complex 17 occurred.

References begin on pg 146
4.8.5 Reduction of \([\text{P}_2\text{N}_2]\text{TiCl}_2, 16,\) under Different Conditions

Reduction of \([\text{P}_2\text{N}_2]\text{TiCl}_2, 16,\) under Argon in Toluene

A flask was charged with \(16\) (0.311 g, 0.477 mmol) and \(\text{KC}_8\) (0.128 g, 0.947 mmol) and flushed with Ar by three evacuate-refill cycles. Degassed toluene (30 mL) was added by cannula to the reaction flask under a flow of Ar. After one hour the red-brown slurry became green-grey and was stirred for an additional 48 hours. The mixture was filtered through Celite under an \(\text{N}_2\) atmosphere and toluene was removed \textit{in vacuo}. The \(^1\text{H}\) NMR spectrum is complicated by many overlapping peaks.

\(^{31}\text{P}^\{^1\text{H}\}\) NMR (\(\text{C}_6\text{D}_6\), 81 MHz): \(\delta -36.8\) (s, \([\text{P}_2\text{N}_2]\text{H}_2\)), \(-17.7\) (s), \(-4.8\) (s, complex 17), 11.0 (s), 20.2 (d, \(J_{pp} 98\) Hz), 22.0 (s), 32.1 (d, \(J_{pp} 98\) Hz)

Reduction of \([\text{P}_2\text{N}_2]\text{TiCl}_2, 16,\) under Argon in THF

A reaction with degassed THF (50 mL), \(16\) (0.656 g, 1.01 mmol) and \(\text{KC}_8\) (0.280 g, 2.07 mmol) was conducted in a similar manner as the analogous reaction in toluene described above. The \(^1\text{H}\) NMR spectrum of the resulting brown-green residues is complicated by many broad overlapping resonances.

\(^{31}\text{P}^\{^1\text{H}\}\) NMR (\(\text{C}_6\text{D}_6\), 81 MHz): \(\delta -36.8\) (s, \([\text{P}_2\text{N}_2]\text{H}_2\)), \(-17.7\) (s), \(-4.8\) (s, complex 17)

Reduction of \([\text{P}_2\text{N}_2]\text{TiCl}_2, 16,\) under Static Vacuum in Toluene

A thick-walled glass flask fitted with a Kontes valve was charged with a mixture of \([\text{P}_2\text{N}_2]\text{TiCl}_2\) (0.191 g, 0.293 mmol) and \(\text{KC}_8\) (0.085 g, 0.629 mmol) and flushed with Ar. Degassed toluene (50 mL) was transferred to the flask under static vacuum at \(-196^\circ\text{C}\). The mixture was warmed to room temperature and stirred overnight under static vacuum. The maroon slurry was filtered through Celite under an Ar atmosphere and toluene was removed \textit{in vacuo}. The \(^1\text{H}\) NMR spectrum of the resulting maroon residues is complicated by many broad overlapping resonances.
Chapter 4: Amidophosphine Complexes of Titanium for the Activation of $N_2$

$^{31}$P{$^1$H} NMR (C$_6$D$_6$, 81 MHz): $\delta$ -36.8 (s, [P$_2$N$_2$]H$_2$), -25.5 (s), 0.8 (s, complex 16)

4.8.6 Synthesis and Characterization of Complexes 18, 19, 20 and 21

Synthesis and Characterization of [NPN]TiCl$_2$, 18

Toluene (30 mL) was added to a flask containing a mixture of TiCl$_4$(THF)$_2$ (1.750 g, 5.24 mmol) and [NPN]Li$_2$(THF)$_2$ (3.103 g, 5.23 mmol). The dark red-orange slurry was stirred for at least one hour (or up to one day) and then filtered through Celite to remove LiCl. The solvent was removed in vacuo, leaving a dark orange residue. Hexanes (5 mL) were added to partially solubilize the residues and then removed in vacuo until the product took on the appearance of orange powder. Yield 1.74 g, 60%. To further purify the sample the solids were scraped into a scintered-glass crucible and washed with a minimal amount of toluene, followed by hexanes. The resulting orange solid was slightly paler than the original residues (Yield 1.50 g, 52%). Red platelet crystals suitable for X-ray diffraction were grown by vapour diffusion of hexanes into a THF solution of [NPN]TiCl$_2$.

Anal. Calcd. for C$_{24}$H$_{31}$Cl$_2$N$_2$PSi$_2$Ti: C, 52.09; H, 5.65; N, 5.06. Found: C, 52.46; H, 5.72; N, 4.73. EI-MS $m/z$: 552 [M$^+$], 517 ([M$^+$] - Cl)

$^1$H NMR (C$_6$D$_6$, 300 MHz): $\delta$ -0.13 (s, 6H, SiCH$_3$), 0.14 (s, 6H, SiCH$_3$), 1.21 (m, 2H, CH$_2$), 1.43 (m, 2H, CH$_2$), 6.88 to 7.13 (overlapping m, 13H, N-phenyl and P-phenyl), 7.84 (m, 2H, o-H P-phenyl).

$^{31}$P{$^1$H} NMR (C$_6$D$_6$, 121 MHz): $\delta$ 3.7 (s)

Synthesis and Characterization of [NPN]TiCl(THF), 19

TiCl$_3$(THF)$_3$ (0.6156 g, 1.662 mmol) was added to a toluene (30 mL) solution of [NPN]Li$_2$(THF)$_2$ (0.9880 g, 1.667 mmol) and shaken vigorously for 1 minute. The dark blue slurry was left undisturbed for 1 hour and then filtered through Celite to remove LiCl. The solvent was removed in vacuo, leaving a dark blue, glassy residue. Hexanes (5 mL) were added to partially solubilize the residues and then removed in vacuo until the product took on

References begin on pg 146
Chapter 4: Amidophosphine Complexes of Titanium for the Activation of \( N_2 \)

the appearance of flaky, gray-blue foam. Yield 0.71 g, 72%. Attempts to grow crystals suitable for X-ray diffraction were unsuccessful. Broad resonances observed in the \(^1\)H NMR spectrum suggest that the complex is paramagnetic. Minor resonances observed in the \(^{31}\)P\(^{\{1\}H}\) NMR spectrum are believed to be a result of diamagnetic impurities in the sample.

Anal. Calcd for \( C_{28}H_{39}ClN_2OPSi_2Ti \): C, 56.99; H, 6.66; N, 4.75. Found: C, 56.59; H, 6.52; N, 5.15. EI-MS \( m/z \): 590 ([M\(^+\] + H), 554 ([M\(^+\] - Cl), 517 ([M\(^+\] - THF)

Synthesis and Characterization of \((N(PN)N)Ti)_2, 20\)

A thick-walled glass flask fitted with a Kontes valve was charged with a mixture of \([NPN]TiCl_2\) (0.147 g, 0.266 mmol) and \( KC_8 \) (0.071 g, 0.526 mmol). The solids were stirred while under vacuum. Degassed THF* (40 mL) was added \textit{in vacuo} by a trap-to-trap transfer at \(-196^\circ\)C. The frozen reaction mixture was flushed with \( N_2 \) (1 atm) while warmed to \(-78^\circ\)C. The flask was sealed once the solvent had fully melted and the slurry was stirred at \(-78^\circ\)C for an additional 2-3 hours. The resulting dark brown/olive green slurry was stirred overnight while gradually warmed to room temperature. The mixture was filtered through Celite to remove graphite and solvent was removed \textit{in vacuo}. The dark green residues (crude yield 0.107 g, 82%) were dissolved in a minimal amount of toluene and set aside to allow for slow evaporation. The olive green solution changed to emerald green over a period of weeks. Prismatic forest green crystals of \((N(PN)N)Ti)_2, 20\), were isolated and suitable for single crystal X-ray diffraction. Crystal yield 0.050 g, 38%. (*Note: when toluene was the reduction solvent there was no evidence for 20 in the \(^1\)H and \(^{31}\)P\(^{\{1\}H}\) NMR spectra of the crude product.)

Anal. Calcd. for \( C_{48}H_{62}N_6P_2Si_4Ti_2 \): C, 58.05; H, 6.29; N, 8.46. Found: C, 57.72; H, 5.89; N, 8.86. EI-MS \( m/z \): 992 [M\(^+\)]

\(^1\)H NMR (\( C_6D_6, 300 \) MHz): \( \delta \) 0.13 (s, 12H, SiCH\(_3\)), 0.44 (s, 12H, SiCH\(_3\)), 0.89 (m, 4H, CH\(_2\)), 1.04 (m, 4H, CH\(_2\)), 6.80 (m, 1H, phenyl), 6.83 (br m, 2H, phenyl), 6.85 (m, 1H, phenyl), 6.94 to 7.15 (overlapping m, 26H, phenyl)

\(^{31}\)P\(^{\{1\}H}\) NMR (\( C_6D_6, 121 \) MHz): \( \delta \) 39.9 (s)

References begin on pg 146
Preparation and Characterization of an Intermediate Titanium Dinitrogen Complex, 21

Degassed THF* (60 mL) was transferred in vacuo to a thick-walled glass flask containing a mixture of \([\text{NPN}]\text{TiCl}_2\) (0.356 g, 0.643 mmol) and \(\text{KC}_8\) (0.173 g, 1.28 mmol) at \(-196^\circ\text{C}\). The reduction and workup were performed in the same manner used to prepare complex 20; however, the resulting slurry was more brown in colour. A brown/olive green powder of the reduction reaction was isolated by the removal of THF in vacuo immediately after filtration. This served to inhibit the formation of 20. (*Note: when toluene was the reduction solvent there was no evidence for 21 in the \(^1\text{H}\) and \(^{31}\text{P}\{^1\text{H}\}\) NMR spectra of the crude product.)

EI-MS \(m/z: 992 ([M^+ - 2 \text{THF})]

\(^1\text{H}\) NMR (\(\text{C}_6\text{D}_6\), 200 MHz): \(\delta\) 0.11 (s, 12H, SiCH\(_3\)), 0.31 (s, 12H, SiCH\(_3\)), 0.89 (m, 4H, CH\(_2\)), 1.21 (m, 12H, CH\(_2\) and THF), 3.66 (br m, 8H, THF), 6.68 to 7.33 (br m, \(\sim26\text{H}, \) phenyl), 8.22 (m, 4H, phenyl)

\(^{31}\text{P}\{^1\text{H}\}\) NMR (\(\text{C}_6\text{D}_6\), 81 MHz): \(\delta\) -18.7 (s, trace), 5.6 (s)

A portion of the olive green powder was dissolved in toluene and a colour change to emerald green was observed over 3 weeks. Toluene was removed in vacuo.

\(^1\text{H}\) NMR (\(\text{C}_6\text{D}_6\), 300 MHz): All major resonances are those observed for 20.

\(^{31}\text{P}\{^1\text{H}\}\) NMR (\(\text{C}_6\text{D}_6\), 121 MHz): \(\delta\) -41.6 (s, trace), -36.8 (s, trace), -34.1 (s, trace), 18.7 (s, trace), 39.9 (s, complex 20)

4.8.7 Additional Reduction Reactions of \([\text{NPN}]\text{TiCl}_2\), 18, and \([\text{NPN}]\text{TiCl}(\text{THF}), 19

Reduction of \([\text{NPN}]\text{TiCl(THF)}, 19, with One Equivalent of \(\text{KC}_8\) under \(^{14}\text{N}_2\)

A thick-walled glass flask fitted with a Kontes valve was charged with a mixture of \([\text{NPN}]\text{TiCl(THF)}\) (0.147 g, 0.249 mmol) and \(\text{KC}_8\) (0.030 g, 0.22 mmol). THF (35 mL) was added by cannula to the flask under N\(_2\) (1 atm) while the mixture was stirred at room temperature. An immediate colour change to brown/olive green was observed. The mixture
was stirred for 1 hr, filtered through Celite and THF was removed in vacuo. The $^1$H NMR spectrum is complicated by many overlapping peaks. Resonances for 20, 21 and [NPN]H$_2$, in addition to several unidentified peaks, are evident in the $^{31}$P{$^1$H} NMR spectrum.

**Reduction of [NPN]TiCl$_2$, 18, under $^{15}$N$_2$; Preparation of $^{15}$N$_2$-20**

Reduction of [NPN]TiCl$_2$ (0.1334 g, 0.2410 mmol) with KC$_8$ (0.0685 g, 0.507 mmol) under $^{15}$N$_2$ was carried out in the same manner as the reduction under one atmosphere of $^{14}$N$_2$ (i.e., vacuum transfer of THF, introduction of N$_2$ at -78°C). The only exception was that the supply of $^{15}$N$_2$ was limited; a 1L ampoule of $^{15}$N$_2$ gas (1 atm) was used. The final pressure of $^{15}$N$_2$ within the reaction vessel, at room temperature, was unknown. The resulting olive green slurry was stirred overnight at room temperature. The mixture was filtered through Celite and brown-green residues resulted from the removal of THF in vacuo. The $^1$H NMR spectrum is complicated by many overlapping resonances. Attempts to obtain a $^{15}$N NMR spectrum were unsuccessful: the $^{15}$N content in the sample was too small to detect a signal.

EI-MS m/z: 994 [M$^+$/]

$^{31}$P{$^1$H} NMR (C$_6$D$_6$, 121 MHz): $\delta$ -41.6 (s, relative integration area = 23), -36.8 (s, relative integration area = 8, [NPN]H$_2$), -34.1 (s, relative integration area = 3), 5.6 (s, relative integration area = 2, intermediate 21), 39.9 (d, $^1$J$_{PN}$ = 22 Hz, relative integration area = 10, $^{15}$N$_2$-20)

**Reduction of [NPN]TiCl$_2$, 18, under Static Vacuum**

A thick-walled glass flask fitted with a Kontes valve was charged with a mixture of [NPN]TiCl$_2$ (0.108 g, 0.195 mmol) and KC$_8$ (0.053 g, 0.39 mmol) and stirred under vacuum. Degassed THF (35 mL) was transferred to the flask under static vacuum at -196°C. The mixture was warmed to room temperature and stirred overnight under static vacuum. The dark brown mixture was filtered through Celite and THF was removed in vacuo. The $^1$H NMR spectrum consists of broad overlapping resonances.

$^{31}$P{$^1$H} NMR (C$_6$D$_6$, 81 MHz): $\delta$ -36.8 (s), -34.1 (s), -11.8 (s), 2.5 (s), 4.5 (s)
Chapter 4: Amidophosphine Complexes of Titanium for the Activation of \( \text{N}_2 \)

4.9 References


Chapter 4: Amidophosphine Complexes of Titanium for the Activation of N\textsubscript{2}


References begin on pg 146


References begin on pg 146
Chapter 4: Amidophosphine Complexes of Titanium for the Activation of \( \text{N}_2 \)


Appendix 1

X-ray Crystal Structure Data

In all cases, suitable crystals were selected and mounted on a glass fiber using Paratone-N oil and freezing to \(-100^\circ\text{C}\). All measurements were made on a Rigaku/ADSC CCD area detector with graphite monochromated Mo-K\(\alpha\) radiation. Data were collected and processed using the d*TREK program.\(^1\) The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods\(^2,3\) and expanded using Fourier techniques.\(^4\) Hydrogen atoms were included but not refined. The non-hydrogen atoms were refined anisotropically. Neutral atom scattering factors were taken from the *International Tables for X-ray Crystallography*.\(^5\) Calculations were performed using the teXsan crystallographic software package.\(^6\) Dr. Brian O. Patrick solved the structures for complexes 8, 9, 13, 17 and 18. Christopher D. Carmichael solved the structure for 20. A summary of all crystal data collection and refinement for compounds 8, 9 and 13 is given in Table A1.1. A summary of all crystal data collection and refinement for compounds 17, 18 and 20 is given in Table A1.2. Crystal structure data CIF files are available.\(^7,8\) Additional information is available through the UBC X-ray laboratory or the Fryzuk research group. The local file name for each structure is listed in Table A1.3. Compound 8 crystallized with one half
molecule of hexane in the asymmetric unit. No solvent molecules crystallized in the asymmetric unit with 13. Compound 17 crystallized as two crystallographically independent half-molecules, each forming an N₂-linked dimer via an inversion centre. Compounds 9, 17 and 20 each crystallized with two molecules of toluene in the asymmetric unit. Compound 18 crystallized with one uncoordinated molecule of THF in the asymmetric unit.

<table>
<thead>
<tr>
<th>Table A1.1. Summary of Crystallographic Data Collection and Refinement for (([P_2N_2]Zr)₂((\mu-\eta^2:\eta^2)-N₂CH=CH(p-Me-C₆H₄))((\mu-C=C(p-Me-C₆H₄))), 8; (([P_2N_2]Zr)₂((\mu-\eta^2:\eta^2)-N₂CH=CH(p-¹Bu-C₆H₄))((\mu-C=C(p-¹Bu-C₆H₄))), 9; and (([NPN]Zrpy)₂((\mu-\eta^2:\eta^2)-N₂), 13</th>
<th>8</th>
<th>9</th>
<th>13</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical Formula</strong></td>
<td>Zr₂P₄Si₂N₆C₆H₁₀₇</td>
<td>Zr₂P₄Si₂N₆C₆H₁₂₈</td>
<td>C₈H₂N₆P₂Si₂Zr₂</td>
</tr>
<tr>
<td><strong>Fw</strong></td>
<td>1551.66</td>
<td>1777.02</td>
<td>1237.98</td>
</tr>
<tr>
<td><strong>Colour, Habit</strong></td>
<td>orange, platelet</td>
<td>clear, needle</td>
<td>Dark green, block</td>
</tr>
<tr>
<td><strong>Crystal size, mm</strong></td>
<td>0.40 x 0.20 x 0.07</td>
<td>0.50 x 0.10 x 0.10</td>
<td>0.20 x 0.20 x 0.20</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>triclinic</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P-1 (#2)</td>
<td>P2₁/a (#14)</td>
<td>C2/c (#15)</td>
</tr>
<tr>
<td><strong>a, Å</strong></td>
<td>12.5329(7)</td>
<td>27.261(1)</td>
<td>24.957(4)</td>
</tr>
<tr>
<td><strong>b, Å</strong></td>
<td>13.3989(5)</td>
<td>12.7830(4)</td>
<td>11.560(2)</td>
</tr>
<tr>
<td><strong>c, Å</strong></td>
<td>25.997(2)</td>
<td>28.343(1)</td>
<td>21.469(3)</td>
</tr>
<tr>
<td><strong>α, deg</strong></td>
<td>91.876(2)</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td><strong>β, deg</strong></td>
<td>103.279(1)</td>
<td>108.920(2)</td>
<td>94.190(10)</td>
</tr>
<tr>
<td><strong>γ, deg</strong></td>
<td>107.544(2)</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td><strong>V, Å³</strong></td>
<td>4026.6(4)</td>
<td>9343.2(6)</td>
<td>6177.3(17)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>2</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td><strong>T, °C</strong></td>
<td>-100 ± 1</td>
<td>-100 ± 1</td>
<td>-100 ± 1</td>
</tr>
<tr>
<td><strong>ρcalc, g/cm³</strong></td>
<td>1.280</td>
<td>1.263</td>
<td>1.331</td>
</tr>
<tr>
<td><strong>F₀₀₀</strong></td>
<td>1630.00</td>
<td>3752.00</td>
<td>2568</td>
</tr>
<tr>
<td><strong>μ (MoKα), cm⁻¹</strong></td>
<td>4.98</td>
<td>4.38</td>
<td>5.10</td>
</tr>
<tr>
<td><strong>correction factors</strong></td>
<td>0.7231 – 1.0000</td>
<td>0.8607 – 1.0000</td>
<td>0.9050 – 0.9050</td>
</tr>
<tr>
<td><strong>20 max, deg</strong></td>
<td>56</td>
<td>55.7</td>
<td>60.9</td>
</tr>
<tr>
<td><strong>total no. of reflns</strong></td>
<td>32629</td>
<td>87468</td>
<td>117554</td>
</tr>
<tr>
<td><strong>no. of unique reflns</strong></td>
<td>15659</td>
<td>21250</td>
<td>9375</td>
</tr>
<tr>
<td><strong>Rint</strong></td>
<td>0.046</td>
<td>0.121</td>
<td>0.0319</td>
</tr>
<tr>
<td><strong>no. observations (I &gt; 2σ(I))</strong></td>
<td>12548</td>
<td>11779</td>
<td>7558</td>
</tr>
<tr>
<td><strong>no. of variables</strong></td>
<td>824</td>
<td>979</td>
<td>338</td>
</tr>
<tr>
<td><strong>R₁ (F², I &gt; 2σ(I))</strong></td>
<td>0.055</td>
<td>0.050</td>
<td>0.032</td>
</tr>
<tr>
<td><strong>R_w (F², all data)</strong></td>
<td>0.136</td>
<td>0.103</td>
<td>0.098</td>
</tr>
<tr>
<td><strong>Gof</strong></td>
<td>1.12</td>
<td>0.88</td>
<td>1.16</td>
</tr>
</tbody>
</table>

Rigaku/ADSC CCD diffractometer, R₁ = Σ||F₀||-|F₁||/Σ|F₀||, R_w = (Σw(‖F₀‖² - ‖F₁‖²)²/Σw‖F₀‖²)¹/²
Table A1.2. Summary of Crystallographic Data Collection and Refinement for ([P2N2]Ti)2(μ-η1:η1-N2), 17; [NPN]TiCl2, 18; and ([N(PN)N]Ti)2 20

<table>
<thead>
<tr>
<th>Complex</th>
<th>File Name</th>
<th>Complex</th>
<th>File Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>mf449</td>
<td>17</td>
<td>mf470</td>
</tr>
<tr>
<td>9</td>
<td>mf496</td>
<td>18</td>
<td>mf488</td>
</tr>
<tr>
<td>13</td>
<td>mf550</td>
<td>20</td>
<td>mf506</td>
</tr>
</tbody>
</table>

Table A1.3. File Name for the Crystallographic Data of each Complex

<table>
<thead>
<tr>
<th>Complex</th>
<th>File Name</th>
<th>Complex</th>
<th>File Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>mf449</td>
<td>17</td>
<td>mf470</td>
</tr>
<tr>
<td>9</td>
<td>mf496</td>
<td>18</td>
<td>mf488</td>
</tr>
<tr>
<td>13</td>
<td>mf550</td>
<td>20</td>
<td>mf506</td>
</tr>
</tbody>
</table>

Rigaku/ADSC CCD diffractometer, R = Σ||Fo||-|Fc||/Σ|Fc|; Rw = (Σw(|Fo|2 - |Fc|2)2)/Σw|Fo|2)1/2
References


Appendix 2

Isotopic Labeling Experiment: Reaction of \([\text{P}_2\text{N}_2\text{Zr}]_2(\mu-\eta^2:\eta^2-\text{N}_2), 1,\) with \text{PhC}≡\text{CH} or \text{PhC}≡\text{CD}

Previous attempts were made to study the kinetics for the reaction of \([\text{P}_2\text{N}_2\text{Zr}]_2(\mu-\eta^2:\eta^2-\text{N}_2), 1,\) with phenylacetylene (PhCCH) by monitoring the system with UV-Visible spectroscopy. Imposing pseudo-first order reaction conditions (minimum ratio of 1:100 for complex 1:PhCCH) did not result in a linear plot. Also, isosbestic points were not apparent in the spectra. Based on this data, the process for forming \(4, ([\text{P}_2\text{N}_2\text{Zr}]_2(\mu-\eta^2:\eta^2-\text{N}_2\text{CH}=\text{CHPh})(\mu-\text{C}=\text{CPh}),\) from 1 is believed to be very complicated and attempts to monitor this reaction are hampered by the possible side reactions of 1, 4 and any unknown intermediates. A comparison of the \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum obtained for a solution with only two equivalents of PhCCH to that of a reaction mixture where an excess of PhCCH was used suggests that the formation of impurities can be reduced by limiting the quantity of PhCCH in solution. For these reasons, a labeling study was undertaken where the effect of PhCCH (~2 equivalents) on the depletion of 1 would be compared relative to that of PhCCD. Phenylacetylene (PhCCH) was filtered through alumina and distilled prior to use. A sample
Appendix 2: Isotopic Labeling Experiment

of d$_1$-phenylacetylene was purchased and used without further purification. Complex 1 was prepared according to the procedure outlined in Chapter 2.

A teal solution of ([P$_2$N$_2$]Zr)$_2$(μ-η$_2$⁻:η$_2$⁻N$_2$)$_1$, 1, (0.0119 g, 0.00933 mmol) in 1.00 mL of toluene was prepared. This solution (0.40 mL, 0.00933 M) was transferred into each of two NMR tubes. A 10 μL syringe was washed with PhCCH (or PhCCD) prior to delivering 1 μL (2.4 equivalents) to one of the NMR samples. A sealed capillary tube containing 30 μL of PEt$_3$ was added to each of the NMR tubes as an internal standard. The samples were mixed at the same moment and monitored by $^{31}$P{$^1$H} NMR spectroscopy every 10-15 minutes over the course of 3 hours. Spectra were also obtained after 5 hours. A colour change from teal to emerald green was apparent for sample A after two hours, while sample B appeared unchanged.

**Table A2.1.** Concentration of ([P$_2$N$_2$]Zr)$_2$(μ-η$_2$⁻:η$_2$⁻N$_2$)$_1$, 1, and PhCCH (or PhCCD) in a Solution of d$_8$-Toluene

<table>
<thead>
<tr>
<th>Sample</th>
<th>Complex 1 (mmol)</th>
<th>PhCCH (mmol)</th>
<th>PhCCD (mmol)</th>
<th>[Complex 1] (M)</th>
<th>[PhCC-H/D] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.00373</td>
<td>0.00911</td>
<td>----</td>
<td>0.00930</td>
<td>0.0227</td>
</tr>
<tr>
<td>B</td>
<td>0.00373</td>
<td>----</td>
<td>0.00910</td>
<td>0.00930</td>
<td>0.0227</td>
</tr>
</tbody>
</table>

Decomposition of 1 was observed over time in both A and B due to the emergence of a peak that corresponds to ([P$_2$N$_2$]Zr)$_2$(μ-η$_2$⁻:η$_2$⁻N$_2$H$_2$)(μ-O), 7 (δ -12.5, s) in the $^{31}$P{$^1$H} NMR spectrum. The integration for this resonance was not monitored because this peak overlaps with the broad resonance of the desired product, 4, ([P$_2$N$_2$]Zr)$_2$(μ-η$_2$⁻:η$_2$⁻N$_2$CH=CHPh)(μ-C≡CPh) or the deuterated product, d$_2$-4, ([P$_2$N$_2$]Zr)$_2$(μ-η$_2$⁻:η$_2$⁻N$_2$CD=CDPh)(μ-C≡CPh) in the $^{31}$P{$^1$H} NMR spectrum at room temperature. Only after a period of 4 weeks was a negligible amount of [P$_2$N$_2$]H$_2$ (δ -36.8, s) observed in the samples.
Plotting the decrease in concentration of $\mathbf{1}$ in both experiments gave virtually identical values over the period indicated (Figure A2.1).

**Table A2.2.** Integration Values for $\mathbf{1}$ in Solution $A$ and Solution $B$ from $^{31}\text{P} \left( ^1\text{H} \right)$ NMR (121 MHz) Spectra Obtained over a Period of 5 Hours

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>$\text{Integration}^1$</th>
<th>$\text{Integration}^2$</th>
<th>Time (min)</th>
<th>$\text{Integration}^1$</th>
<th>$\text{Integration}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Complex $\mathbf{1}$</td>
<td>PEt$_3$ Impurity</td>
<td></td>
<td>Complex $\mathbf{1}$</td>
<td>PEt$_3$ Impurity</td>
</tr>
<tr>
<td>21</td>
<td>293.8</td>
<td>105.9</td>
<td>28</td>
<td>238.2</td>
<td>113.4</td>
</tr>
<tr>
<td>36</td>
<td>170.4</td>
<td>113.8</td>
<td>42</td>
<td>188.1</td>
<td>98.9</td>
</tr>
<tr>
<td>51</td>
<td>148.8</td>
<td>104.0</td>
<td>61</td>
<td>140.6</td>
<td>108.2</td>
</tr>
<tr>
<td>71</td>
<td>129.4</td>
<td>98.5</td>
<td>80</td>
<td>142.3</td>
<td>118.6</td>
</tr>
<tr>
<td>87</td>
<td>112.0</td>
<td>100.1</td>
<td>94</td>
<td>123.2</td>
<td>97.4</td>
</tr>
<tr>
<td>100</td>
<td>118.7</td>
<td>117.4</td>
<td>109</td>
<td>134.4</td>
<td>122.0</td>
</tr>
<tr>
<td>115</td>
<td>108.6</td>
<td>112.5</td>
<td>122</td>
<td>129.0</td>
<td>107.5</td>
</tr>
<tr>
<td>128</td>
<td>100.5</td>
<td>102.3</td>
<td>137</td>
<td>116.7</td>
<td>117.6</td>
</tr>
<tr>
<td>144</td>
<td>109.3</td>
<td>95.8</td>
<td>152</td>
<td>124.2</td>
<td>109.9</td>
</tr>
<tr>
<td>158</td>
<td>90.1</td>
<td>92.1</td>
<td>166</td>
<td>120.7</td>
<td>115.0</td>
</tr>
<tr>
<td>282</td>
<td>88.0</td>
<td>103.2</td>
<td>288</td>
<td>102.8</td>
<td>87.8</td>
</tr>
</tbody>
</table>

$^1$Integration values for $\mathbf{1}$ are relative to a value of 1000 assigned to the area for the PEt$_3$ resonance at $\delta$ -62.5 in each of the $^{31}\text{P} \left( ^1\text{H} \right)$ NMR spectra. The resonance for $\mathbf{1}$ was integrated from $\delta$ -16.0 to $\delta$ -16.5 and that of PEt$_3$ was integrated from $\delta$ -62.1 to $\delta$ -62.9 in each of the spectra.

$^2$The relative amount of an impurity ($\delta$ -30.9, s) in the PEt$_3$ sample was also determined by an integration of $\delta$ 31.1 to $\delta$ 30.6. The variation of this integration value between spectra was used to estimate that the data is accurate to ±10%.
Figure A2.1. Decrease in the integrated area for the $^{31}$P{$^1$H} NMR signal of 1 over time following the addition of PhCCH (Solution A) or PhCCD (Solution B).

Although each solution was monitored over a period of 5 hours, the reaction is known to be moderately slow and a week is required for 1 to be fully consumed. Within the first 3 hours of the reaction, the amount of unreacted PhCCH (or PhCCD) in solution is in excess. Although these conditions were not pseudo-first order, this type of plot ($\ln(I)$ vs. time) was used as a tool to estimate the difference in the reaction rate constant ($k_{obs}$) between a solution with PhCCH or PhCCD. The concentration of complex 1 is proportional to the integrated area for the resonance of complex 1, I, in the $^{31}$P{$^1$H} NMR spectrum. So, the integration data in Table A2.2 were used to determine the values for the y-axis in Figure A2.2. The value for I at ~5 hours was used as an approximation for “I(infinity)” (the value of I when time = infinity). The presence of a kinetic isotope effect was expected to be apparent from this simple plot.
Appendix 2: Isotopic Labeling Experiment

Figure A2.2. A first-order plot of the integration data for the depletion of 1 over time following the addition of PhCCH (Solution A) or PhCCD (Solution B).

In a first-order reaction plot the rate constant is obtained from the slope. The slope resulting from a plot of the data for Solution A (−3.12x10⁻⁴ s⁻¹) is slightly larger than that for Solution B (−2.497x10⁻⁴ s⁻¹). However, this slight difference is not large enough to suggest it is the result of a primary kinetic isotope effect. As a result, it appears that the cleavage and formation of C-H bonds is not part of the rate-determining step in the formation of 4.