Group 4 Complexes of an Arene-Bridged Diamidophosphine Ligand for Nitrogen Activation

by

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B. Sc., University of Toronto, 1999
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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

September 2006

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Abstract

Molecular nitrogen comprises about 80% of the earth’s atmosphere, but is only used as a starting material in one industrial reaction: NH₃ synthesis from N₂ and H₂ by the Haber-Bosch process. Dinitrogen is generally unreactive, however, N₂ complexes of most transition metals and lanthanides are known, and the challenge remains to discover metal dinitrogen complexes that can functionalize N₂. This thesis describes a new ligand, [NPN]⁺, its coordination to Zr and Hf, and the use of [NPN]⁺Zr complexes to transform N₂.

Arene-bridged diamidophosphine ligand [NPN]⁺Li₂ ([NPN]⁺ = [{N-(2,4,6-Me₃C₆H₂)(2-N-5-Me-C₆H₃)}₂PPh]²⁻) is synthesized from simple organic compounds and PhPCl₂ in high yield. Zr and Hf complexes, [NPN]⁺MCl₂ (M = Zr, Hf), are prepared via protonolysis from [NPN]⁺H₂, M(NMe₂)₄, and Me₃SiCl. Organometallic [NPN]⁺MR₂ (R = Me, CH₂Ph, CH₂SiMe₃) are prepared from [NPN]⁺MCl₂ and Grignard or organolithium reagents. [NPN]⁺ZrR₂ (R = CH₂Ph, CH₂SiMe₃) are light- and heat-sensitive, and decompose to cyclometalated [NPNC]⁺ZrR ([NPNC]⁺ = [{2-(MesN-5-MeC₆H₄)P(Ph)(2-(NC₆H₂-2,4-CH₃-6-CH₂)-5-MeCH₃)}₃]) and RH via an intramolecular σ-bond metathesis mechanism.

A Zr-N₂ complex, ([NPN]⁺Zr(THF))₂(µ-η²:η²-N₂), is synthesized in high yield from [NPN]⁺ZrCl₂ and 2.2 equiv. of KC₈ in THF under 4 atm of N₂. By single crystal X-ray analysis, N₂ has been reduced to N₂⁺ and is side-on bound to two Zr atoms. Excess Py and PMe₂R (R = Me, Ph) reacts with the Zr-N₂ complex to furnish ([NPN]⁺Zr(Py))₂(µ-η²:η²-N₂), and ([NPN]⁺Zr(PMe₂R))(µ-η²:η²-N₂){Zr[NPN]⁺}, respectively. The PMe₂R adducts react with H₂ to provide ([NPN]⁺Zr(PMe₂R))(µ-H)(µ-η²:η²-N₂)NHNH(NH)₂ with a new N-H bond. A new N-Si bond forms upon addition of PhSiH₃ to the Py adduct to give ([NPN]⁺Zr(Py))(µ-H)(µ-η²:η²-NNSiH₂Ph){Zr[NPN]⁺} in high yield. The reaction of 4,4'-dimethylbenzophenone with the THF adduct provides ([NPN]⁺Zr)₂(µ-O)(µ-η¹:η²-NN=NC(4-MeC₆H₄))₂ with a new N=C bond, and benzophenone imine reacts with the Py adduct to generate ([NPN]⁺Zr(N=CPh₂))₂(µ-η²:η²-N₂H₂) with two new N-H bonds.

The dilithium complex of Ph₄Ar[NPN]⁺ (Ar = 4-PrC₆H₄) is prepared in two steps from commercially available reagents. Ph₄Ar[NPN]⁺Li₂(S) (S = THF, dioxane) is similar to [NPN]⁺Li₂(S) in solution and in the solid state, and is converted to Ph₄Ar[NPN]⁺Zr(NMe₂)₂ via protonolysis. Future directions for research are also suggested.
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## Glossary of Terms

<table>
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<tr>
<td>Å</td>
<td>Ångström ($10^{-10}$ m)</td>
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<tr>
<td>Anal.</td>
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<tr>
<td>Ar</td>
<td>aryl group (unless context indicates argon)</td>
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<tr>
<td>atm</td>
<td>atmosphere</td>
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<tr>
<td>b</td>
<td>broad</td>
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<td>Bn</td>
<td>benzyl group (-CH$_2$C$_6$H$_5$)</td>
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<td>'Bu</td>
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</tr>
<tr>
<td>2D</td>
<td>two-dimensional</td>
</tr>
<tr>
<td>δ</td>
<td>delta</td>
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<tr>
<td>Δ</td>
<td>heat</td>
</tr>
<tr>
<td>dd</td>
<td>doublet of doublets</td>
</tr>
<tr>
<td>ddd</td>
<td>doublet of doublets of doublets</td>
</tr>
<tr>
<td>deg (°)</td>
<td>degrees</td>
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<td>dens or ρ</td>
<td>density</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>ΔG$^\ddagger$</td>
<td>free energy of activation</td>
</tr>
<tr>
<td>ΔH$^\ddagger$</td>
<td>enthalpy of activation</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>DME</td>
<td>dimethoxyethane (MeOCH₂CH₂OMe)</td>
</tr>
<tr>
<td>dₙ</td>
<td>n-deuterated</td>
</tr>
<tr>
<td>ΔSᵗ</td>
<td>entropy of activation</td>
</tr>
<tr>
<td>dt</td>
<td>doublet of triplets</td>
</tr>
<tr>
<td>e or e⁻</td>
<td>electron(s)</td>
</tr>
<tr>
<td>E or E⁺</td>
<td>element</td>
</tr>
<tr>
<td>E</td>
<td>energy</td>
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<tr>
<td>E</td>
<td>entgegen or <em>trans</em></td>
</tr>
<tr>
<td>EI</td>
<td>electron impact</td>
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<tr>
<td>ESI</td>
<td>electrospray ionization</td>
</tr>
<tr>
<td>ESR or EPR</td>
<td>electron spin resonance or electron paramagnetic resonance</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl group (-CH₂CH₃)</td>
</tr>
<tr>
<td>EtO</td>
<td>ethoxide group (-OCH₂CH₃)</td>
</tr>
<tr>
<td>Et₂O</td>
<td>diethyl ether</td>
</tr>
<tr>
<td>EtOAc</td>
<td>ethyl acetate</td>
</tr>
<tr>
<td>fw</td>
<td>formula weight</td>
</tr>
<tr>
<td>g</td>
<td>gram(s)</td>
</tr>
<tr>
<td>gof</td>
<td>goodness of fit</td>
</tr>
<tr>
<td>h</td>
<td>hour(s)</td>
</tr>
<tr>
<td>'H</td>
<td>proton</td>
</tr>
<tr>
<td>{'H}</td>
<td>proton decoupled</td>
</tr>
<tr>
<td>ηⁿ</td>
<td>hapticity of order n</td>
</tr>
<tr>
<td>HMDSO</td>
<td>hexamethyldisiloxane [(CH₃)₃Si]₂O</td>
</tr>
<tr>
<td>HMQC</td>
<td>heteronuclear multiple quantum coherence</td>
</tr>
<tr>
<td>HMSC</td>
<td>heteronuclear single quantum coherence</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz, seconds⁻¹</td>
</tr>
<tr>
<td>I</td>
<td>nuclear angular momentum quantum number (spin)</td>
</tr>
<tr>
<td>I</td>
<td>intensity</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>`J_AB</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
</tbody>
</table>

*xvi*
kcal  kilocalories  
k_b  Boltzmann constant  
kJ  kilojoules  
^7Li  lithium-7  
LUMO  lowest unoccupied molecular orbital  
m  multiplet  
m^-  meta- position of aryl ring  
M  metal  
M^+  parent ion  
\(\mu\)  bridging, absorption coefficient, or micro  
Me  methyl group, (-CH\(_3\))  
Mes  mesityl group, (-2,4,6-C\(_6\)H\(_2\)(CH\(_3\))\(_3\))  
mg  milligram(s)  
MHz  megaHertz  
min.  minute(s)  
mL  millilitre(s)  
mm  millimetre(s)  
mmol  millimole(s)  
MO  molecular orbital  
mol  mole(s)  
MS  mass spectrometry  
\((m/z)\)  mass-to-charge ratio  
\(^{15}\)N  nitrogen-15  
v  stretch  
nm  nanometre(s)  
NMR  nuclear magnetic resonance  
NOE  nuclear overhauser effect  
NOESY  nuclear overhauser enhancement spectroscopy  
\([\text{NPN}]\)  \([\text{PhP(CH}_2\text{SiMe}_2\text{NPh)}_2]^{2-}\)  
\([\text{NPN}]^+\)  \([\text{\{N-(2,4,6-Me}_3\text{C}_6\text{H}_3\}{2-N-5-MeC}_6\text{H}_3})_2\text{PPh}]^{2-}\)  
o-  ortho- position of aryl ring  
ORTEP  Oakridge Thermal Ellipsoid Plotting Program  
xvii
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Full Form</th>
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</thead>
<tbody>
<tr>
<td>$p$</td>
<td>para-position of aryl ring</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>[(R$_2$PCH$_2$SiMe$_2$)N] R = Me, 'Pr</td>
</tr>
<tr>
<td>[P$_2$Nd]</td>
<td>[PhP(CH$_2$SiMe$_2$)$_2$NSiMe$_2$CH$_2$]$_2$PPh]$^2$</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>'Pr</td>
<td>isopropyl group (-CH(CH$_3$)$_2$)</td>
</tr>
<tr>
<td>$^n$Pr</td>
<td>normal propyl group (-CH$_2$CH$_2$CH$_3$)</td>
</tr>
<tr>
<td>Py</td>
<td>Pyridine (C$_5$H$_5$N)</td>
</tr>
<tr>
<td>R</td>
<td>alkyl or aryl group</td>
</tr>
<tr>
<td>refl</td>
<td>reflections</td>
</tr>
<tr>
<td>$R_f$</td>
<td>retention factor</td>
</tr>
<tr>
<td>RR</td>
<td>resonance Raman</td>
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<tr>
<td>rt</td>
<td>room temperature</td>
</tr>
<tr>
<td>s</td>
<td>singlet</td>
</tr>
<tr>
<td>s</td>
<td>second(s)</td>
</tr>
<tr>
<td>$^{29}$Si</td>
<td>silicon-29</td>
</tr>
<tr>
<td>syst</td>
<td>system</td>
</tr>
<tr>
<td>t</td>
<td>time</td>
</tr>
<tr>
<td>t</td>
<td>triplet</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TLC</td>
<td>thin layer chromatography</td>
</tr>
<tr>
<td>tmeda</td>
<td>tetramethylethylenediamine (Me$_2$NCH$_2$CH$_2$NMe$_2$)</td>
</tr>
<tr>
<td>TMS</td>
<td>tetramethylsilane ((CH$_3$)$_4$Si)</td>
</tr>
<tr>
<td>Tol</td>
<td>tolyl group (-C$_6$H$_5$CH$_3$)</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>ultraviolet-visible</td>
</tr>
<tr>
<td>V</td>
<td>Volt</td>
</tr>
<tr>
<td>V</td>
<td>Volume (of unit cell)</td>
</tr>
<tr>
<td>VT</td>
<td>variable temperature</td>
</tr>
<tr>
<td>xs</td>
<td>excess</td>
</tr>
<tr>
<td>$Z$</td>
<td>number of formula units in the unit cell</td>
</tr>
</tbody>
</table>
Acknowledgements

I would like to thank Mike Fryzuk for being an excellent supervisor. His research ideas and patient support were invaluable for the past five years.

I am greatly indebted to past and present members of the Fryzuk group for creating a supportive and fun lab environment, and for all of their help showing me techniques and sharing in the group jobs. I would especially like to thank Howie Jong and Liam Spencer for many productive discussions about chemistry and crystallography, and for making the lab a great place to be. I am very grateful to have worked alongside Lara Morello, a great labmate and friend. Thanks are due to Mike Petrella, Bruce MacKay, Scott Winston, Thorsten von Fehren, and Mike Shaver for many hours showing me the ropes. I have also had the good fortune to supervise many talented undergraduates including Shiva Shoai, Sharonna Greenberg, Nelly Ousatiouk, and Malte Wohlfart. Thanks for all of the hard work, enthusiasm, patience and new ideas.

Many thanks are due to the excellent support staff at the Chemistry Department at U.B.C.: Dr. Brian Patrick, our very talented departmental crystallographer, for his patient instruction, Minaz Lakha and Marshall Lapawa and all of the staff at the mass spectrometry/microanalysis facility for their patience and skill with my finicky air-sensitive samples. Thank you to Zorana Danilovic, Maria Ezhova, Marietta Austria, Liane Darge, and Nick Burlinson for their incredible knowledge and assistance with NMR spectroscopy. Thanks very much to the excellent support staff in the mechanical and electronic/computing shop, glassblowing shop, chemistry stores, and in the front office. I am especially indebted to Ken Love for many hours of tireless detective work in front of the Fryzuk lab’s glovebox.

Thanks are due to Peter Legzdins for reading my thesis, and for support through the years. I would also like to acknowledge Peter Wassell for allowing me to teach in the inorganic undergraduate lab — it's been a fun five years! Thanks are also due to Doug Stephan at the University of Windsor for help with one of the crystal structures, and general supportiveness. I am very grateful to Sharonna Greenberg for editing this entire thesis, and
for her friendship. Thank you to Britta Boden, Tracey Stott, Amanda Gallant, Meghan Dureen, and Carolyn Moorlag for friendship and support. I'm going to miss all of the good cooking!

Thank you to my parents and my brother for being such good role models, and for your generosity, love, and support.

Thank you to Mark for being such a fun and kind husband, and for curing my allergies!
To my parents and Mark…
Chapter One

Synthesis and Reactivity of Side-on Bound Dinitrogen

1.1 Introduction.

Transition-metal complexes that incorporate dinitrogen as a ligand have enjoyed a special status in inorganic coordination chemistry. In contrast to isoelectronic carbon monoxide, which is reactive and binds strongly to many transition-metal ions, \( \text{N}_2 \) is remarkably stable and a poor ligand.\(^1\) Although more is known about \( \text{CO} \) as a ligand,\(^2\) since the first \( \text{N}_2 \) complex, \([\text{Ru(NH}_3)_5\text{N}_2]\)\(^{2+}\), was discovered in 1965, a great deal has been learned about how \( \text{N}_2 \) binds to a metal, and the reactivity of coordinated \( \text{N}_2 \).\(^3\) Early investigations into the reactivity of coordinated \( \text{N}_2 \) focused on protonation in an effort to mimic the conversion of \( \text{N}_2 \) to ammonia by the enzyme nitrogenase.\(^4\)\(^5\) Another reaction of interest is the addition of organic and inorganic electrophiles, such as acyl halides or main group halides, to dinitrogen complexes. The displacement of \( \text{N}_2 \) by better donor ligands is also a well known, albeit unproductive reaction of coordinated dinitrogen. Until relatively recently, research on dinitrogen coordination chemistry has focused on these three types of reactions.\(^6\)

In the past decade, the chemistry of coordinated dinitrogen has been reinvigorated by the discovery of new reactions, including \( \text{N}-\text{N} \) bond cleavage, and functionalization of coordinated \( \text{N}_2 \).\(^1\)\(^7\) What has also emerged as significant is the binding mode of the \( \text{N}_2 \) unit to one or more metals, and the extent of activation of coordinated \( \text{N}_2 \) (Table 1.1). While the end-on bonding mode is the most common for coordinated \( \text{N}_2 \), in 1988, the first planar side-on bound \( \text{N}_2 \) complex \((\text{Cp}^*\text{Sm})_2(\mu-\eta^3:\eta^2-\text{N}_2)\) was communicated.\(^8\) The \( \text{N}_2 \) unit is only weakly activated in this dinuclear compound, and

\(^{†}\) A version of this chapter has been published: MacLachlan, E. A.; Fryzuk, M. D. Organometallics 2006, 25, 1530.
its reactivity is limited by the fact that N₂ dissociates from the complex in solution and in the solid state. Since 1988, however, many other side-on bound dinitrogen complexes have been discovered and their reactivity is beginning to be investigated. What is apparent so far is that side-on N₂ complexes show enhanced reactivity compared to end-on N₂ complexes. This chapter will focus on the side-on bound N₂ unit in metal complexes, with some discussion of the side-on–end-on bonding mode of N₂ (E in Table 1.1).

Table 1.1. General bonding modes of N₂ in mononuclear and dinuclear metal complexes. Only connectivity is indicated, along with extremes in N–N bond activation from weak activation (N–N triple bond) to strong activation (N–N double and single bonds).

<table>
<thead>
<tr>
<th>Weak Activation</th>
<th>Strong Activation</th>
<th></th>
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</thead>
<tbody>
<tr>
<td>M—N=N</td>
<td>M—N=N=N=M</td>
<td>End-on</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mononuclear</td>
</tr>
<tr>
<td>M—N=N=N=M</td>
<td>M—N=N=N=M</td>
<td>End-on</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dinuclear</td>
</tr>
<tr>
<td>M—N=N=N=M</td>
<td>M—N=N=N=M</td>
<td>Side-on</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dinuclear</td>
</tr>
<tr>
<td>M—N=N=N=M</td>
<td>M—N=N=N=M</td>
<td>Side-on</td>
</tr>
<tr>
<td></td>
<td></td>
<td>End-on</td>
</tr>
<tr>
<td>M—N=N=N=M</td>
<td>M—N=N=N=M</td>
<td>End-on</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dinuclear</td>
</tr>
<tr>
<td>M—N=N=N=M</td>
<td>M—N=N=N=M</td>
<td>Side-on</td>
</tr>
<tr>
<td></td>
<td></td>
<td>End-on</td>
</tr>
<tr>
<td>M—N=N=N=M</td>
<td>M—N=N=N=M</td>
<td>End-on</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dinuclear</td>
</tr>
<tr>
<td>M—N=N=N=M</td>
<td>M—N=N=N=M</td>
<td>Side-on</td>
</tr>
<tr>
<td></td>
<td></td>
<td>End-on</td>
</tr>
<tr>
<td>M—N=N=N=M</td>
<td>M—N=N=N=M</td>
<td>End-on</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dinuclear</td>
</tr>
<tr>
<td>M—N=N=N=M</td>
<td>M—N=N=N=M</td>
<td>Side-on</td>
</tr>
<tr>
<td></td>
<td></td>
<td>End-on</td>
</tr>
<tr>
<td>M—N=N=N=M</td>
<td>M—N=N=N=M</td>
<td>End-on</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dinuclear</td>
</tr>
<tr>
<td>M—N=N=N=M</td>
<td>M—N=N=N=M</td>
<td>Side-on</td>
</tr>
<tr>
<td></td>
<td></td>
<td>End-on</td>
</tr>
<tr>
<td>M—N=N=N=M</td>
<td>M—N=N=N=M</td>
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<td></td>
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<td>Side-on</td>
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<tr>
<td>M—N=N=N=M</td>
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<td>Side-on</td>
</tr>
<tr>
<td></td>
<td></td>
<td>End-on</td>
</tr>
</tbody>
</table>
1.2 Side-On Coordination of N\textsubscript{2} Prior to 1988.

Orgel was the first to propose the side-on bonding mode of N\textsubscript{2} in 1960, many years before any such complexes existed.\textsuperscript{9} In 1970, the side-on bonding mode was invoked when [(H\textsubscript{3}N)\textsubscript{5}Ru(\textsuperscript{14}N\textsuperscript{15}N)]Br\textsubscript{2} and [(H\textsubscript{3}N)\textsubscript{5}Ru(\textsuperscript{15}N\textsuperscript{14}N)]Br\textsubscript{2} were observed to interconvert over a few hours at room temperature by IR spectroscopy.\textsuperscript{10} Because isomerization is faster than the dissociation of N\textsubscript{2} from (NH\textsubscript{3})\textsubscript{5}Ru\textsuperscript{2\textsuperscript{+}}, the isomerization reaction is intramolecular and proceeds via a mononuclear transition state with N\textsubscript{2} bound side-on to Ru. In 1973, the isolation of triatomic Co(\eta\textsuperscript{2}-N\textsubscript{2}) in a matrix containing Co atoms and N\textsubscript{2} at 10 K was reported.\textsuperscript{11} A single peak is observed in the IR spectrum when \textsuperscript{14}N\textsuperscript{15}N gas is used, indicating that a symmetric species with N\textsubscript{2} bound side-on to Co is present. In 1978, a mononuclear side-on N\textsubscript{2} complex was reported on the basis of evidence obtained by EPR spectroscopy.\textsuperscript{12} Cp\textsubscript{2}ZrR(N\textsubscript{2}) (R = CH(SiMe\textsubscript{3})\textsubscript{2}) is prepared from Cp\textsubscript{2}ZrR(Cl) and Na/Hg amalgam in THF under N\textsubscript{2}. There is a quintet in the EPR spectrum of the Zr(III) complex due to coupling to two equivalent \textsuperscript{14}N nuclei (I = 1). Cp\textsubscript{2}ZrR(\textsuperscript{15}N\textsubscript{2}) is prepared analogously and a triplet is observed in its EPR spectrum due to coupling to two equivalent \textsuperscript{15}N nuclei (I = 1/2). Unfortunately, the solid-state molecular structure of the complex has not been reported, so this result has not been widely acknowledged.

The first crystallographically characterized side-on N\textsubscript{2} complex, [{(C\textsubscript{6}H\textsubscript{5}Li)\textsubscript{3}Ni}\textsubscript{2}N\textsubscript{2}(OEt\textsubscript{2})\textsubscript{2}],\textsubscript{1}\textsuperscript{4} was reported in 1973; 1 is synthesized from \textit{all-trans}-1,5,9-cyclooctatetraene-nickel, [(CDT)Ni], and PhLi in Et\textsubscript{2}O under N\textsubscript{2}.\textsuperscript{13} N\textsubscript{2} is bound side-on to a Ni–Ni bond, and end-on to four Li atoms, and the N–N bond is elongated to 1.35 Å. Similarly, [{(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}Na(OEt\textsubscript{2})\textsubscript{2}}\textsubscript{2}]{(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}Ni}\textsubscript{2}Na-Li\textsubscript{4}(OEt\textsubscript{4})(OEt\textsubscript{2})\textsubscript{2}, 2, is prepared from PhLi, PhNa, and [(CDT)Ni] under N\textsubscript{2}.\textsuperscript{14} The N–N bond length is 1.359(18) Å, and N\textsubscript{2} is bound side-on to a Ni–Ni bond, and associated with Na and Li atoms (see D in Table 1.1).\textsuperscript{4}

\textsuperscript{4} The numbering scheme for compounds in chapter one differs from that used in the remaining chapters.
An intriguing example of N$_2$ bound to multiple metals, a component of which has N$_2$ bound side-on–end-on (E in Table 1.1), was reported in 1982. Upon exposure of solutions of [µ-η$^1$·η$^5$-C$_5$H$_4$]($\eta^5$-C$_5$H$_5$)$_3$Ti$_2$ to N$_2$ a tetranuclear compound, (µ$_3$-η$^1$·η$^5$-N$_2$)($\eta^5$-C$_5$H$_5$)$_2$Ti$_2$[(η$^1$·η$^5$-C$_5$H$_4$)($\eta^5$-C$_5$H$_5$)$_3$Ti$_2$], 3, forms.$^{15}$ N$_2$ is coordinated side-on to one Ti, and end-on to two Ti atoms, with an N–N bond length of 1.301(12) Å.$^{16}$

In an early theoretical investigation, side-on bonding of N$_2$ was predicted to be favourable for group 4 complexes.$^{17}$ If two group 4 transition-metal ions (e.g., Zr(II)) donate two electrons each to bridging N$_2$, one π bond, and either a δ bond (if N$_2$ is coordinated side-on) or a second π bond (if N$_2$ is coordinated end-on) will form. If more than two electrons are available from each metal, the formation of π-bonding interactions will stabilize the complex to a greater extent than the formation
of a $\delta$ bond. The authors challenged synthetic chemists to focus their attention on early transition
metals in the quest for side-on complexes of $\text{N}_2$.

In the examples described above, side-on bonding of $\text{N}_2$ is just a part of the larger picture. The side-on bound $\text{N}_2$ may be in a larger multinuclear complex, or in some cases the complex could not be isolated and characterized in the solid state. In 1988, a simple unequivocal example of a side-on bound $\text{N}_2$ complex was reported. For this reason, this date stands as a milestone in dinitrogen coordination chemistry.

1.3 Side-On Coordination of $\text{N}_2$ Since 1988.

In 1988, the first discrete dinuclear $\text{N}_2$ complex in which the $\text{N}--\text{N}$ bond is perpendicular to, and coplanar with, the $\text{M}--\text{M}$ axis was reported. $^8$ ($\text{Cp}^{\ast}_2\text{Sm})_2(\mu-\eta^2:\eta^2-\text{N}_2)$, 4, forms when toluene solutions of $\text{Cp}^{\ast}_2\text{Sm}$ are exposed to $\text{N}_2$; 4 loses $\text{N}_2$ under vacuum. In the solid-state molecular structure of 4, the $\text{N}--\text{N}$ bond length is 1.088(12) Å, not elongated over free $\text{N}_2$ (1.0975(2) Å) (see A in Table 1.1). The $\text{Cp}^{\ast}_2\text{Sm}$ units are perpendicular to each other, and the $\text{N}_2$ unit is canted: the $\text{Sm}_2\text{N}_2$ plane is at an angle of 62.9° to the Sm1-Cp$^{\ast}$ (centroid)$_2$ plane. Although $\text{N}_2$ appears to be neutral in this structure, the Sm–C bond lengths are typical for a Sm$^{3+}$ species, as are the chemical shifts observed by $^{13}$C NMR spectroscopy. To maintain charge neutrality, $\text{N}_2^{2-}$ with an elongated N–N bond would have to be present. The discrepancy between the expected and observed N–N bond lengths has not been fully rationalized.
In 1990, the second discrete dinuclear complex with side-on bound N$_2$ was reported.$^{18}$ Dark blue ([PNP]ZrCl)$_2$(μ-η$_2^*$:η$_2^*$-N$_2$) ([PNP] = [(Pr$_2$PCH$_2$SiMe$_2$)$_2$N$]$), 5, is prepared from [PNP]ZrCl$_3$ and Na/Hg amalgam in toluene under 4 atm of N$_2$. The N–N bond length is 1.548(7) Å, longer than the N–N single bond in hydrazine, and the longest measured to date for an N$_2$ complex (C in Table 1.1). Since 4 and 5 were reported, many other lanthanide, actinide, and transition-metal complexes that contain side-on bound N$_2$ have been discovered. In some cases, side-on N$_2$ complexes display interesting new reactions for coordinated dinitrogen.

![Diagram of complex 5](image)

1.4 Side-On N$_2$ Complexes of the Lanthanides.

Since the report of 4 in 1988, many other lanthanide dinitrogen compounds have been discovered. Tm$_2$I$_2$ reacts with two equivalents of KCp* in Et$_2$O under N$_2$ to give (Cp*$_2$Tm)$_2$(μ-η$_2^*$:η$_2^*$-N$_2$), 6, in 55% yield.$^{19}$ The low-resolution solid-state molecular structure of 6 shows N$_2$ bound side-on to two Tm centres in a planar Tm$_2$N$_2$ core. Side-on N$_2$ complexes have been synthesized with [C$_5$H$_3$(SiMe$_3$)$_2$]$^-$ and [C$_5$H$_4$(SiMe$_3$)]$^-$ ancillary ligands; N$_2$ is moderately activated in \{[C$_5$H$_3$(SiMe$_3$)$_2$]$_2$Tm$_2$(μ-η$_2^*$:η$_2^*$-N$_2$) (N–N bond: 1.259(4) Å), 7, and \{[C$_5$H$_4$(SiMe$_3$)]$_2$Tm(THF)$_2$\}$_2$(μ-η$_2^*$:η$_2^*$-N$_2$) (N–N bond: 1.236(8) Å), 8.$^{19}$ N$_2$ may be more strongly activated in these complexes because Tm(II) is more reducing (−2.3 V) than Sm(II) (−1.5 V). N$_2$ is also side-on bound in \{[C$_5$H$_3$(SiMe$_3$)$_2$]$_2$Dy$_2$\}$_2$(μ-η$_2^*$:η$_2^*$-N$_2$), 9, prepared from DyI$_2$ and K[C$_5$H$_3$(SiMe$_3$)$_2$] under N$_2$.$^{20}$
The synthesis of a neodymium N₂ complex required the use of harder ligands than Cp, i.e., [(Me₃Si)₂N] and (O₂,6-tBu₂C₆H₃), and these ligands also support Tm and Dy dinitrogen complexes. Two equivalents of NaN(SiMe₃)₂ react with TmI₂(THF)₃ or DyI₂ in THF under N₂ to give \{[(Me₃Si)₂N]₂Ln(THF)\}_2(μ-η²:η²-N₂) (Ln = Tm, 10, and Dy, 11). The two complexes have analogous solid-state structures with N–N bond lengths of 1.264(7) Å and 1.305(6) Å, respectively. The first example of a Nd-N₂ complex, blue-green [(ArO)₂Nd(THF)₂(μ-η²:η²-N₂) (Ar = 2,6-tBu₂C₆H₃), 12, is prepared from NdI₂ and two equivalents of KOAr in THF under N₂ (N–N bond: 1.242(7) Å). The use of Tm²⁺, Dy²⁺, and Nd²⁺ was significant since these species are extremely reducing and their molecular chemistry had been relatively unexplored. A versatile route to Ln-N₂ complexes is via reduction of Ln[N(SiMe₃)₂], with one equivalent of KC₈ in THF under N₂ to give \{[(Me₃Si)₂N]₂Ln(THF)\}_2(μ-η²:η²-N₂), 13, (Ln = Tm, Dy, Nd, Gd, Ho, Tb, Y, Er, Lu, La) (Equation 1.1). The N–N bond lengths range from 1.258(3) Å for Ln = Nd, to 1.305(6) Å for Ln = Dy (11).
Although KC₈ reduction of Ln[N(SiMe₃)₂]₃ has provided many new Ln-N₂ complexes, single crystals of \{[(Me₃Si)₂N]₂La(THF)\}₂(μ-η²:η²-N₂), an attractive diamagnetic target, could not be obtained by this route. Crystalline La-N₂ complexes could be prepared, however, with a different ancillary ligand.\(^\text{24}\) \{C₅Me₄H\}₂La(THF) \(\text{N}_2\), 14, and \{Cp²La(THF)\}₂(μ-η²:η²-N₂), 15, are obtained by KC₈ reduction of La(C₅Me₄H)₃ and [Cp²La][(μ-Ph)₂BPh₃], respectively. The N–N bond in 15 is 1.233(5) Å, corresponding to reduction to N₂²⁻, and there is a singlet at δ 569 in the \(^{15}\)N NMR spectrum. The discovery of these dinuclear side-on Ln-N₂ complexes has been recently recounted.\(^\text{25}\) The synthesis and reduction of Lu(C₅Me₄H)₃ to give \{(C₅Me₄H)₂Lu(THF)\}₂(μ-η²:η²-N₂) was recently reported.\(^\text{26}\)

The second Ln-N₂ compound was reported in 1994. In one pot, [(THF)₂Li\{[Et₂C(α-C₄H₂N)]₄\}Sm(THF), 16, is prepared from \{[Et₂C(α-C₄H₂N)]₄\}Li₄(THF), SmCl₃(THF), Li metal, and N₂. In the solid state, N₂ is encapsulated in an Sm₂Li₄ octahedron and the N–N bond length of 1.525(4) Å indicates that N₂⁺, or hydrazide, is present.\(^\text{27}\)
When $\left\{\left(\text{CH}_2\right)_6\text{C}\left(\alpha\text{-C}_4\text{H}_2\text{N}\right)\right\}_{4}$ is the ancillary ligand, a labile Sm$_2$N$_2$ complex, $\left\{\left(\text{CH}_2\right)_6\text{C}\left(\alpha\text{-C}_4\text{H}_2\text{N}\right)\right\}_{4}\text{Sm}\left[\text{Li}\left(\text{THF}\right)\right]_4\left(\mu^3\text{-Cl}\right)_2\left(\mu\text{-}\eta^3\text{-N}_2\right)(\text{THF})_2$, 17, with weakly activated N$_2$ (N–N bond: 1.08(3) Å) forms from the Sm(II) reduction product, $\left\{\left(\text{CH}_2\right)_6\text{C}\left(\alpha\text{-C}_4\text{H}_2\text{N}\right)\right\}_{4}\text{Sm}\left(\text{THF}\right)\left[\text{Li}\left(\text{THF}\right)\right]_2\left[\text{Li}\left(\text{THF}\right)\right]_2\left(\mu^3\text{-Cl}\right)$, 18. Solutions of 17 readily lose N$_2$ to regenerate 18, and concentrating solutions of 18 under N$_2$ yields the Sm$_3$N$_2$ complex, $\left\{\left(\text{CH}_2\right)_6\text{C}\left(\alpha\text{-C}_4\text{H}_2\text{N}\right)\right\}_{4}\text{Sm}\left[\text{Li}\left(\text{THF}\right)\right]_2\left(\mu\text{-N}_2\right)(\text{THF})_2$, 19. N$_2$ is bound side-on to three Sm centres and end-on to two Li centres with an N–N bond length of 1.502(5) Å.

When dipyrrrolide ancillary ligands are used, N$_2$ is once again strongly activated by Sm(II). $\text{K}_2\left[\text{Ph}_2\text{C}\left(\alpha\text{-C}_4\text{H}_3\text{N}\right)\right]$ reacts with SmI$_2$(THF)$_2$ under N$_2$ to give $\left\{\left[\text{Ph}_2\text{C}\left(\alpha\text{-C}_4\text{H}_3\text{N}\right)\right]_2\text{Sm}\right\}_4\left(\mu\text{-N}_2\right)(\text{THF})_2$, 20, in high yield. Dinitrogen is bound side-on to two Sm atoms and end-on to two Sm atoms in an Sm$_4$N$_2$ coplanar array, and the N–N bond is 1.412(17) Å. A similar Sm$_4$N$_2$ complex, $\left\{\left(\text{CH}_2\right)_6\text{C}\left(\alpha\text{-C}_4\text{H}_3\text{N}\right)\right\}_{4}\text{Sm}_{4}\left(\text{THF}\right)_2\left(\mu\text{-N}_2\right)[\text{Na}(\text{THF})]_3(\text{THF})_2$ (N–N bond: 1.371(19) Å), 21, is prepared in two steps from 1,1-dipyrrrolylcyclohexane, KH, SmCl$_3$(THF)$_3$, and Na/naphthalene.
Complex 21 can also be prepared by Na reduction of \(\{(\text{CH}_2)\text{C}(\alphaC_4\text{H}_3\text{N})\}_2\text{Sm}_4(\text{THF})_2\text{N}_2\) (N–N bond: 1.392(16) Å), 22, which is prepared from \([\text{(Me}_3\text{Si})_2\text{N}]_2\text{Sm}(\text{THF})_2\) and 1,1-dipyrrolylcylohexane.\(^{31}\) \([\text{(Me}_3\text{N})_2\text{Si}]_2\text{Sm}(\text{THF})_2\) has proven to be a versatile Sm(II) starting material. The reaction of \([\text{Et}_2\text{C}(\alphaC_4\text{H}_3\text{NH})_2]\) with \([\text{(Me}_3\text{N})_2\text{Si}]_2\text{Sm}(\text{THF})_2\) under N\(_2\) gives \(\{(\text{Et}_2\text{C}(\alphaC_4\text{H}_3\text{N})\}_4\text{Sm}(\text{THF})_2\}\text{N}_2(\text{THF})_2\), 23. N\(_2\) is bound side-on to two Sm atoms and end-on to two Sm atoms with an N–N bond length of 1.415(3) Å.\(^{32}\)

![Image of molecular structures](image)

Pr and Nd tetrapyrrroliide complexes also activate N\(_2\). Reduction of \(\{(\text{Et}_2\text{C}(\alphaC_4\text{H}_3\text{NH})\}_4\text{M}(\text{THF})\}[\text{Na}(\text{THF})_2\] (M = Pr, Nd) with Na/naphthalene under N\(_2\) gives the side-on N\(_2\) complexes 25 (M = Pr) and 26 (M = Nd) upon crystallization. In the solid state, the complexes contain \(\eta^1\eta^5\)-bound pyrrole ligands, planar \(\text{M}_2\text{N}_2\) cores, and moderately activated N\(_2\) (N–N bonds: 1.254(7) Å (25), 1.234(8) Å (26)).\(^{33}\)

![Image of molecular structures](image)
Since 1988, side-on binding of \( \text{N}_2 \) has been found to be ubiquitous for lanthanide complexes. The coordinated \( \text{N}_2 \) unit varies from unactivated to highly activated, and there will likely be many more reports of \( \text{N}_2 \) coordination by lanthanides. Research into other aspects of lanthanide dinitrogen chemistry also continues. For example, side-on coordination of \( \text{N}_2 \) to lanthanides has also been observed by IR spectroscopy using matrix isolation techniques.\(^{34}\)

### 1.5 Side-On \( \text{N}_2 \) Complexes of the Actinides.

The first actinide dinitrogen complex was reported in 1998.\(^ {35}\) Reduction of \([\text{N}_3\text{N}]\text{UCl} ([\text{N}_3\text{N}] = \text{[N(CH}_2\text{CH}_2\text{NSi}^3\text{BuMe}_2)_3])\) with \text{K} in pentane produces \([\text{N}_3\text{N}]\text{U(III)}, 27, \) upon sublimation. Under 1 atm of \( \text{N}_2 \), \{\([\text{N}_3\text{N}]\text{U} \}_{2}(\mu-\eta^2:\eta^2-\text{N}_2), 28, \) forms (Equation 1.2). \( \text{N}_2 \) binding is reversible, and 27 is regenerated under vacuum. At 1.109(7) Å, the N–N bond is essentially unactivated in 28 and UV/visible spectroscopy and magnetic susceptibility measurements show that the complex contains U(III).

![Diagram of complexes](image)

Although it may seem that the \( \pi \) bond of \( \text{N}_2 \) is a \( \sigma \) donor to U in 28, calculations suggest that \( \pi \) back-bonding from U to \( \text{N}_2 \) is the most important U–N bonding interaction.\(^ {36}\) By DFT, the \( \pi \)-bond of \( \text{N}_2 \) is too low in energy to interact with U in the model compound, \([\text{(NH}_2)_3\text{(NH}_2\text{)U} \}_{2}(\mu-\eta^2:\eta^2-\text{N}_2), 29. \) The bulky \([\text{N}_3\text{N}] \) ligand may hinder U f and \( \text{N}_2 \) \( \pi^* \) orbital overlap and prevent strong
activation of \( \text{N}_2 \); compared to 28, complex 29 is predicted to have a long N–N bond and short U–N bonds.\(^{37}\)

Moderate activation of \( \text{N}_2 \) by an actinide was reported in 2002.\(^{38}\) The N–N bond is 1.232(10) Å in \{Cp\(^*\)U(C\(_6\)H\(_4\)(Si\(_3\)Pr\(_3\)))\}\(_2\)(\(\mu-\eta^2:\eta^2\)-N\(_2\)), 30, although \( \text{N}_2 \) binding is reversible: starting complex Cp\(^*\)U(C\(_6\)H\(_4\)(Si\(_3\)Pr\(_3\))) is regenerated under vacuum. DFT calculations on the model complex \([\eta^5\text{Cp}]\([\eta^8\text{C}_8\text{H}_8]\)]\(_2\)(\(\mu-\eta^2:\eta^2\)-N\(_2\)) indicate that U(5f)→N\(_2\)(\(\pi\)) \( \pi \) back-bonding is substantial.\(^{39}\)

![Diagram of complex 30]

In contrast to Ln-N\(_2\) complexes, which generally feature \( \text{N}_2 \) coordinated in the bridging side-on mode, actinide dinitrogen chemistry is diverse. Since the first report of \( \text{N}_2 \) fixation by an organouranium complex,\(^{40}\) a heterodinuclear U-N\(_2\) compound,\(^{41}\) a mononuclear end-on U-N\(_2\) compound,\(^{42}\) and \( \text{N}_2 \) cleavage by U\(^{43}\) and Th compounds\(^{44}\) have been reported.

### 1.6 Side-On \( \text{N}_2 \) Complexes of the Transition Metals.

Since the discovery\(^{18}\) of \([\text{PNP}Zr\text{Cl}]_2(\mu-\eta^2:\eta^2\)-N\(_2\)), 5, many transition-metal complexes with side-on \( \text{N}_2 \) have been reported. Since the early 1990s, there has been speculation on the binding mode of \( \text{N}_2 \) in nitrogenase. Some have suggested that \( \text{N}_2 \) binds side-on to Fe in the FeMo cofactor.\(^{45}\) In 1991, an intriguing pair of \( \text{N}_2 \) complexes showed how capricious \( \text{N}_2 \) bonding could be.\(^{46}\) \{[(Me\(_3\)Si)\(_2\)]TiCl(tmeda)\}\(_2\)(\(\mu-\eta^1:\eta^1\)-N\(_2\)) (tmeda = Me\(_2\)NCH\(_2\)CH\(_2\)NMMe\(_2\)) (N–N bond: 1.289(9) Å), 31, with end-on bound \( \text{N}_2 \) forms from mixtures of (tmeda)\(_2\)TiCl\(_2\) and one equivalent of (Me\(_3\)Si)\(_2\)NLi
When $(\text{tmeda})_2\text{TiCl}_2$ reacts with 2.5 equivalents of $(\text{Me}_3\text{Si})_2\text{NLi}$ and excess tmeda under $\text{N}_2$, purple $[\text{Li}(\text{tmeda})_2]\{[\{(\text{Me}_3\text{Si})_2\text{N}\}_2\text{Ti}\}_2(\mu-\eta^2:\eta^1-\text{N}_2)_2\}$, 32, forms (anion shown below). To date, 32 is unique because two molecules of $\text{N}_2$ are bound side-on to two metals. The $\text{N}–\text{N}$ bonds are 1.379(21) Å.

Since 1990, other $[\text{PNP}]\text{Zr}-\text{N}_2$ complexes have been discovered. When $[\text{PNP}]\text{ZrCl}_2(\text{15-C}_5\text{H}_5)$ is reduced with Na/Hg amalgam under $\text{N}_2$, $([\text{PNP}]\text{ZrCp})_2(\mu-\eta^1:\eta^1-\text{N}_2)$, 33, forms, wherein $\text{N}_2$ is coordinated end-on to two Zr centres and the $\text{N}–\text{N}$ bond length is 1.301(3) Å. $\text{N}_2$ may adopt the end-on bonding mode in 33 because the Cp ligand interacts with the d orbitals required for $\delta$ bonding to $\text{N}_2$; in addition, steric factors may be important. In contrast, Na/Hg reduction of $[\text{PNP}]\text{Zr}(\text{O}-2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{Cl}_2$ under $\text{N}_2$ gives $\{[\text{PNP}]\text{Zr}(\text{O}-2,6\text{-Me}_2\text{C}_6\text{H}_3)\}_2(\mu-\eta^2:\eta^2-\text{N}_2)$, 34. In the solid state, $\text{N}_2$ is bound side-on to two Zr atoms with a 1.528(7) Å $\text{N}–\text{N}$ bond. In contrast to 5, the $\text{Zr}_2\text{N}_2$ core in 34 is not planar, but has a butterfly distortion (D in Table 1.1); the angle between the two $\text{ZrN}_2$ planes is 156°. A peak at 751 cm$^{-1}$ in the RR spectrum of 34 is assigned to the symmetric ν($\text{N}–\text{N}$) mode, consistent with the presence of a long $\text{N}–\text{N}$ bond. KC$_8$ reduction of $[\text{P}_2\text{N}_2]\text{ZrCl}_2$ ($[\text{P}_2\text{N}_2] = [\text{PhP(\text{CH}_2\text{SiMe}_2\text{NSiMe}_2\text{CH}_2}_2\text{PPh})]$) under $\text{N}_2$ generates dark-blue $([\text{P}_2\text{N}_2]\text{Zr})(\mu-\eta^2:\eta^2-\text{N}_2)$, 35. In the solid state, one macrocyclic $[\text{P}_2\text{N}_2]$ coordinates to each Zr atom, and $\text{N}_2$ is bound side-on in a planar $\text{Zr}_2\text{N}_2$ core ($\text{N}–\text{N}$ bond: 1.43(1) Å).
Side-on $\text{N}_2$ complexes have been implicated as intermediates in $\text{N}_2$ cleavage by a Nb calixarene. The end-on Nb-N$_2$ complex, $\{[\text{p-}^\text{Bu-calix}[4]-\text{O}_4]\text{Nb}\text{$_2$}(\mu-\eta^1:\eta^1\text{-N}_2)[\text{Na(diglyme)}]_2\}$, 36, reacts with Na to give $\{[\text{p-}^\text{Bu-calix}[4]-\text{O}_4]\text{Nb}\text{$_2$}(\mu-\text{N})_2[\text{Na(DME)}]_4\}$, with two bridging nitrides. The side-on Nb-N$_2$ complex, $\{[\text{p-}^\text{Bu-calix}[4]-\text{O}_4]\text{Nb}\text{$_2$}(\mu-\eta^1:\eta^2\text{-N}_2)[\text{Na(DME)}]_4(D\text{ME})\}$, 37, a possible intermediate in the N–N cleavage reaction, is prepared from 36 and Na. In the solid-state, $\text{N}_2$ is perpendicular to a Nb–Nb bond, and the N–N bond length is 1.403(8) Å. Because the N–N bond length is similar in 36 and 37, Na has reduced Nb(V) to Nb(IV), and the formation of a Nb–Nb bond has forced $\text{N}_2$ to become side-on bound.
The side-on–end-on bonding mode of N₂ is known for [NPN]Ta complexes ([NPN] = [PhP(CH₂SiMe₂NPh)₂]²).⁵² [NPN]TaMe₃ reacts with H₂ to provide ([NPN]Ta₂(μ-H)₄, which reacts with N₂ to give ([NPN]Ta₂(μ-H)(μ-η¹:η²-N₂), 38 (Equation 1.3). In 38, N₂ is bound side-on to one Ta and end-on to the other Ta, and N₂ is moderately activated (N–N bond: 1.319(6) Å). This reaction is remarkable for two reasons. First, H₂ is the relatively mild reducing agent that generates the strongly reducing tetrahydride dimer. Thus, the use of alkali metal reductants (e.g., KCu, Na) or strongly reducing metal starting materials (e.g., Sm(II)) is avoided. Second, this is a rare example⁵₃ of an early transition-metal hydride complex that coordinates N₂ via displacement of H₂, although this reaction is known for late transition metals.⁵⁴ The IR and RR spectra of 38 confirm that N₂ is strongly activated in this complex.⁵⁵

In 2001, another early transition-metal hydride was observed to coordinate N₂.⁵⁶ The side-on Zr-N₂ complex, (rac-BpZr)₂(μ-η²:η²-N₂) (rac-Bp = [rac-Me₂Si(2-SiMe₂-4'-Bu-η²-C₆H₄)₂]²), 39, is synthesized from rac-BpZrH₂ and N₂, and rac-BpZrH₂ is prepared from rac-BpZrMe₂ and H₂. The Zr₂N₂ core is planar, and the N–N bond length is 1.241(3) Å.
An intermediate in the formation of a Zr-N₂ complex was discovered in 2003.\textsuperscript{57} Two equivalents of 'BuLi add to Cp\textsubscript{2}ZrCl\textsubscript{2} (Cp\textsuperscript{2} = [1,3-(Me\textsubscript{3}Si)\textsubscript{2}-η\textsuperscript{5}-C\textsubscript{5}H\textsubscript{5}]) to yield [Cp\textsubscript{2}Zr]_2(μ-η\textsuperscript{5}:η\textsuperscript{2}-N\textsubscript{2}), 40, (N–N bond: 1.47(3) Å). Low temperature NMR spectroscopy shows that cyclometalated (Cp\textsuperscript{2})[1-(Me\textsubscript{3}Si)-η\textsuperscript{5}-C\textsubscript{5}H\textsubscript{5}-3-μ-SiMe\textsubscript{2}CH\textsubscript{2}]ZrH, 41, is an intermediate in the formation of 40. Related cyclometalated zirconocenes, such as (Cp\textsuperscript{2})[1-(Me\textsubscript{3}Si)-η\textsuperscript{1}-C\textsubscript{5}H\textsubscript{5}-3-μ-SiMe\textsubscript{2}CH\textsubscript{2}]ZrH, do not react with N\textsubscript{2}.

In 1974, the reduction of Cp\textsuperscript{*}ZrCl\textsubscript{2} to give [Cp\textsuperscript{*}Zr(η\textsuperscript{1}-N\textsubscript{2})]_2(μ-η\textsuperscript{1}:η\textsuperscript{1}-N\textsubscript{2}) was reported.\textsuperscript{58} With a slight modification to the ancillary ligand, from pentamethyl to tetramethyl Cp, a complex in which N\textsubscript{2} coordinates side-on to two Zr atoms is isolated. Thus, the reduction of (η\textsuperscript{5}-C\textsubscript{5}Me\textsubscript{4}H\textsubscript{2})ZrCl\textsubscript{2} with Na/Hg amalgam under N\textsubscript{2} gives [(η\textsuperscript{5}-C\textsubscript{5}Me\textsubscript{4}H\textsubscript{2})Zr]_2(μ-η\textsuperscript{2}:η\textsuperscript{2}-N\textsubscript{2}), 42.\textsuperscript{59} The N–N bond length in the planar Zr\textsubscript{2}N\textsubscript{2} array is 1.377(3) Å. With one additional methyl group per zirconocene, the end-on dinitrogen complex is obtained; Cp\textsuperscript{*}(η\textsuperscript{5}-C\textsubscript{5}Me\textsubscript{4}H)ZrI\textsubscript{2} reduction gives [Cp\textsuperscript{*}(η\textsuperscript{5}-C\textsubscript{5}Me\textsubscript{4}H)Zr(η\textsuperscript{1}-N\textsubscript{2})]_2(μ-η\textsuperscript{1}:η\textsuperscript{1}-N\textsubscript{2}), 43.\textsuperscript{60} The hafnium analogue of 42, [(η\textsuperscript{5}-C\textsubscript{5}Me\textsubscript{4}H\textsubscript{2})HfI\textsubscript{2}(μ-η\textsuperscript{5}:η\textsuperscript{2}-N\textsubscript{2})], was recently prepared.\textsuperscript{61} Complex 43 is the first Hf-N\textsubscript{2} complex characterized in the solid state; 43 is prepared by the same route used to prepare 42 and N\textsubscript{2} is strongly activated (N–N bond: 1.423(11) Å).

Whereas most side-on N\textsubscript{2} complexes are multinuclear, there is evidence for a metastable mononuclear side-on N\textsubscript{2} complex of Os(II). Photolysis of single crystals of [(H\textsubscript{3}N)\textsubscript{5}Os(η\textsuperscript{1}-N\textsubscript{2})][PF\textsubscript{6}]\textsubscript{2} causes partial formation of [(H\textsubscript{3}N)\textsubscript{5}Os(η\textsuperscript{2}-N\textsubscript{2})][PF\textsubscript{6}]\textsubscript{2}.\textsuperscript{62} Analysis by X-ray crystallography and IR
spectroscopy confirms the presence of side-on N₂. Although the change in the N–N bond length is within error for the structure, the Os–N₁ bond lengths are 0.263(17) Å longer than Os–N₁ in the starting material, and the N–N stretching frequency is decreased by 187 cm⁻¹. ¹⁵N NMR spectroscopy has also been used to observe transient side-on N₂; intramolecular isomerization of Cp′Re(CO)(L)(¹⁵N¹⁴N) (for Cp′ = Cp, L = CO; for Cp′ = Cp*, L = CO, PMe₃, P(OMe)₃) occurs via an η²-N₂ intermediate, similar to isomerization of [Ru(NH₃)₅N₂]²⁺ observed by IR spectroscopy.¹⁰

Side-on [NPN]Zr-N₂ complexes were recently reported;⁶⁴ KC₈ reduction of [NPN]ZrCl₂ in THF under N₂ gives purple {[NPN]Zr(THF)}₂(µ-η¹-η¹-N₂), 44. N₂ is bound side-on to two Zr atoms and N₂ is strongly activated; the N–N bond length is 1.503(3) Å.

1.7 Reactivity of Side-On Dinitrogen Complexes.

Prior to 1997, few reactions were known for side-on N₂ complexes, and most involved the addition of acid to a complex to yield hydrazine. To date, no reactions have been reported for N₂ bound side-on to a lanthanide or actinide; reactivity of side-on N₂ has only been observed in transition-metal complexes. In 1997, the first functionalization reactions of side-on N₂ were reported (Scheme 1.1). Under H₂, ([P₂N₂]Zr)(µ-η²:η²-N₂) (35) transforms to ([P₂N₂]Zr)(µ-H)(µ-η²:η²-N₂H), 45.⁴⁹ Neutron diffraction analysis confirms that new N–H and Zr–H bonds form, and that the N–N bond length in side-on bound hydrazide (NNH) is 1.39(2) Å.⁵⁵ In a similar fashion, a new N–Si
bond is produced upon addition of °BuSiH3 to 35. ([P2N2]Zr)2(µ-H)(µ-η2:η2-N2SiH2°Bu), 46, features side-on bound NNSiH2°Bu with a 1.530(4) Å N–N bond.49

Scheme 1.1.

The hydrogenation and hydrosilylation of 35 represent new transformations for coordinated dinitrogen that transcend the reaction of end-on N2 complexes with electrophiles. The formation of an N–H bond in 45 was the first report of this kind of reaction; typically, H2 displaces N2 in a dinitrogen complex. DFT calculations on the addition of H2 and SiH4 to model complex ([p2n2]Zr)2(µ-η2:η2-N2) ([p2n2] = [(PH3)2H]+) show that the reactions proceed via σ-bond metathesis.66 The addition of a second equivalent of H2 to give ([p2n2]Zr)2(µ-η2:η2-N2H2)(µ-H)2 is predicted to be spontaneous, although this has not been observed experimentally.67
Another new reaction for coordinated N₂, N–C bond formation, is observed upon addition of two equivalents of ArC≡CH (Ar = Ph, p-MeC₆H₄, p-‘BuC₆H₄), to 35 to give ([P₂N₂]Zr)[(μ-CCR)(μ-η²:η²-N₂CH=CHAr)], 47, with bridging acetylide and p-Me-styryl-hydrazide (N–N bond = 1.457(4) Å) groups (Equation 1.4). The proposed mechanism involves [2 + 2] cycloaddition of ArCCH across Zr–N to give a zirconaazacyclobutene intermediate, followed by protonolysis of the Zr–C bond with the second ArCCH; the arylacetylide anion bridges the Zr atoms.

\[
\begin{align*}
\text{Ar} & \quad (\text{Me's on Si omitted}) \\
\text{Zr} & \quad (\text{Ar} = \text{Ph, p-MeC}_6\text{H}_4, \ p-\text{BuC}_6\text{H}_4)
\end{align*}
\]

Recently, the functionalization of N₂ side-on bound to a zirconocene complex has been observed. When \([\eta^5-C_5Me_5(H)]_2Zr[\eta^2-N_2], 42, is exposed to H₂, [(\eta^5-C_5Me_5(H))_2Zr(H)]_2(\mu-\eta^2:\eta^2-N_2H_2), 48, is produced with side-on bound hydrazide (N–N bond = 1.475(3) Å) and two terminal zirconium hydrides (Scheme 1.2). Heating 48 under H₂ yields a small amount of ammonia, whereas heating 48 in the absence of H₂ generates \([(\eta^5-C_5Me_5(H))_2Zr(\mu-N)(\mu-NH_2), 49, in which the N–N bond has been cleaved. This discovery illustrates how a small change to an ancillary ligand can impact not only the extent of activation of coordinated N₂, but also the reactivity of the N₂ complex. Whereas the addition of H₂ to \([\text{Cp}^*Zr(\eta^1-N_2)],(\mu-\eta^1:\eta^1-N_2)\) liberates N₂, the hydrogenation of \(\{(\eta^5-C_5Me_5(H))_2Zr\}_2(\mu-\eta^2:\eta^2-N_2)\) enables new N–H bonds to form. Predictably, \([\text{Cp}^*(\eta^5-C_5Me_5(H))Zr(\eta^1-N_2)],(\mu-\eta^1:\eta^1-N_2)\), 43, reacts with H₂ to liberate N₂. The effect of Cp substituents on N₂ activation was recounted recently.
An investigation into the mechanism of H₂ addition to [(η⁵-C₅Me₄H)(η⁵-C₅Me₃H)Zr₂(μ-η²:η²-N₂)], 50, shows the reaction is first order in both H₂ and 50 with a large negative entropy of activation.⁷⁰ The primary kinetic isotope effect indicates that H–H bond breaking is the rate-determining step. Together these observations are consistent with 1,2-addition of H₂ across Zr–N via an ordered transition state with simultaneous Zr–H and N–H bond formation. New N–H bonds also form during the reaction of [(η⁵-C₅Me₄H)₂Hf₂(μ-η²:η²-N₂)] with H₂ to give [(η⁵-C₅Me₄H)₂HfH₂(μ-η¹:η²-N₂H₂)].⁶¹

In addition to the hydrogenation of 42, its reactivity with terminal alkynes, amines, ethanol, and water has been explored.⁷¹ When two equivalents of a terminal acetylene, R'CCH (R' = Ph, 'Bu, "Bu) are added to 42, the hydrazide complex, [(η⁵-C₅Me₄H)Zr(CCR')](μ-η²:η²-N₂H₂), 51, forms. The production of N–H bonds from a dinitrogen complex and an alkyne is a new reaction, and it stands in contrast to the N–C bond formation observed upon addition of alkynes to 35.⁶⁸ The solid-state molecular structure of 51 (R' = 'Bu) shows that hydrazide is side-on bound with an N–N bond length of 1.454(2) Å, and one η¹-acetylde coordinates to each Zr.⁷¹
Water adds to 42 to give hydrazine and \((\eta^5-C_5Me_5H)_2Zr(OH)_2\). In contrast, the addition of H$_2$O to end-on bound \([\text{Cp}^*\text{Zr}(\eta^1-N_2)]_2(\mu-\eta^1:\eta^1-N_2)\) produces N$_2$ and \([\text{Cp}^*\text{ZrH}]_2(\mu-O)\). The addition of excess EtOH to 42 gives hydrazine and \((\eta^5-C_5Me_5H)_2Zr(OEt)_2\). When dimethylamine or 1,1-dimethylhydrazine is added to 42, the end-on hydrazide complex \(\{(\eta^5-C_5Me_5H)_2Zr(NR''_2)\}_2(\mu-\eta^1:\eta^1-N_2H_2)\) (NR''$_2$ = NMe$_2$, NHNMe$_2$), 52, forms (Scheme 1.3), which also yields hydrazine upon treatment with EtOH. In these reactions, N$_2$ in 42 acts as a strong base.

Scheme 1.3.

The side-on–end-on dinitrogen complex, \([\text{NPN}]\text{Ta}((\text{Ph})_2(\mu-\eta^1:\eta^1-N_2)\) (38), is remarkable in its breadth of reactivity. Some reactions involve only the bridging hydrides; for example, the reaction with propene results in migratory insertion and the formation of a propyl complex with end-on N$_2$, \([\text{NPN}]\text{Ta}((\text{Pr})_2(\mu-\eta^1:\eta^1-N_2)\), 53. N$_2$ in 38 is displaced by phenylacetylene, and \([\text{NPN}]\text{Ta}_2(\mu-H)_2(\mu-\eta^1:\eta^1-HCCPh)\), 54, with a bridging bis(\mu-alkylidene) is generated. Coordinated N$_2$ in 38 can also act as a nucleophile: benzyl bromide reacts with 38 to give the N-benzyl derivative.
The reactions of 38 with boranes, silanes, and alanes provide even more dramatic transformations. Hydride reagents with the general formula E-H (E-H = 9-BBN (HBR₂), DIBAL (HAlR₂), and H₂SiBu³) add to 38 to give the intermediate ([NPN]TaH)((μ-H)₂((μ-η¹:η²-N₂)N₄E)Ta[NPN]), 56 (Equation 1.5). The solid-state molecular structure of 56 (E = BR₂ or SiH₄Bu³) confirms the solution spectroscopic data; for E = AlBu¹₂, 56 has only been characterized in solution. Thus, E-H addition across N₂ in 38 is another new transformation of coordinated dinitrogen and represents a starting point for further chemistry.
Solutions of intermediate 56 yield different products depending on the identity of E. Upon hydroboration of 38 (E = BC₈H₁₄), the [NPN] ligand degrades and [(PhNSiMe₂CH₂P(Ph)CH₂SiMe₂-μ-N)Ta(=NBC₈H₁₄)](μ-N)(Ta[NPN]), 58, eventually forms;⁷⁵ one equivalent of benzene, from N-Ph of [NPN] and B–H, and one equivalent of H₂ from the bridging hydrides are also produced. In this transformation, N₂ is cleaved and functionalized. Hydroalumination (E = Al'Bu₂) also results in N–N bond cleavage and functionalization, and ([NPN]TaH)(μ-H)₂(μ-η¹:η²-N₂Al(μ-H)⁵Bu)(Ta[NPN]), 59 is produced;⁷⁷ although [NPN] does not degrade, one amide donor migrates from Ta to Al, and one equivalent of isobutene is eliminated. Hydrosilylation (E = H₂SiBu") produces the very symmetrical disilylimide species ([NPN]Ta₂(μ-NSiH₂Bu")₂, 60.⁷⁶ In this case N₂ has been cleaved and functionalized, and the ancillary ligand remains intact. The addition of E–H to 38 is summarized in Scheme 1.5.
N–N bond cleavage appears to be triggered by H₂ elimination from intermediate 57. DFT calculations for \( E = \text{SiH}_3 \) suggest that the transition state along the path to 57 is a species with a Ta–Ta bond, such as 61. Thus, the Ta–Ta bond contains the electrons required for N–N cleavage.
1.8 Conclusions and Scope of Thesis.

The side-on bonding mode of $\text{N}_2$ is no longer rare, and there are approximately fifty complexes where the side-on mode has been confirmed using X-ray crystallography (see Table 1.2). In terms of the extent of activation of $\text{N}_2$, there are no obvious trends. Lanthanide and transition-metal side-on $\text{N}_2$ complexes show wide variation in the extent of activation as measured by $\text{N}–\text{N}$ bond distances, although in general, more transition-metal $\text{N}_2$ complexes than lanthanide $\text{N}_2$ complexes contain long $\text{N}–\text{N}$ bonds. What is evident is that more investigations into the reactivity of side-on $\text{N}_2$ are warranted. In the cases described above, it is clear that new reactions have been discovered that seem to correlate with the bonding mode. Whether these reactions can be harnessed to produce useful organonitrogen products catalytically remains to be seen.

In this thesis, a new dinitrogen complex with $\text{N}_2$ coordinated in the side-on mode will be described. In chapter two, the synthesis and characterization of a new diamidophosphine ligand is presented. $\text{[NPN]}^*$ ($\text{[NPN]}^* = \{\text{N}-(2,4,6-\text{Me}_3\text{C}_6\text{H}_2)(2-\text{N}-5-\text{MeC}_6\text{H}_3)\}_2\text{PPh}_2^+$) is an arene-bridged analogue of $\text{[NPN]}$ previously reported by the Fryzuk group. Complexes of this ligand are expected to be more robust than those of $\text{[NPN]}$ because they lack the reactive $\text{N}–\text{Si}$ bond and the flexible $\text{CH}_2\text{SiMe}_2$ backbone. In chapter two, the synthesis and characterization of $\text{Zr(IV)}$ and $\text{Hf(IV)}$ complexes of $\text{[NPN]}^*$ are described. In particular, $\text{[NPN]}^*\text{ZrCl}_2$ is a useful starting material in the synthesis of organometallic and dinitrogen complexes. In chapter three, the synthesis, characterization, and reactivity of $\text{[NPN]}^*\text{Hf}$ and $\text{[NPN]}^*\text{Zr}$ organometallic complexes is discussed. In chapter four, the synthesis of $\text{([NPN]}^*\text{Zr(THF)})_2(\mu-\eta^2:\eta^2-\text{N}_2)$ from $\text{[NPN]}^*\text{ZrCl}_2$ and $\text{KC}_8$ in THF is introduced. The synthesis of Py and $\text{PMe}_2\text{R}$ (R = Me, Ph) adducts of the Zr-$\text{N}_2$ complex is also presented. In chapter five, the reactivity of the side-on bound $\text{N}_2$ complexes with $\text{H}_2$, $\text{PhSiH}_3$, 4,4'-dimethylbenzophenone, $(\text{CH}_3)_3\text{CC}(-\text{O})\text{H}$, benzophenone imine, and $\text{Ph}_3\text{P} = \text{O}$ is discussed.
Table 1.2. A selection of side-on N$_2$ complexes and related species for which N-N bond lengths are known; also included are $^{15}$N NMR chemical shifts along with IR and Raman data if available.

<table>
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<th>Compound</th>
<th>$^{15}$N NMR (δ)</th>
<th>Bond length (Å)</th>
<th>vNN (cm$^{-1}$)</th>
<th>Reference</th>
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<tr>
<td>N$_2$</td>
<td>293.4$^{a, c}$</td>
<td>1.0975(2)$^{d}$</td>
<td>2331$^{e}$</td>
<td></td>
</tr>
<tr>
<td>$T_{warn}$-PhN=NPh</td>
<td>129.0$^{f}$</td>
<td>1.255$^{g}$</td>
<td>1441 (R)$^{h}$</td>
<td></td>
</tr>
<tr>
<td>H$_2$NNH$_2$</td>
<td>689.7$^{i}$</td>
<td>1.47$^{d}$</td>
<td>1111 (R)$^{k}$</td>
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<td>[(C$_6$H$_5$Li)$_3$Ni]$_2$N$_2$(OEt)$_2$$_2$ (1)</td>
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<tr>
<td>[(C$_6$H$_5$)Na(OEt)$_2$]$_2$[(C$_6$H$_5$)$_2$Ni]$_2$N$_2$.</td>
<td></td>
<td>1.359(18)</td>
<td>14</td>
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<tr>
<td>NaLi$_4$(OEt)$_4$(OEt)$_2$$_2$ (2)</td>
<td>1.301(12)</td>
<td>1282($^{15}$N$_2$: 15, 16</td>
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<tr>
<td>(μ-η$^1$:η$^2$:N$_2$)[η$^1$:η$^2$:C$_5$H$_4$i][η$^1$:η$^2$:C$_5$H$_5$_2]Tl$_2$] &amp; (3)</td>
<td>1.088(12)</td>
<td>731 (R)</td>
<td>18</td>
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<td>{[PNP]ZrC$_1$}$_2$(THF)$_2$$_2$N$_2$ (5)</td>
<td>619.9$^{i}$</td>
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<td>{[C$_5$H$_5$(SiMe$_3$)$_3$]$_2$Tm$_2$}[μ-η$^2$:η$^2$:N$_2$] (7)</td>
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<tr>
<td>{[C$_5$H$_5$(SiMe$_3$)$_3$]$_2$Tm$_2$}[μ-η$^2$:η$^2$:N$_2$] (8)</td>
<td>1.236(8)</td>
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<td></td>
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<tr>
<td>{[Me$_5$Si]$_2$N$_2$Tm(THF)}$_2$[μ-η$^2$:η$^2$:N$_2$] (9)</td>
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<td>{[Me$_5$Si]$_2$N$_2$Dy(THF)}$_2$[μ-η$^2$:η$^2$:N$_2$] (10)</td>
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<td>{[O-2,6-But$_2$C$_5$H$_2$]$_2$Nd(THF)}$_2$[μ-η$^2$:η$^2$:N$_2$] (12)</td>
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26
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<th>Chemical Formula</th>
<th>δ (ppm)</th>
<th>JNN (Hz)</th>
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<td>{(N_2N)U}_2(μ-η^2:η^2-N_2)</td>
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<td>[(NPN)Ta]_2(Qi-H)_2(μ-η^1:η^2-N_2)</td>
<td>-20.4, 163.6</td>
<td>1.319(6)</td>
<td>1165 (R)</td>
</tr>
<tr>
<td>(rac-BpZr)_2(μ-η^2:η^2-N_2)</td>
<td>1.241(3)</td>
<td></td>
<td>56</td>
</tr>
<tr>
<td>[Cp^*Zr]_2(μ-η^2:η^2-N_2)</td>
<td>1.47(3)</td>
<td></td>
<td>57</td>
</tr>
<tr>
<td>{[η^1-C_5MesH_2]Zr}_2(μ-η^2:η^2-N_2)</td>
<td>621.1</td>
<td>1.377(3)</td>
<td>59</td>
</tr>
<tr>
<td>{[η^1-C_5MesH_2]Hf}_2(μ-η^2:η^2-N_2)</td>
<td>590.5</td>
<td>1.423(11)</td>
<td>61</td>
</tr>
<tr>
<td>{[NPN]Zr(THF)}_2(μ-η^2:η^2-N_2)</td>
<td>1.503(3)</td>
<td></td>
<td>64</td>
</tr>
</tbody>
</table>

\* Liquid MeNO_2 is δ 361 relative to aqueous NH_4^+ (5 M NH_4NO_3/2 M HNO_3). See Mason, J. Chem. Rev. 1981, 81, 205, for more information on Nitrogen NMR.

\* Originally δ -67.6 as referenced to NO_3^- in a 5 M solution of NH_4NO_3 in 2 M HNO_3.


\* Originally measured as δ 350.9 referenced to formamide at 0 ppm.
1.9 References.


Chapter Two

Zirconium and Hafnium Complexes of an Arene-Bridged Diamidophosphine Ligand

2.1 Introduction.‡

At the core of inorganic chemistry is the idea that the structure and reactivity of a metal complex may be controlled by the ancillary ligand. With the appropriate ligand, chemists prepare metal complexes that catalyze organic transformations,¹ readily change oxidation state,² impart chiral environments for asymmetric synthesis,³ attain unusual electronic states,⁴ and absorb light for energy transfer.⁵ Although it is not yet possible to predict reactivity based on the choice of ancillary ligand, research into ligand design continues guided by ideas of geometry control, donor atom properties, and substituent effects. The importance of ligand choice was dramatically illustrated in 2004 when Chirik et al. reported that the reduction of (η⁵-C₅Me₄H)₂ZrCl₂ under N₂ yields [(η⁵-C₅Me₄H)₂Zr]₂(μ-η²:η²-N₂) in which N₂ bridges two Zr atoms side-on. The activated N₂ in this complex reacts with H₂ to yield [(η⁵-C₅Me₄H)₂Zr(H)]₂(μ-η²:η²-N₂H₂) with two new N-H bonds.⁶ About three decades earlier, the reduction of (η⁵-C₅Me₅)₂ZrCl₂ was reported to yield the end-on dinuclear complex, [(η⁵-C₅Me₅)₂Zr(η¹-N₂)]₂(μ-η¹:η¹-N₂), which releases N₂ when it is exposed to H₂.⁷ The difference of one methyl group in the ancillary ligand changed the extent of activation of N₂, its coordination mode to Zr, and its reactivity, thus exemplifying

‡ A portion of this chapter has been published: MacLachlan, E. A.; Fryzuk, M. D. Organometallics 2005, 24, 1112.
the challenges chemists face in trying to design ancillary ligands to change a complex in a predictable way.

Research in the Fryzuk group has focused on creating multidentate ligands that incorporate amide and phosphine donors. Chelating amidophosphine ligands allow simultaneous coordination by amide donors, which stabilize high-valent, electron-poor metal complexes, and phosphine donors, which stabilize low-valent, electron-rich metal complexes, to a single metal centre. These ligands can facilitate nitrogen activation by early transition metals because they stabilize the metal complex in the presence of strong reducing agents. As described in chapter one, the tridentate anionic [PNP] ligand ([PNP] = [N(SiMe₂CH₂PR₂)], R = 'Pr) stabilizes one of the earliest examples of a side-on N₂ complex: ([PNP]ZrCl₂(μ-η²:η²-N₂) (Figure 2.1) contains the longest intact N–N bond in a metal complex (1.548(7) Å). A side-on Zr₂N₂ complex also forms when macrocyclic [P₂N₃] ([P₂N₃] = [PhP(CH₂SiMe₂NSiMe₂CH₂)₂PPh]²⁻) is the ancillary ligand: ([P₂N₃]Zr₂(μ-η²:η²-N₂) has a 1.43(1) Å N–N bond, consistent with the presence of an N–N single bond, or an N₂⁺ unit, in the complex (Figure 2.1). In 1997, ([P₂N₃]Zr₂(μ-η²:η²-N₂) became the first transition-metal N₂ complex to react with H₂ to yield new N–H bonds. Previously, the addition of H₂ to an N₂ complex had only been observed to liberate N₂ gas and produce a metal hydride complex. This [P₂N₃] stabilized complex also reacts with silanes and terminal acetylenes to yield new N–Si and N–C bonds.
The Fryzuk group reported the synthesis of a tridentate dianionic ligand [{NPN}] \(([{\text{NPN}}]} = [{\text{PhP(\text{CH}_2\text{SiMe}_2\text{NPh})}_2}]^2\) and its Ta complexes in 1998.\(^{15}\) The reaction of [{NPN}]TaMe\(_3\) with dihydrogen provides the Ta(IV) hydride \(([{\text{NPN}}]\text{Ta})_2(\mu-\text{H})_4\). The tetrahydride reacts with \(\text{N}_2\) to yield \(([{\text{NPN}}]\text{Ta})_2(\mu-\text{H})_2(\mu-\eta^1:\eta^2-\text{N}_2)\), the first dinuclear complex with \(\text{N}_2\) coordinated in the side-on–end-on bonding mode (see Figure 2.1). The addition of boranes, alanes, and silanes to this complex results in the formation of a new N–E (where E = B, Si, or Al) bond and cleavage of the \(\text{N}_2\) unit.\(^{16}\) Zr–\(\text{N}_2\) complexes of the [{NPN}] ligand have also been reported.\(^{17}\)

Although \(\text{N}_2\) coordinated to an early transition-metal amidophosphine complex undergoes a variety of transformations, ancillary ligand decomposition often accompanies these reactions. For example, the addition of 9-BBN to \(([{\text{NPN}}]\text{Ta})_2(\mu-\text{H})_2(\mu-\eta^1:\eta^2-\text{N}_2)\) (9-BBN = 9-borabicyclo[3.3.1]nonane) leads to N–N bond cleavage and the formation of a new B–N bond.\(^{18}\) However, [{NPN}] is degraded in the course of the reaction; benzene is
eliminated from one of the two phenylamido substituents and the amido N bridges the two Ta centres as a nitride ligand (Scheme 2.1).

Scheme 2.1.

It should be noted here that the Fryzuk group has also explored the chemistry of –CH$_2$SiMe$_2$– bridged [NPN] ligands with non-phenyl substituents on N and P, such as mesitylamide (MesN) and cyclohexylphosphine (CyP), and that decomposition reactions of these ligands are also observed. For brevity, when there are one or two non-phenyl substituents on [NPN], they are specified before the square brackets as superscripts in the following order: P substituent, N substituent. In other words, the –CH$_2$SiMe$_2$– bridged [NPN] ligand with CyP and MesN substituents is abbreviated: Cy$_x$Mes$_y$[NPN].
Other undesirable reactions observed for the [NPN] ligand include the formation of a phosphinimide ([NP(=N)N]) complex from a Ti-N₂ complex, the migration of the N donor of [NPN] from Ta to Al when DIBAL-H is added to the Ta₂N₂ complex, the formation of \( \text{Cy}^{\text{Me}}[\text{NPN}]\text{V} = \text{N-Mes} \) and a cyclic \( \text{Cy}^{\text{Me}}[\text{PN}] \) compound \( \text{Cy}^{\text{Me}}[\text{PN}] = \text{CyP(CH₂SiMe₃)₂NMes} \) when \( \text{Cy}^{\text{Me}}[\text{NPN}]\text{V}_2(\mu-\text{Cl})_2 \) is reduced with K₂C₂, \( \text{Cy}^{\text{Ph}}[\text{PN}] \) elimination and \( \text{Cy}^{\text{Ph}}[\text{NPN}]\text{NbCl}(=\text{NPh}) \) formation when \( \text{Cy}^{\text{Ph}}[\text{NPN}]\text{NbCl}_₂ \) is reduced with K₂C₂ as well as several other uncharacterized decomposition reactions of [NPN] metal complexes. Similarly, side-reactions of [PNP] and [P₂N₂] have also been reported. Decomposition of these complexes may result from the reactivity of the N–Si bond and the flexibility of the –CH₂SiMe₂– backbone. [PNP], [P₂N₂], and [NPN] ligands all contain N–Si bonds to facilitate ligand synthesis, and to reduce the basicity of the amidino nitrogen donor.

Ancillary ligand decomposition is a major barrier to the development of a catalytic cycle based on N₂ functionalization, and for this reason the synthesis of a more robust tridentate amidophosphine ligand was initiated. This new ligand should mimic the electronic and steric properties of [NPN], but lack the reactive and extremely moisture-sensitive N–Si bond. An early analogue of [NPN] contained a –CH₂CH₂– linker, \([\text{PhNCH₂CH₂}]₂\text{PPh}²⁻ \). Although Ta complexes can be prepared with this ligand, attempts to hydrogenate or reduce these complexes give mixtures of products. The seemingly minor substitution of one CH₂ group for SiMe₂ in the backbone of [NPN] has a dramatic impact on the reactivity of the corresponding metal complexes. One possible explanation is that the reduction of [NPN]Ta complexes is facilitated by the slightly electron-withdrawing silylamide substituents, whereas the reduction of \([\text{PhNCH₂CH₂}]₂\text{PPh}]Ta \) complexes is hindered by the presence of the more electron-donating alkylamide substituents. Secondary
alkylamines are generally stronger bases than secondary silyl-substituted amines. The pKₐ of diisopropylamine is 36,²⁴ whereas the pKₐ of bis(trimethylsilyl)amine is 26.²⁵ An arene-bridged diamidophosphine ligand may be electronically similar to [NPN], and the amido donors are expected to have similar basicity. The pKₐ of diphenylamine is 25.²⁶ In addition, an arene-bridged diamidophosphine would lack the reactive N–Si bond of [NPN], and should not be readily decomposed by nucleophiles or H₂O. An arene-bridged diamidophosphine ligand may also be less flexible than [NPN], which may hinder the migration of N and P donors that is observed under some conditions. A comparison of –CH₂SiMe₂– bridged [NPN] and an arene-bridged diamidophosphine ligand is given in Figure 2.2. This chapter describes the synthesis of an arene-bridged diamidophosphine ligand and its Zr(IV) and Hf(IV) complexes.

![Figure 2.2](image-url)

**Figure 2.2.** Comparison of two diamidophosphine ligands: Attributes of the –CH₂SiMe₂– bridged and arene-bridged diamidophosphine ligands [NPN]Li₂ and [NPN⁺]Li₂.
2.2 Results and Discussion.

2.2.1 Synthesis of a phenyl-bridged diamidophosphine [NPN]'.

The phenyl-bridged diamidophosphine ligand [NPN]’, ([NPN]’ = \{N-(4-MeC₆H₄)(2-NC₆H₄)₂PhP\}_2\) can be prepared in three steps from (2-NH₂C₆H₄)₂PhP.⁷ The 2,2'-diaminotriphenylphosphine starting material is synthesized by a Pd-catalyzed P–C coupling reaction from phenylphosphine (PhPH₂) and 2-iodoaniline in the presence of Pd(PPh₃)₄ and the water-soluble triarylphosphine GUAP-3 (GUAP-3 = [\{3-GuanN(H)C₆H₄\}_3P\}]·3HCl, Guan = C(H)(NH₂)(NMe₂)).²⁷ The N-arylation of (2-NH₂C₆H₄)₂PhP with aryliodides via Cu- or Pd-catalyzed C–N coupling is unsuccessful, possibly because the chelating diaminophosphine substrates and products coordinate to the metal catalyst. To decrease the likelihood of catalyst poisoning, (2-NH₂C₆H₄)₂PhP was first oxidized by H₂O₂ to provide (2-NH₂C₆H₄)₂PhP=O as a beige solid in high yield. The phosphine oxide reacts with 2.2 equivalents of 4-iodotoluene and catalytic CuI(Phen)(PPh₃) to give [N-(4-MeC₆H₄)(2-N(H)C₆H₄)]₂PhP=O, 2.1, as a beige powder in high yield (Scheme 2.2).

There is a singlet at δ 42.4 in the ³¹P{¹H} NMR spectrum of 2.1, which is in the range expected for a triarylphosphine oxide. The ¹H NMR spectrum of 2.1 shows a singlet at δ 2.26 that is assigned to two equivalent p-CH₃ groups on the NTol substituents, a broad singlet at δ 8.52 assigned to the NH groups, as well as resonances in the aromatic region that are consistent with the proposed C₄ symmetric compound. Overall, this two-step procedure provides the N-arylated diaminophosphine oxide in 85% yield.

* The abbreviations [NPN], [NPN]', and [NPN]* are used to distinguish three different diamidophosphine ligands. [NPN] = \{[PhNSiMe₂CH₂]₂PPh\}², [NPN]' = \{[N-(4-MeC₆H₄)(2-NC₆H₄)₂PhP]\}², and [NPN]* = \{[N-(2,4,6-Me₃C₆H₃)(2-N-5-MeC₆H₄)₂PPh]\}².
Scheme 2.2.

There are several drawbacks to the Cu-catalyzed route to 2.1 described above. The reaction must be heated at a high temperature for several days before it goes to completion. Moreover, a by-product forms when the reaction is conducted on scales larger than 5 g. The by-product, 

\[ [N,N-(4-\text{MeC}_6\text{H}_4)_2(2-\text{NC}_6\text{H}_4)] [N-(4-\text{MeC}_6\text{H}_4)(2-\text{N(H)}\text{C}_6\text{H}_4)]\text{PhP=O}, \]

results from the reaction of three equivalents of \( p\)-\text{CH}_3\text{C}_6\text{H}_4\text{I} with \( (2-\text{NH}_2\text{C}_6\text{H}_4)_2\text{PhP=O} \). Compound 2.2 is isolated as a white microcrystalline solid after it is separated from 2.1 by silica gel chromatography and recrystallized. It was characterized by multinuclear NMR spectroscopy, EI-MS, and microanalysis. The formation of the by-product, and the chromatography required to separate it from 2.1 decrease the yield of the desired diarylated compound to \( \sim 55\% \) when the reaction is carried out on a 5 g scale.
Compound 2.1 is reduced to [NPN]'H₂, 2.3, using standard phosphine oxide reduction conditions (see Scheme 2.2). The reaction is quenched with degassed H₂O, and 2.3 is obtained as a translucent white residue in high yield upon work-up. The singlet in the ³¹P{¹H} NMR spectrum is at ð —30.9 for 2.3, typical for a triarylphosphine. In the ¹H NMR spectrum, resonances diagnostic of NH (ð 6.36) and ArCH₃ (ð 2.06) groups are present, as well as the expected ArH resonances. Finally, addition of two equivalents of °BuLi to 2.3 in a mixture of hexanes and THF provides [NPN]'Li₂(THF)₂, 2.4, in 53% yield as small yellow crystals (see Scheme 2.2). The ³¹P{¹H} NMR spectrum of 2.4 is similar to that of [NPN]Li₂(THF)₂; a quartet is observed at ð —33.0 (I(°Li) = 3/2, JPLi = 41 Hz). As expected, there are a doublet and a singlet in the ⁷Li{¹H} NMR spectrum of [NPN]'Li₂(THF)₂, indicating that one Li ion is bound to P (ð —0.35) and the other is not (ð —1.72). By ¹H NMR spectroscopy, two equivalents of THF are coordinated to 2.4.

In addition to the problems noted above for the Cu-catalyzed arylation, there are several other drawbacks to the synthesis of [NPN]' outlined above. First, the reaction requires four steps from phenylphospbine, which is odious to prepare. The purification of 2.1 is labour intensive and any impurities that remain are difficult to remove after subsequent steps. Also, the presence of small amounts of H₂O and NEt₃ remaining after the work-up of 2.3, which are difficult to eliminate completely from the oily residue, are incompatible with the lithiation reaction to give 2.4. Despite many attempts to modify the conditions, multi-gram quantities of pure 2.4 could not be obtained. It was clear that a new route to arene-bridged diamidophosphines was needed.

In 2003, Liang and co-workers described the synthesis of arene-bridged [PNP] and [NP] ligand precursors by the reaction of an alkali metal phosphide with an aryl fluoride.
This reaction is sometimes referred to as nucleophilic phosphanylation. Stelzer and co-workers prepared a series of substituted triarylphosphines in an earlier example of nucleophilic phosphanylation. The aminophosphine \([\text{NP}]\text{H}\) \((\text{NP}]\text{H} = (2-\text{Ph}_2\text{PC}_6\text{H}_4)\text{NH}(2,6-\text{R}_2\text{C}_6\text{H}_3); \text{R} = \text{Me}, \text{Pr}\) is synthesized by heating \((2-\text{FC}_6\text{H}_4)\text{NH}(2,6-\text{R}_2\text{C}_6\text{H}_3)\) and \(\text{KPPh}_2\) in dimethoxyethane (DME) to reflux for several days. The aminodiphosphine \([\text{PNP}]\text{H}\) \((\text{PNP}]\text{H} = (2-\text{R}_2\text{PC}_6\text{H}_4)_2\text{NH}, \text{R} = \text{Ph}, \text{Pr}, \text{Bu}, \text{Cy}\) is prepared in a similar manner from \((2-\text{FC}_6\text{H}_4)_2\text{NH}\) and two equivalents of \(\text{MPR}_2\) \((\text{M} = \text{Li}, \text{K})\) (Figure 2.3). Following this report, the synthesis of an arene-bridged dianaminophosphine by nucleophilic phosphanylation was attempted in the Fryzuk group. Thus, two equivalents of \((2-\text{FC}_6\text{H}_4)\text{NH}(\text{Ph})\) in DME are added to a clear red solution formed from the addition of two equivalents of \(\text{K}\) to \(\text{PhPH}_2\) in DME, and the solution is heated to reflux for several days. In the \(^{31}\text{P}\{^1\text{H}\}\) NMR spectra of aliquots taken from the reaction mixture, the peak due to starting material disappears, and several new peaks grow in. To date, attempts to separate the products of this reaction for further characterization have been unsuccessful.

![Figure 2.3. Arene-bridged [NP]H and [PNP]H.](image)

In 2004, a second route to arene-bridged aminophosphines was reported. \([\text{PNP}]\text{H}\) \((\text{PNP}]\text{H} = (2-\text{Pr}_2\text{P}-4-\text{MeC}_6\text{H}_3)_2\text{NH}\) is prepared in two steps. First, \((4-\text{MeC}_6\text{H}_3)_2\text{NH}\) is brominated to yield \((2-\text{Br}-4-\text{MeC}_6\text{H}_3)_2\text{NH}\). Addition of three equivalents of \(^9\text{BuLi}\) and two
equivalents of \( \text{Pr}_2\text{PCl} \) to the bis(bromoaryl)amine, followed by treatment with deoxygenated water yields \([\text{PNP}]\text{H}\) (Scheme 2.3). The synthesis of these proligands and their Li and transition-metal complexes was recently reviewed.35

Scheme 2.3.

\[
\begin{align*}
\text{NH} & \quad \text{AcOH} \\
\text{Br}_2 & \quad 1) \quad \text{3 BuLi, 2 Pr}_2\text{PCl} \\
\text{NH} & \quad 2) \quad \text{H}_2\text{O} \\
\text{[PNP]}\text{H} & \quad
\end{align*}
\]

2.2.2 Metathesis approach to \([\text{NPN}]^*\).

As an alternative to the Cu-catalyzed route described above, the synthesis of a diamidophosphine ligand by a metathesis pathway, similar to that used to prepare \([\text{PNP}]\text{H}\) (see Scheme 2.3) was undertaken. The brominated diarylamine, \((2,4,6-\text{Me}_3\text{C}_6\text{H}_2)(2-\text{Br}-4-\text{MeC}_6\text{H}_3)\text{NH}\), 2.5, can be readily prepared from \((\text{Mes})\text{(Tol)}\text{NH}\)36 and N-bromosuccinimide (NBS) in acetonitrile.37 To determine if 2.5 undergoes complete NH deprotonation and Li/Br exchange in the presence of "BuLi, 2.1 equivalents of "BuLi are added to a solution of 2.5 and 2.1 equivalents of tmeda (tmeda = Me_2NCH_2CH_2NMe_2) in Et_2O at \(-35^\circ\text{C}\). The product of this reaction, light yellow \((2,4,6-\text{Me}_3\text{C}_6\text{H}_2)(2-\text{Li}-4-\text{MeC}_6\text{H}_3)\text{NLi}(\text{tmeda})\), 2.6, has been characterized by \(^1\text{H}\) and \(^{13}\text{C}\{\text{H}\}\) NMR spectroscopy.

To form the diamidophosphine ligand \([\text{NPN}]^*\) ([NPN] = \{[N-(2,4,6-\text{Me}_3\text{C}_6\text{H}_2)(2-N-5-\text{MeC}_6\text{H}_3)]_2\text{PPh}\}^2, or a ligand bridged with a 5-MeC_6H_3 group), 2.5 is lithiated in Et_2O solution (no tmeda is used) and reacted \textit{in situ} with 0.48 equivalents of PhPCl_2 (Scheme 2.4). Upon work-up, \([\text{NPN}]^*\text{Li}_2\cdot(\mu-\text{C}_4\text{H}_6\text{O}_2), 2.7\cdot(\mu-\text{C}_4\text{H}_6\text{O}_2),\) is obtained in 85% yield as a yellow
powder that is somewhat soluble in toluene and freely soluble in THF. Compound 2.7·(p-C₄H₈O₂) is thermally unstable and can decompose to a brown powder over a few days in an N₂-filled glovebox. Single crystals suitable for X-ray analysis of the THF adduct, 2.7·2THF, were grown from a concentrated solution of 2.7·(p-C₄H₈O₂) in benzene with a few drops of THF added.

Scheme 2.4.

Although the formation of 2.7·(p-C₄H₈O₂) proceeds in one pot from an easily synthesized organic starting material and a commercially available phosphine, PhPCl₂, the reaction is quite sensitive to changes in certain reaction conditions. For example, a change in solvent from Et₂O to THF or hexanes gives a mixture of products that does not contain a resonance attributable to 2.7 in its ³¹P{¹H} NMR spectrum. When more than two equivalents of "BuLi are added, 2.7 cannot be separated from a brown hexanes-soluble impurity. Thus, determining the exact concentration of "BuLi in hexanes by titration is essential. It is also important to add slightly less than 0.5 equivalents of PhPCl₂ dropwise, very slowly, to the solution of lithiated 2.5 at −35 ± 5 °C. Regardless of the scale of the reaction, if the PhPCl₂ addition is carried out over less than 2 h, a low yield of 2.7 is obtained. As yet, it is unclear why the synthesis of 2.7 is so sensitive to the conditions used, or by what mechanism the reaction proceeds.
Similar to other [NPN] lithium derivatives,\textsuperscript{15,20} the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 2.7-(p-
C$_4$H$_8$O$_2$) shows a quartet at $\delta$ —35.2 ($J_{PL} = 40$ Hz), and the $^7\text{Li}\{^1\text{H}\}$ NMR spectrum shows a
doublet at $\delta$ —0.07 and a singlet at $\delta$ —1.97 (Figure 2.4). The $^1\text{H}$ NMR spectrum of 2.7-(p-
C$_4$H$_8$O$_2$) in C$_6$D$_6$ (with a drop of THF added to increase solubility) is notable because four
singlets are observed in the ArCH$_3$ region ($\delta \sim 2.0$). The two ortho-Me groups of each MesN
substituent are inequivalent to each other because of restricted rotation about the N—C$_{o\text{,o}}$
bond on the NMR timescale at 298 K. In addition, two singlets are observed for the
inequivalent meta C—H groups on each MesN. The other resonances in the aromatic region
of the $^1\text{H}$ NMR spectrum are consistent with the proposed C$_5$ symmetric compound.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{31P_7Li_NMR_spectra.png}
\caption{$^{31}\text{P}\{^1\text{H}\}$ and $^7\text{Li}\{^1\text{H}\}$ NMR spectra of 2.7-(p-C$_4$H$_8$O$_2$) in C$_6$D$_6$.}
\end{figure}

The solid-state molecular structure of 2.7-2THF (Figure 2.5) as determined by single-
crystal X-ray diffraction shows two distinct Li environments: Li1 is coordinated to N1, N2,
and P1 of [NPN]$^+$, and O1 of THF, whereas Li2 is coordinated to N1 and N2, and O2 of
the second coordinated THF. The P—Li1 bond is 2.510(3) Å, the Li1—N bonds (2.08 Å) are

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the same within error, and the Li1–O1 bond is 1.908(3) Å. The Li2–N bonds (2.05 Å) are the same within error, and the Li2–O2 bond is 1.932(3) Å. The Li1–Li2 separation is 2.518(4) Å. The stereochemistry at Li1 is best described as distorted tetrahedral and the stereochemistry at Li2 is distorted trigonal. The remaining bond lengths and angles in the [NPN]* ligand are unremarkable. Crystallographic supporting information is in appendix one. Although spectroscopic and X-ray diffraction techniques confirmed the identity of 2.7·2THF, several attempts to characterize this compound by microanalysis have shown it to be low in carbon. This may be due incomplete combustion, or to the extreme air- and moisture-sensitivity of this material.

![Figure 2.5. ORTEP drawing of the solid-state molecular structure of [NPN]*Li2·2THF, 2.7·2THF (ellipsoids drawn at the 50% probability level). All hydrogen atoms, and the carbon atoms of THF have been omitted for clarity. Selected bond lengths (Å) and angles (°): P1–Li1 2.510(3), N1–Li1 2.078(3), N1–Li2 2.046(4), Li1–Li2 2.518(4), O1–Li1 1.908(3), O2–Li2 1.932(3), N2–Li2 2.051(3), N2–Li1 2.076(3), P1–Li1–Li2 77.01(11), N1–Li2–N2 105.76(15), O1–Li1–Li2 144.07(18).](image-url)
The solid-state and solution data indicate that the structures of 2.7 and [NPN]Li₂·2THF are remarkably similar. A diamond-shaped Li₂N₂ core in the solid state, and a quartet due to Li-P coupling in the ³¹P{¹H} NMR spectrum have also been observed for lithium diamidophosphines with other substituents at N and P. For example, Cy₅Mes[NPN]Li₂(THF) is structurally analogous to 2.7 with similar bond lengths and angles (N–Li1 bonds average to 2.12 Å, N–Li2 bonds average to 1.95 Å). However, there is only one equivalent of THF coordinated to Li in the complex, and Li-P coupling is not detected at ambient temperature in C₆D₆ by NMR spectroscopy for this compound.

2.2.3 Synthesis of group 4 complexes of [NPN]⁺.

Dichlorozirconium complexes of [NPN]⁺ are prepared in a three-step route from 2.7·(p-C₄H₈O₂). First, the lithiated ligand is protonated; then the proligand reacts with Zr(NMe₂)₄ via elimination of Me₂NH to give the bis(dimethylamido)zirconium complex. Excess Me₃SiCl is added to this Zr complex to obtain [NPN]⁺ZrCl₂. To prepare the proligand [NPN]⁺H₂, 2.8, excess Me₂NHCl was stirred with 2.7·(p-C₄H₈O₂) in THF (Scheme 2.5). Taking the reaction mixture to dryness and extracting the product with toluene easily removes LiCl and Me₂NH from 2.8, which is obtained as an air-stable white powder in high yield. There is a singlet at 6 –31.4 in the ³¹P{¹H} NMR spectrum of 2.8 in C₆D₆. The ¹H NMR spectrum acquired at 298 K shows broad singlets attributable to the ortho-Me and meta-
CH groups of MesN, as well as resonances for the other ArCH$_3$ and ArH groups, and a doublet at $\delta$ 5.88 ($J_{HF} = 5$ Hz) assigned to NH in the C$_s$ symmetric compound. The broad singlets seen for the MesN substituents indicate that rotation about the N–C$_{ps}$ bond to MesN is hindered. In the variable-temperature $^1$H NMR (VT-NMR) experiment, coalescence of the broad Me singlets is observed at 320 K. Thus, $\Delta G^\#_{rot}$ is 15.5 ± 0.3 kcal mol$^{-1}$. A stacked-plot of the VT-NMR spectra for 2.8 and the calculation of $\Delta G^\#_{rot}$ are included in appendix two.

$[^{NPN}]Zr(NMe_2)_2$, 2.9, is synthesized by adding toluene to a 1:1 mixture of 2.8 and Zr(NMe$_2$)$_4$. Upon work-up, 2.9 is obtained as a toluene-soluble yellow powder in high yield (Scheme 2.5). The $^{31}$P{$_1$H} NMR spectrum of 2.9 in C$_6$D$_6$ shows a singlet at $\delta$ –11.5, and the $^1$H NMR spectrum (Figure 2.6) shows four singlets for the [NPN]* ArCH$_3$ groups, indicating that rotation about N–C$_{ps}$ of MesN does not occur at 298 K on the NMR timescale. There are two NMe$_2$ resonances at $\delta$ 3.06 and 2.31, corresponding to two different amidomethyl environments. Complex 2.9 appears to be a C$_s$ symmetric trigonal-bipyramidal complex in solution, with one NMe$_2$ apical and the other equatorial. Addition of THF, Py or PMe$_3$ to 2.9 in benzene produces no color change or shift in the peak in the $^{31}$P{$_1$H} NMR spectrum, which suggests that a sixth neutral donor ligand cannot coordinate to Zr. The $^1$H and $^{31}$P{$_1$H} NMR spectra of 2.9 are similar to those reported for [PhP(CH$_2$CH$_2$:NSiMe$_3$)$_2$]Zr(NMe$_2$)$_2$.40
Figure 2.6. 300 MHz $^1$H NMR spectrum of 2.9 in C₆D₆.

[NPN]$^*$ZrCl₂, 2.10, is synthesized from 2.9 and excess Me₃SiCl in toluene and is isolated in 89% yield as a bright yellow powder (Scheme 2.5). No attempt has been made to observe the expected by-product of the reaction, Me₃SiNMe₂, which is likely eliminated from the reaction mixture upon removal of the volatiles under vacuum. A singlet at $\delta$ = 2.8 is observed in the $^{31}$P{$^1$H} NMR spectrum of 2.10 in C₆D₆. By $^1$H NMR spectroscopy (Figure 2.7), 2.10 has the expected characteristics of a C₃ symmetric monomer, although the formulation of this complex as a C₂v symmetric dimer in solution, ([NPN]$^*$ZrCl)(μ-Cl)₂, cannot be ruled out based on the available evidence. In the $^1$H NMR spectrum of 2.10, there
are signals due to four distinct ArCH₃ groups, similar to 2.7 and 2.9, as well as the expected ArH resonances.

Scheme 2.5.
The ORTEP representation of the solid-state molecular structure of 2.10 is shown in Figure 2.8. The stereochemistry around Zr is distorted trigonal bipyramidal with Cl2 and P1 apical, and N1, N2, and Cl1 equatorial. [NPN]* coordinates to Zr facially, and the two chlorides are cis to each other. Facial coordination of [NPN]* is not unexpected because the phosphine donor should prevent the ligand from coordinating in a meridional fashion. The P–Zr–N1, P–Zr–N2 angles are noticeably smaller than 90° with the two amido donors appearing to be hinged out of the equatorial plane by the arene bridge of [NPN]*. The Zr–N (average 2.07 Å), Zr–Cl (average to 2.42 Å), Zr–P (2.7229(8) Å), and other bond lengths in 2.10 are typical.41 In addition, angles about N1 and N2 add to 359.25 and 359.97°, respectively, indicating that the amide N atoms are planar and sp² hybridized.
Figure 2.8. ORTEP drawing of the solid-state molecular structure of [NPN]$^+$ZrCl$_2$, 2.10 (ellipsoids at 50% probability). All hydrogen atoms and the proximal Mes substituent (except C$_{prox}$) have been omitted for clarity. Selected bond lengths (Å) and angles (°): Zr1–N1 2.060(2), Zr1–N2 2.072(2), Zr1–P1 2.7229(8), Zr1–Cl1 2.4279(8), Zr1–Cl2 2.4099(8), N1–Zr1–N2 113.96(9), Cl1–Zr1–Cl2 96.23(3), N1–Zr1–P1 72.73(7), N2–Zr1–P1 70.38(7), N1–Zr1–Cl1 106.25(7), P1–Zr1–Cl1 178.63(3), P1–Zr1–Cl2 85.02(3).

The synthesis of 2.10 from proligand 2.8 is an example of a protonolysis reaction. Although group 4 complexes are often prepared by a metathesis reaction between the Li, Na, or K salt of the ligand and a metal halide complex, such as ZrCl$_4$(THF)$_2$, this reaction is sometimes unselective; the desired complex may form in low yield, or be present in a mixture of products from which it cannot be readily separated. Protonolysis, or the reaction of a proligand with a metal amide or alkyl compound to yield a new metal complex, and a volatile amine or alkane by-product, is used to prepare Zr complexes when the metathesis
route is unsuccessful.\textsuperscript{42} For example, \textit{ansa}-zirconocene dichloride catalyst precursors for olefin polymerization are synthesized from substituted cyclopentadiene ligands, Zr(NMe\textsubscript{2})\textsubscript{4}, and Me\textsubscript{3}SiCl.\textsuperscript{43} When a simple metathesis reaction between 2.7-(\textit{p}-C\textsubscript{6}H\textsubscript{5}O\textsubscript{2}) and ZrCl\textsubscript{4}(THF)\textsubscript{2} is carried out, the product mixture is dark brown with several peaks in its \textsuperscript{31}P{\textsuperscript{1}H} NMR spectrum. Despite extensive effort, the products of this reaction could not be separated.

\textbf{2.2.4 Adducts of [NPN]\textsuperscript{*}ZrCl\textsubscript{2}.}

When one or two drops of THF are added to 20 mg of 2.10 in C\textsubscript{6}D\textsubscript{6} in an NMR tube, an instant yellow to red colour change occurs. The red product, [NPN]\textsuperscript{*}ZrCl\textsubscript{2}(THF), 2.11, was only characterized by solution NMR spectroscopy because the compound could not be isolated. Attempts to concentrate solutions of 2.11, or to precipitate 2.11 from THF with pentane, for example, result in the precipitation of 2.10. The singlet in the \textsuperscript{31}P{\textsuperscript{1}H} NMR spectrum of 2.11 in C\textsubscript{6}D\textsubscript{6} is at \(\delta 2.7\), shifted downfield relative to the starting material. In the \textsuperscript{1}H NMR spectrum, there are two sharp resonances that can be assigned to free THF. As well, there are only four singlets in the ArCH\textsubscript{3} region of the spectrum, and not the eight singlets that would be predicted if 2.11 is a C\textsubscript{1} symmetric complex. Thus, coordinated THF appears to exchange rapidly with excess THF in solution on the NMR timescale, and this fluxionality is responsible for the apparent plane of symmetry in the product.

The addition of a slight excess of PMe\textsubscript{3} to 20 mg of 2.10 in C\textsubscript{6}D\textsubscript{6} in an NMR tube also produces an instant yellow to red colour change. As for 2.11, the adduct is not isolable, and [NPN]\textsuperscript{*}ZrCl\textsubscript{2}(PMe\textsubscript{3}), 2.12, could only be characterized via solution NMR spectroscopy. The singlet due to [NPN]\textsuperscript{*} in the \textsuperscript{31}P{\textsuperscript{1}H} NMR spectrum is shifted downfield from \(\delta \approx 2.8\) to 3.4 upon addition of PMe\textsubscript{3}, and there is a broad singlet that integrates as \(\approx 2P\) at \(\delta \approx 50\). The
bound and free PMe₃ average to give the broad singlet at δ -50 that shifts to δ -59 upon addition of another drop of PMe₃ to the sample tube, closer to the value expected for free PMe₃ (δ -62). The ¹H NMR spectrum displays four singlets in the ArCH₃ region, and there is no resonance diagnostic of coordinated PMe₃. These observations suggest that bound and free PMe₃ are exchanging rapidly on the NMR timescale in samples of 2.12.

The addition of Py to a toluene solution of 2.10 produces a yellow to red-orange colour change. Upon taking the reaction mixture to dryness, [NPN]*ZrCl₂(Py), 2.13, is isolated. As for 2.11 and 2.12, the singlet in the ³¹P{¹H} NMR spectrum (δ 2.7) is shifted downfield relative to the starting material 2.10. There are four ArCH₃ singlets in the ¹H NMR spectrum, indicative of a plane of symmetry in the six-coordinate complex. If Py coordinates to Zr in the equatorial plane of trigonal-bipyramidal 2.10, then 2.13 is expected to be a racemic mixture of C₁ symmetric complexes. The loss of the plane of symmetry would give eight inequivalent ArCH₃ groups that should be observable as eight singlets in the ArCH₃ region of the ¹H and ¹³C{¹H} NMR spectra. The presence of only four ArCH₃ singlets indicates that either a C₅ symmetric product is present in solution, in other words Py coordinates axially and the two chlorides are equatorial, or that 2.13 appears C₅ symmetric because it is fluxional on the NMR timescale at 298 K. The reactions of 2.10 with THF, Py and PMe₃ are summarized in Scheme 2.6.
The ORTEP representation of the solid-state molecular structure of 2.13 is shown in Figure 2.9. Two nearly identical molecules of $C_1$ symmetry are located in the asymmetric unit (only one is presented here), related by a centre of inversion to two complexes of opposite configuration in the unit cell. The geometry around Zr is distorted octahedral with facially coordinated $[\text{NPN}]^+$, and the chlorides are cis disposed, with one trans to P and the other cis. As was observed for 2.10, the P–Zr–N1 and P–Zr–N2 angles are less than 90°, at 70.00(4) and 73.45(4)°, respectively. The Zr–N bonds (to $[\text{NPN}]^+$) in 2.13 average to 2.14 Å, slightly longer than the Zr–N bonds in 2.10 (average to 2.07 Å). Similarly, the Zr–Cl bonds are longer in 2.13 (average to 2.48 Å) than in 2.10 (average to 2.42 Å). As expected, the Zr–N3 bond (2.3889(16) Å) to Py is longer than the Zr–N_{amido} bonds.
Figure 2.9. ORTEP drawing of the solid-state molecular structure of [NPN]⁺ZrCl₂(Py), 2.13 (ellipsoids drawn at the 50% probability level). Hydrogen atoms and carbon atoms of the proximal Mes substituent (except C₁₇) have been omitted for clarity. Selected bond lengths (Å) and angles (°): Zr₁–P₁ 2.7131(5), Zr₁–N₁ 2.1081(15), Zr₁–N₂ 2.1693(16), Zr₁–N₃ 2.3889(16), Zr₁–Cl₁ 2.4418(5), Zr₁–Cl₂ 2.5257(5), N₁–C₁ 1.455(2), P₁–Zr₁–N₁ 70.00(4), P₁–Zr₁–N₂ 73.45(4), P₁–Zr₁–Cl₁ 176.657(18), P₁–Zr₁–Cl₂ 82.142(17), N₁–Zr₁–N₂ 97.87(6), Cl₁–Zr₁–Cl₂ 99.062(19), C₁–N₁–C₁₀ 117.42(15), C₁₅–P₁–C₁₇ 109.59(9).

2.2.5 Synthesis and structure of [NPN]⁺HfCl₂.

Hafnium complexes of [NPN]⁺ are prepared by the same protonolysis route used to synthesize [NPN]⁺Zr complexes. [NPN]⁺Hf(NMe₂)₂, 2.14, is synthesized from 2.8 and Hf(NMe₂)₄ in toluene solution, and is isolated as a pale yellow toluene-soluble powder in high yield (Scheme 2.7). The NMR spectra of 2.14 are similar to those of its Zr analogue, 2.9. There is a singlet at δ ~ -4.5 in the ³¹P{¹H} NMR spectrum of 2.14 in C₆D₆. The ¹H NMR
spectrum features four singlets that are assigned to [NPN]*ArCH₃ groups. Two inequivalent NMe₂ groups are assigned to two singlets in the ¹H NMR spectrum in the δ ~ 2 – 3 range. Overall, the ¹H and ¹³C{¹H} NMR spectra show the expected resonances for a C₂ symmetric complex.

Scheme 2.7.

The ORTEP representation of the solid-state molecular structure of 2.14 is shown in Figure 2.10. The geometry about Hf is distorted trigonal bipyramidal with [NPN]* coordinated facially to Hf. Unsurprisingly, the P–Hf–N₁ and P–Hf–N₂ angles of 72.89(4)° and 70.71(4)°, respectively, deviate from 90° because of strain imposed by the arene bridge. Two inequivalent NMe₂ groups are apparent in the solid state: one NMe₂ is apical and trans to P, and the other is equatorial. The Hf–P and Hf–N bond lengths are unremarkable.⁴⁴
Figure 2.10. ORTEP drawing of the solid-state molecular structure of [NPN]*Hf(NMe)2, 2.14 (ellipsoids drawn at the 50% probability level). All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Hf–P1 2.7721(5), Hf–N1 2.1366(17), Hf–N2 2.1585(16), Hf–N3 2.0632(18), Hf–N4 2.0173(17), N1–C1 1.449(3), P1–Hf–N1 72.89(4), P1–Hf–N2 70.71(4), P1–Hf–N3 163.60(6), P1–Hf–N4 95.11(5), N1–Hf–N2 120.91(6), N3–Hf–N4 100.92(8), C1–N1–C10 117.05(16), C15–P1–C17 107.82(9).

[NPN]*HfCl2, 2.15, is isolated as a pale yellow powder in quantitative yield from the reaction of 2.14 and excess chlorotrimethylsilane in toluene (see Scheme 2.7). The NMR spectra of 2.15 in C₆D₆ are analogous to those observed for its Zr congener, 2.10: there is a singlet at δ 0.1 in the ³¹P{¹H} NMR spectrum, and four singlets attributable to the ArCH₃ substituents in the ¹H NMR spectrum. The ORTEP drawing of the solid-state molecular structure of 2.15 is shown in Figure 2.11. The geometry around Hf is distorted trigonal.
bipyramidal, with two chlorides cis-disposed; one is apical and trans to P. The structure resembles that of 2.10 with small differences in bond lengths and angles.

![Diagram of molecular structure](image)

**Figure 2.11.** ORTEP drawing of the solid-state molecular structure of \([\text{NPN}]^+\text{HfCl}_2\), 2.15 (ellipsoids drawn at the 50% probability level). All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Hf–P1 2.7059(9), Hf–N1 2.072(3), Hf–N2 2.076(3), Hf–Cl1 2.3903(10), Hf–N4 2.4003(9), N1–C1 1.450(4), P1–Hf–N1 73.75(8), P1–Hf–N2 71.81(9), P1–Hf–Cl1 86.14(3), P1–Hf–Cl2 176.49(3), N1–Hf–N2 115.05(11), Cl1–Hf–Cl2 97.36(4), C1–N1–C10 115.0(3), C15–P1–C17 108.5(2).

Similar to 2.10, compound 2.15 coordinates a sixth donor ligand (Equation 2.1). \([\text{NPN}]^+\text{HfCl}_2(\text{Py}),\) 2.16, is prepared from 2.15 and Py in toluene solution, and is isolated as an orange powder in high yield. There is a singlet at δ 3.2 in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 2.16 in $\text{C}_6\text{D}_6$. As for 2.11, 2.12, and 2.13, the P resonance of 2.16 is shifted downfield from that of the \([\text{NPN}]^+\text{MCl}_2\) starting material. Although there are only three resonances in the
ArCH<sub>3</sub> region of the <sup>1</sup>H NMR spectrum, one is broad and integrates to 12H, indicating that two of the ArCH<sub>3</sub> signals are coincident.

When a toluene-<em>d</em> solution of 2.16 is cooled to 220 K, a loss of symmetry in the complex is apparent in the <sup>1</sup>H NMR spectrum. The presence of eight singlets in the ArCH<sub>3</sub> region is diagnostic of a C<sub>1</sub> symmetric complex, and the ArH region also shows the expected resonances for a C<sub>1</sub> symmetric structure. At 360 K, there are three ArCH<sub>3</sub> resonances (again two singlets appear to overlap), and the ArH resonances are consistent with a C<sub>s</sub> symmetric solution structure for 2.16. The apparent plane of symmetry in 2.16 at 298 K in solution is consistent with either intra- or intermolecular exchange of Py.

### 2.2.6 Synthesis and structure of [NPN]<sup>+</sup>HfL<sub>2</sub>

[NPN]<sup>+</sup>HfL<sub>2</sub>, 2.17, is prepared from 2.15 and excess iodotrimethylsilane in toluene solution and is isolated in quantitative yield as a yellow powder (Equation 2.2). In C<sub>6</sub>D<sub>6</sub> solution, the <sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H NMR spectra closely resemble those of 2.10 and 2.15, and are consistent with a C<sub>s</sub> symmetric trigonal-bipyramidal structure for 2.17. The ORTEP representation of the solid-state molecular structure of 2.17 is shown in Figure 2.12. The geometry at Hf is distorted trigonal bipyramidal, and the bond lengths and angles are
unremarkable. In particular, at about 2.77 Å, the Hf–I bond lengths agree well with others reported in the literature.45

Figure 2.12. ORTEP drawing of the solid-state molecular structure of [NPN]⁺Hf₂, 2.17 (ellipsoids drawn at the 50% probability level). All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Hf1–P1 2.6994(13), Hf1–N1 2.061(4), Hf1–N2 2.068(4), Hf1–I1 2.7924(5), Hf1–I2 2.7573(4), P1–Hf1–N1 70.94(12), P1–Hf1–N2 73.56(12), P1–Hf1–I1 177.36(3), P1–Hf1–I2 86.03(3), N1–Hf1–N2 112.94(16), I1–Hf1–I2 96.605(14).
2.3 Conclusions.

In this chapter, two new routes to diamidophosphine ligands are reported. Although it was possible to prepare small quantities of $[\text{NPN}]^+\text{Li}_2(\text{THF})_2$ using Cu-catalyzed C–N coupling to obtain an $N,N$-diarylated diaminotriphenyolphosphine ligand precursor, the purity and overall yield provided by this route were disappointing. In contrast, the metathesis method provides a good overall yield of $[\text{NPN}]^+\text{Li}_2(p-\text{C}_6\text{H}_4\text{O}_2)$ from (Mes)(2-Br-4-MeC$_6$H$_3$)NH, $^7$BuLi, and PhPCl$_2$ in three simple steps. This reaction has been reproduced several times on a large scale (up to 25 g). $[\text{NPN}]^+\text{Li}_2$ has been characterized in solution and in the solid state.

The metathesis route is used extensively in the Fryzuk group to make early transition-metal complexes by the reaction of $[\text{PNP}]\text{Li}$, $[\text{P}_2\text{N}_2]\text{Li}_2$, or $[\text{NPN}]\text{Li}_2$ with $\text{MCl}_x(\text{THF})_x$. Zirconium complexes of $[\text{NPN}]^+$ cannot be prepared by salt metathesis because multiple metal-containing products form; however, Zr and Hf complexes are prepared in high yield by protonolysis. The proligand $[\text{NPN}]^+\text{H}_2$ is synthesized in high yield from $[\text{NPN}]^+\text{Li}_2(p-\text{C}_6\text{H}_4\text{O}_2)$ and NMe$_3$HCl. Zr and Hf complexes of $[\text{NPN}]^+$ are prepared from $[\text{NPN}]^+\text{H}_2$ and M(NMe$_2$)$_4$ ($M = \text{Zr, Hf}$). The reaction of $[\text{NPN}]^+\text{M(NMe}_2)_2$ with excess Me$_3$SiCl furnishes the dichloride complexes, $[\text{NPN}]^+\text{MCl}_2$. Overall, this three-step route provides $[\text{NPN}]^+\text{ZrCl}_2$ and $[\text{NPN}]^+\text{HfCl}_2$ in 78% and 85% yield, respectively, from $[\text{NPN}]^+\text{Li}_2(p-\text{C}_6\text{H}_4\text{O}_2)$. Both metal dichloride complexes, as well as the hafnium bis(dimethylamide) complex, have been characterized in the solid state by single-crystal X-ray diffraction. $[\text{NPN}]^+\text{HfI}_2$ can also be prepared in high yield from $[\text{NPN}]^+\text{HfCl}_2$ and excess TMSI.

The trigonal-bipyramidal complexes, $[\text{NPN}]^+\text{MCl}_5$, coordinate small neutral donor ligands such as Py to give racemic mixtures of $C_1$ symmetric six-coordinate complexes.
[NPN]*ZrCl₂(Py) has been characterized crystallographically, and the solid-state molecular structure is consistent with the low temperature ¹H NMR data obtained for [NPN]*HfCl₂(Py). In chapter three, [NPN]*ZrCl₂ and [NPN]*HfCl₂ are used as starting materials for the preparation of organometallic complexes [NPN]*MR₂ (M = Zr, Hf; R = Me, CH₂Ph, and CH₂SiMe₃). The attempted synthesis of Zr and Hf hydride complexes from [NPN]*MMe₂ is also described. In chapter four, the preparation of an N₂ complex from [NPN]*ZrCl₂, and the attempted preparation of an N₂ complex from [NPN]*HfI₂ is described.

2.4 Experimental.

2.4.1 General experimental.

Unless otherwise stated, all manipulations were performed under an atmosphere of dry, oxygen-free N₂ or Ar by means of standard Schlenk or glovebox techniques (Vacuum atmospheres HE-553-2 glovebox equipped with an MO-40-2H purification system and a −35 °C freezer). Ar and N₂ were dried and deoxygenated by passing the gases through a column containing molecular sieves and MnO. Hexanes, toluene, tetrahydrofuran, pentane, benzene, and diethyl ether were purchased anhydrous from Aldrich, sparged with N₂, and passed through columns containing activated alumina and Ridox catalyst. Dioxane was dried over sodium-benzophenone ketyl and distilled. THF-d₆, C₇D₈, and C₆D₆ were dried over Na/K alloy under partial pressure, trap-to-trap distilled, and freeze-pump-thaw degassed three times. ¹H, ³¹P{¹H}, and ¹³C{¹H} NMR spectra were recorded on a Bruker AV-300, Bruker AV-400, or Bruker AMX-500 spectrometer, operating at 300.1, 400.0, and 500.1 MHz for ¹H spectra, respectively. ⁷Li{¹H} NMR spectra were recorded on the AV-400 or
AMX-500. Unless otherwise noted, all spectra were recorded at room temperature. $^1$H NMR spectra were referenced to residual protons in the deuterated solvent: $C_6D_6$ ($\delta$ 7.16), CDCl$_3$ ($\delta$ 7.24), $C_7D_8$ ($\delta$ 2.09), or THF-$d_8$ ($\delta$ 3.58). $^{31}$P{$^1$H} NMR spectra were referenced to external $P(OMe)_3$ ($\delta$ 141.0 with respect to 85% $H_3PO_4$ at $\delta$ 0.0). $^{13}$C{$^1$H} NMR spectra are referenced to residual solvent: $C_6D_6$ ($\delta$ 128.0), CDCl$_3$ ($\delta$ 77.23), or THF-$d_8$ ($\delta$ 67.4). $^7$Li{$^1$H} NMR spectra were referenced to external LiCl in $D_2O/H_2O$ at $\delta$ 0.0. Chemical shifts ($\delta$) listed are in ppm, and absolute values of the coupling constants are in Hz. Mass spectrometry (EI-MS) and microanalyses (C, H, N) were performed at the Department of Chemistry at the University of British Columbia. Microanalysis of compound 2.17 was performed at CHEMISAR laboratories in Guelph, Ontario.

2.4.2 Starting materials and reagents.

Me$_3$SiCl, Me$_3$SiI, Cl$_3$SiH, and PhPCl$_4$ (Aldrich) were distilled prior to use. Pyridine, triethylamine and tetramethylethylenediamine (tmeda) were dried over CaH$_2$ and distilled prior to use. Me$_3$NHCl was suspended in benzene and heated to reflux in a Dean-Stark apparatus to remove water. (2-NH$_2$C$_6$H$_4$)$_2$PPh, $^{31}$Hf(NMe$_2$)$_4$ and Zr(NMe$_2$)$_4$ were prepared by literature methods. $^3$BuLi (~1.6 M in hexanes) was titrated against benzoic acid in THF with o-phenanthroline as an indicator. All other compounds were purchased from commercial suppliers and were used as received.

$[N-(4-MeC_6H_4)(2-N(H)C_6H_4)]_2$PhP=O (2.1). In air, (2-NH$_2$C$_6$H$_4$)$_2$PPh (1.00 g, 3.42 mmol) was dissolved in hexanes (30 mL) and acetone (5 mL). $H_2O_2$ (30% w/v, 0.5 mL, 4.4
mmol) was added dropwise to the stirred solution. The beige reaction mixture was taken to dryness, and the pale brown residue so obtained was dissolved in CH₂Cl₂ and washed with water (3 × 50 mL). The organic layer was separated, dried over Na₂SO₄, filtered, and concentrated under vacuum to obtain (2-NH₂C₆H₄)₂PhP=O as a beige solid (1.03 g, 3.34 mmol, 98%). (2-NH₂C₆H₄)₂PhP=O can be recrystallized from acetone/EtOAc.

³¹P{¹H} NMR (CDCl₃, 81 MHz): δ = 40.8 (s).


In air, (2-NH₂C₆H₄)₂PhP=O (1.03 g, 3.34 mmol) was dissolved in xylenes (30 mL) and THF (10 mL), and to this solution was added K₂CO₃ (2.00 g, 14.5 mmol), 4-iodotoluene (1.64 g, 7.52 mmol), and CuI(Phen)(PPh₃) (0.220 g, 0.35 mmol). The reaction mixture was stirred and heated to reflux for 4 d at 120 °C and appeared as white and orange solids suspended in a brown solution over the course of the reaction. Because no visible changes occurred, the reaction was followed by TLC in 9:1 petroleum ether:EtOAc (Rₜ = 0.8). The reaction mixture was cooled to rt and taken to dryness to obtain a beige residue that was purified by silica gel chromatography (9:1 petroleum ether:EtOAc). Compound 2.1 was isolated as a beige powder (1.42 g, 2.91 mmol, 85% relative to (2-NH₂C₆H₄)₂PhP).

³¹P{¹H} NMR (CDCl₃, 121 MHz): δ = 42.4 (s).
\[^{13}\text{C}\{^1\text{H}\} \text{ NMR} (\text{CDCl}_3, 75 \text{ MHz}): \delta = 150.9 \text{ (d, 5 Hz)}, 139.0, 133.8, 133.7, 133.6 \text{ (d, 2 Hz), 132.4, 132.3, 132.2, 129.9, 128.7 (d, 23 Hz), 121.7, 118.0 \text{ (d, 13 Hz), 115.2 \text{ (d, 8 Hz), and 113.6 (ArC)}, 20.9 \text{ (ArCH}_3)\}.

\text{EI-MS (m/\chi): 488 (100, [M]^+), 305 (50, [M - (Tol)(Ph)NH]^+), 183 (40, [(Tol)(Ph)NH]^+).}

\[{\text{[N,N-(4-MeC}_6\text{H}_4)\text{)(2-NC}_6\text{H}_4}\text{][N-(4-MeC}_6\text{H}_4)(2-N(\text{H})\text{C}_6\text{H}_4)\text{]PhP=O (2.2).}}\] Compound 2.2 was obtained as an impurity when the synthesis of 2.1 was repeated with >5 g of (2-NH\text{C}_6\text{H}_4)\text{)}_2\text{PPh.} \text{ The off-white product was purified by silica gel chromatography (4:1 petroleum ether/EtOAc, Rf = 0.8), followed by recrystallization from EtOH/H}_2\text{O to yield white crystals.}

\[^1\text{H} \text{ NMR} (\text{CDCl}_3, 300 \text{ MHz}): \delta = 7.41 \text{ (m, 4H), 7.31-7.07 (m, 9H), 7.03 \text{ (d, 2H, 8 Hz), 6.94 \text{ (d, 2H, 8 Hz), and 6.71 (br, 8H) (ArH)}, 6.54 \text{ (t, 1H, 7 Hz, NH), 2.27 (s, 3H) and 2.12 (s, 6H) (ArCH}_3).}

\[^{31}\text{P}\{^1\text{H}\} \text{ NMR} (\text{CDCl}_3, 121 \text{ MHz}): \delta = 34.1 \text{ (s).}

\[^{13}\text{C}\{^1\text{H}\} \text{ NMR} (\text{CDCl}_3, 75 \text{ MHz}): \delta = 152.2 \text{ (d, 3 Hz), 149.8 \text{ (d, 4 Hz), 145.8, 139.3, 135.4 (d, 11 Hz), 133.5 (d, 2 Hz), 133.2 (d, 11 Hz), 132.6 \text{ (d, 3 Hz), 132.5, 132.4 (d, 2 Hz), 132.0 \text{ (d, 10 Hz), 131.4, 131.2 (d, 6 Hz), 131.1 (d, 3 Hz), 130.9, 129.7, 129.2, 128.1 (d, 12 Hz), 124.7 \text{ (d, 13 Hz), 123.8, 120.4, 117.4 (d, 7 Hz), 116.4 and 115.0 (ArC), 20.9 and 20.8 (ArCH}_3).}

\text{EI-MS (m/\chi): 578 (100, [M]^+).}

\text{Anal. Calcd. for C}_{39}\text{H}_{35}\text{N}_2\text{OP: C, 80.95; H, 6.10; N, 4.84; Found: C, 80.63; H, 6.22; N, 5.24.}

\[{\text{[N-(4-MeC}_6\text{H}_4)(2-N(\text{H})\text{C}_6\text{H}_4)\text{]PhP, [NPN]P}^\text{2}} \text{ (2.3).}}\] Toluene (30 mL), trichlorosilane (1.2 g, 8.9 mmol), and triethylamine (0.62 g, 6.1 mmol) were added to 2.1 (1.00 g, 2.04 mmol)
under N\textsubscript{2} in a long Schlenk tube. The translucent light brown mixture was heated to reflux overnight, whereupon an off-white suspension formed. The reaction mixture was cooled, degassed H\textsubscript{2}O (3 mL) was added, and the mixture was taken to dryness to obtain a beige residue. The residue was triturated with toluene (25 mL), and the solution was filtered through Celite. The colourless solution was taken to dryness to obtain a translucent white residue (0.890 g, 1.88 mmol, 92%).

\textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}, 300 MHz): \(\delta = 7.48 \text{ (bd, 2H)}, 7.29 \text{ (m, 4H)}, 7.04 \text{ (m, 5H)}, 6.82 \text{ (d, 4H, 8 Hz)}, 6.76 \text{ (d, 4H, 8 Hz)}, \text{ and } 6.72 \text{ (m, 2H) (ArH)}, 6.36 \text{ (bs, 2H, NH)}, 2.06 \text{ (s, 6H, ArCH\textsubscript{3})}.

\textsuperscript{31}P\textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}, 121 MHz): \(\delta = -30.9 \text{ (s)}\).

\textsuperscript{13}C\textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}, 75 MHz): \(\delta = 148.5 \text{ (bs)}, 140.4, 135.2 \text{ (bs)}, 134.6, 134.3 \text{ (bs)}, 131.5, 130.8, 130.1, 129.2, 129.1, 122.5, 121.2, 120.5, and 116.6 \text{ (ArC), 20.7 (ArCH\textsubscript{3})}.

\[N-(4-MeC\textsubscript{6}H\textsubscript{4})(2-N(Li)C\textsubscript{6}H\textsubscript{4})\textsubscript{2}PhP-2THF, [NPN]\textsuperscript{'Li\textsubscript{2}2THF (2.4).} \textsuperscript{3}BuLi (1.6 M in hexanes, 1.10 mL, 1.75 mmol) was added dropwise to a solution of 2.3 (0.37 g, 0.78 mmol) in hexanes (10 mL) and THF (1 mL) at \(-35 \text{ °C}. The yellow clear solution was shaken thoroughly to mix, and was stored overnight at \(-35 \text{ °C}. A yellow precipitate formed overnight that was collected on a frit, washed with pentane (3 \times 1 mL), and dried. Compound 2.4 was recrystallized from THF/toluene layered with pentane. Small yellow crystals were collected on a frit and dried (0.26 g, 0.41 mmol, 53%).

\textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}, 500 MHz): \(\delta = 7.81 \text{ (bt, 2H, 6 Hz)}, 7.74 \text{ (t, 2H, 7 Hz)}, 7.66 \text{ (t, 2H, 7 Hz)}, 7.38 \text{ (d, 4H, 8 Hz)}, 7.13 \text{ (m, 8H)}, 7.02 \text{ (t, 1H, 7 Hz)}, \text{ and } 6.67 \text{ (t, 2H, 7 Hz) (ArH)}, 2.96 \text{ (bs, 8H, THF)}, 2.27 \text{ (s, 6H, ArCH\textsubscript{3})}, 0.87 \text{ (bs, 8H, THF)}.

\textsuperscript{31}P\textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}, 202 MHz): \(\delta = -33.0 \text{ (q, } J_{PL} = 41 \text{ Hz)}\).
$^7$Li{¹H} NMR (C₆D₆, 194 MHz): $\delta = -0.35$ (d, 1Li, $J_{Li} = 41$ Hz), $-1.72$ (s, 1Li).

(2,4,6-Me₃C₆H₂)(2-Br-4-MeC₆H₃)NH (2.5). In a flask shielded from the light and open to the air, N-bromosuccinimide (3.00 g, 16.9 mmol) was added portion-wise to a stirred pale yellow solution of (Mes)(Tol)NH (3.80 g, 16.9 mmol) in CH₃CN (100 mL) at 0 °C over 30 min. The brown suspension was allowed to warm to rt, and a saturated solution of NaHSO₃ (5 mL) was added. The beige reaction mixture was taken to dryness to obtain a beige solid that was dissolved in a minimum amount of petroleum ether and filtered through silica powder about 5 cm deep in a 60-mL glass frit. The silica was rinsed with petroleum ether until the washings were colourless. Beige crystals were obtained when the filtrate was taken to dryness. The crystals were isolated, washed with petroleum ether (2 × 5 mL), and dried (4.94 g, 16.2 mmol, 96%).

¹H NMR (CDCl₃, 300 MHz): $\delta = 7.33$ (s, 1H), 6.96 (s, 2H), 6.83 (d, 1H, 8 Hz), and 6.07 (d, 1H, 8 Hz) (ArH), 5.51 (bs, 1H, NH), 2.33 (s, 3H), 2.23 (s, 3H), 2.17 (s, 6H) (ArCH₃).

¹³C{¹H} NMR (CDCl₃, 75 MHz): $\delta = 141.5$, 136.5, 136.0, 135.5, 132.9, 129.4, 129.1, 128.1, 112.6, and 109.4 (ArC), 21.1, 20.2, and 18.3 (ArCH₃).

EI-MS (m/z): 303 (100, [M]⁺).

Anal. Calcd. for C₁₆H₁₈NBr: C, 63.17; H, 5.96; N, 4.60; Found: C, 62.81; H, 5.99; N, 4.72.

(2,4,6-Me₃C₆H₂)(2-Li-4-MeC₆H₃)NLitmeda (2.6). A stirred solution of 2.5 (0.790 g, 2.59 mmol) and tmeda (0.80 mL, 0.62 g, 5.3 mmol) in Et₂O (5 mL) was cooled to −35 °C, and $^9$BuLi (3.4 mL, 1.6 M in hexanes, 5.4 mmol) was added dropwise. A light yellow
precipitate formed immediately that was collected on a frit, washed with hexanes (5 mL), and
dried (0.680 g, 1.92 mmol, 74%).

$^1$H NMR (THF-$d_8$, 300 MHz): $\delta = 6.93$ (d, 1H, 2 Hz), 6.74 (s, 2H), 6.38 (dd, 1H, 8 Hz, 2
Hz), and 5.54 (d, 1H, 8 Hz) (ArH), 2.31 (s, 4H, tmeda), 2.17 (s, 3H, CH$_3$), 2.15 (s, 12H,
tmeda), 2.02 (s, 3H), and 2.00 (s, 6H) (ArCH$_3$).

$^{13}$C($^1$H) NMR (THF-$d_8$, 75 MHz): $\delta = 153.8, 152.1, 133.5, 132.2, 129.4, 129.3, 128.4, 116.4,$
113.3, and 111.5 (ArC), 58.8 and 46.2 (tmeda), 21.0, 20.0, and 18.9 (ArCH$_3$).

Satisfactory elemental analysis could not be obtained; samples darkened instantly in the
modified N$_2$-filled glovebox used in the microanalytical facility of the UBC Chemistry Dept.

$[\text{NPN}]^+\text{Li}_2(p$-$C_4H_8O_2)(2.7p$-$C_4H_8O_2)$. To a stirred solution of 2.5 (4.84 g, 15.9 mmol) in
Et$_2$O (100 mL) at $-35$ °C was added $^6$BuLi (1.55 M in hexanes, 20.5 mL, 31.8 mmol)
dropwise over 15 min. The clear yellow solution was allowed to warm to rt and stirred for 3
h. The solution was chilled ($-35$ °C), and PhPCl$_2$ (1.40 g, 7.82 mmol) in Et$_2$O (10 mL) was
added dropwise over 2 – 3 h at this temperature. The yellow solution became dark orange
throughout the addition. The reaction mixture was warmed slowly to rt and stirred for 24 h
to obtain a pale orange suspension that was taken to dryness to obtain an orange foam.

Hexanes (30 mL) were added to the foam to obtain a translucent orange solution. 1,4-
Dioxane (5 mL) was added to the solution to obtain a yellow precipitate that was collected
on Celite $\sim$3 cm deep in a frit. The precipitate was washed with hexanes and the dark orange
filtrate was concentrated and chilled to induce the formation of yellow crystals. The solid
trapped on Celite in the frit was eluted through the Celite with a mixture of toluene (50 mL)
and THF (0.1 mL) to obtain a yellow filtrate that was taken to dryness. The yellow powder
so obtained can be recrystallized from toluene (with a drop of THF to dissolve) layered with hexanes. The combined powder and crystals (4.37 g, 6.65 mmol, 85% isolated yield based on PhPCl2) were stored at —35 °C because thermal decomposition has been observed. NMR spectroscopy was facilitated by the addition of a drop of THF to the suspension of 2.7·(p-C4H8O2) in C6D6. Resonances for free (not coordinated to Li) p-C4H8O2, and free and coordinated THF were observed in the 1H NMR spectrum. Signals due to coordinated THF appear as shoulders on the peaks for free THF in the 1H NMR spectrum and cannot be integrated accurately. Elemental analyses of 2.7·(p-C4H8O2) were hampered by its sensitivity to moist air; the yellow powder darkened instantly upon opening sample vials in the modified glovebox used for microanalysis at U.B.C. Despite many attempts, results that were low in carbon were found. X-ray quality crystals of 2.7·2THF were obtained by slow evaporation of a benzene solution of 2.7·(p-C4H8O2) with a small amount of THF added.

1H NMR (C6D6, 300 MHz): δ = 7.81 (t, 2H, 7 Hz), 7.72 (bd, 2H, 3 Hz), 7.19 (t, 2H, 7 Hz), 7.02 (t, 1H, 8 Hz), 6.97 (s, 2H), 6.87 (s, 2H), 6.85 (d, 2H, 8 Hz), and 6.52 (dd, 2H, JHH = 6 Hz, JHP = 8 Hz) (ArH), 2.35 (s, 6H), 2.33 (s, 6H), 2.28 (s, 6H), and 2.16 (s, 6H) (ArCH3).

31P{1H} NMR (C6D6, 121 MHz): δ = —35.2 (q, JPL = 40 Hz).

7Li{1H} NMR (C6D6, 155 MHz): δ = —0.07 (d, 1Li, J LiLi = 40 Hz), —1.97 (s, 1Li).

13C{1H} NMR (C6D6, 75 MHz): δ = 162.1 (d, 28 Hz), 152.0, 140.2, 134.9 (d, 3 Hz), 133.8, 132.3 (d, 14 Hz), 132.2, 132.1, 131.8, 130.8, 129.0, 128.8, 126.8, 122.9, 120.9 (d, 12 Hz), and 117.9 (d, 5 Hz) (ArC), 20.9, 20.7, 20.4, and 20.2 (ArCH3).

The data for one representative attempt at microanalysis is reported below.

Anal. Calcd. for C46H55N2Li2O2P: C, 77.51; H, 7.78; N, 3.93; Found: C, 74.75; H, 7.59; N, 4.02.
[NPN]⁺H₂ (2.8). Trimethylammonium chloride (0.319 g, 3.34 mmol) was added all at once to a stirred yellow solution of 2.7-(p-C₄H₈O₂) (1.06 g, 1.61 mmol) in THF (15 mL). After 15 min., the reaction mixture was a white suspension. After 1 h, the reaction mixture was taken to dryness to obtain a white solid that was extracted with warm toluene (20 mL). The toluene suspension was filtered through Celite, the Celite was washed with additional warm toluene (10 mL), and the filtrate was taken to dryness to obtain a white solid. The solid was washed with pentane and dried to yield a white powder (0.872 g, 1.57 mmol, 97%). Compound 2.8 is air-stable as a solid for weeks and in solution for days, although in our laboratory it is stored in the glovebox to keep it water-free.

¹H NMR (C₆D₆, 300 MHz, 300 K): δ = 7.68 (dd, 2H, J_{HP} = 7 Hz, J_{HH} = 7 Hz), 7.29 (d, 2H, J_{HP} = 7 Hz), 7.12 (d, 2H, 6 Hz), 7.02 (t, 1H, 8 Hz), 6.88 (d, 2H, 7 Hz), 6.78 (bs, 2H), 6.74 (bs, 2H), and 6.38 (dd, 2H, J_{HP} = 5 Hz, J_{HH} = 9 Hz) (ArH), 5.98 (d, 2H, J_{HP} = 5 Hz, NH), 2.12 (s, 6H), 2.04 (bs, 6H), 1.98 (s, 6H), and 1.90 (bs, 6H) (ArCH₃).

¹H NMR (C₇D₈, 500 MHz, 273 K): δ = 7.63 (t, 2H, 7 Hz), 7.26 (d, 2H, 7 Hz), 7.10 (m, 3H), 6.84 (d, 2H, 7 Hz), 6.75 (s, 2H), 6.69 (s, 2H), and 6.35 (dd, 2H, J_{HP} = 5 Hz, J_{HH} = 9 Hz) (ArH), 5.91 (d, 2H, 5 Hz, NH), 2.16 (s, 6H), 2.08 (s, 6H), 2.01 (s, 6H), and 1.93 (s, 6H) (ArCH₃).

¹H NMR (C₇D₈, 300 MHz, 370 K): δ = 7.59 (t, 2H, 8 Hz), 7.12 (m, 4H), 6.95 (m, 1H), 6.82 (d, 2H, 8 Hz), 6.73 (s, 4H), and 6.23 (dd, 2H, J_{HP} = 5 Hz, J_{HH} = 9 Hz) (ArH), 5.88 (bd, 2H, J_{HP} = 5 Hz, NH), 2.12 (s, 6H), 2.01 (s, 6H), and 1.98 (s, 12H) (ArCH₃).

³¹P{¹H} NMR (C₆D₆, 121 MHz): δ = −31.4 (s).
\[ ^{13}\text{C} \{ ^{1}\text{H} \} \text{ NMR (C}_6\text{D}_6, 75 \text{ MHz}) : \delta = 147.7 \ (d, \ 16 \text{ Hz}), 136.5, 135.7 \ (bs), 135.5 \ (bs), 135.1, 135.0, 134.8, 134.7, 134.5, 131.8, 129.6, 129.1, 129.0, 128.9, 117.9 \ (d, \ 7 \text{ Hz}), \text{ and } 112.5 \ (d, \ 3 \text{ Hz}) \ (\text{ArC}), 20.6, 20.1, 18.0 \ (bs), \text{ and } 17.7 \ (bs) \ (\text{ArCH}_3). \]

IR (KBr): 3360 (m), 3012 (m), 2917 (m), 2854 (m), 1601 (m), 1491 (s), 1389 (m), 1310 (s), 1293 (s), 1268 (m), and 1028 (m) cm\(^{-1}\).

EI-MS \((m/z)\): 556 (20, [M\(^+\)], 541 (100, [M – Me\(^+\)]).

Anal. Calcd. for C\(_{38}\)H\(_{41}\)N\(_2\)P: C, 81.98; H, 7.42; N, 5.03; Found: C, 82.04; H, 7.46; N, 4.87.

\([\text{NPNI}^\dagger\text{Zr(NMe}_2)_2\ (2.9). \text{ Zr(NMe}_2)_4\ (0.580 \text{ g, 2.17 mmol}) \text{ and 2.8 (1.21 g, 2.17 mmol}) \text{ were mixed together, and toluene (15 mL) was added to obtain a lemon yellow solution that was stirred for 2 h. The reaction mixture was taken to dryness to obtain a yellow residue. Upon addition of pentane (5 mL), a light yellow precipitate formed that was collected on a frit and dried (1.43 g, 1.95 mmol, 90%).} \]

\(^1\text{H} \text{ NMR (C}_6\text{D}_6, 300 \text{ MHz}) : \delta = 7.60 \ (t, 2H, 8 \text{ Hz, o-PPh}), 7.52 \ (d, 2H, 7 \text{ Hz, m-Tol}), 7.11 \ (m, 3H, 7 \text{ Hz, m-, p-PPh}), 7.02 \ (s, 2H, m-Mes), 6.97 \ (s, 2H, m-Mes), 6.93 \ (d, 2H, 9 \text{ Hz, o-Tol}), 6.19 \ (dd, 2H, 8 \text{ Hz, m-Tol}), 3.06 \ (s, 6H, N(CH}_3)_2\), 2.42 \ (s, 6H), \text{ and } 2.32 \ (s, 6H) \ (\text{ArCH}_3), 2.31 \ (s, 6H, N(CH}_3)_2\), 2.25 \ (s, 6H), \text{ and } 2.08 \ (s, 6H) \ (\text{ArCH}_3). \]

\(^{31}\text{P} \{ ^{1}\text{H} \} \text{ NMR (C}_6\text{D}_6, 121 \text{ MHz}) : \delta = -11.5 \ (s). \]

\[^{13}\text{C} \{ ^{1}\text{H} \} \text{ NMR (C}_6\text{D}_6, 75 \text{ MHz}) : \delta = 161.5 \ (d, 31 \text{ Hz}), 145.2, 144.6, 137.2, 136.4, 135.0, 134.7, 134.3, 133.3, 133.1, 130.3, 130.2, 118.0, 117.6, 115.1, \text{ and } 115.0 \ (\text{ArC}), 43.6 \text{ and } 43.5 \ (\text{N(CH}_3)_2\), 21.0, 20.4, 19.3, \text{ and } 19.2 \ (\text{ArCH}_3). \]

EI-MS \((m/z)\): 732 (1, [M\(^+\)], 688 (30, [M – NMe\(_2\)]\(^+\)), 556 (30, [2.8\(^+\)]), 541 (100, [2.8 – Me\(^+\)].

Anal. Calcd. for C\(_{45}\)H\(_{45}\)N\(_4\)PZr: C, 68.72; H, 7.00; N, 7.63; Found: C, 68.42; H, 6.99; N, 7.38. 

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[NPN]¹ZrCl₂ (2.10). To a stirred yellow toluene solution (40 mL) of 2.9 (1.20 g, 1.63 mmol) was added chlorotrimethylsilane (1.77 g, 16.3 mmol) dropwise. The clear yellow solution was stirred overnight, whereupon a yellow precipitate formed. The reaction mixture was taken to dryness to obtain a yellow powder that was collected on a frit, washed with pentane (3 × 5 mL), and dried (1.04 g, 1.45 mmol, 89%). X-ray quality crystals of 2.10 were grown by slow evaporation of a benzene solution of the compound.

¹H NMR (C₆D₆, 400 MHz): δ = 7.60 (dd, 2H, JHH = 7 Hz, JHP = 7 Hz), 7.45 (d, 2H, 8 Hz), 7.05 (m, 3H), 6.91 (s, 2H), 6.84 (d, 2H, 8 Hz), 6.80 (s, 2H), and 6.05 (dd, 2H, JHH = 7 Hz, JHP = 7 Hz) (ArH), 2.46 (s, 6H), 2.34 (s, 6H), 2.09 (s, 6H), and 1.94 (s, 6H) (ArCH₃).

³¹P{¹H} NMR (C₆D₆, 121 MHz): δ = -2.8 (s).

¹³C{¹H} NMR (C₆D₆, 75 MHz): δ = 159.9 (d, 32 Hz), 138.5, 138.3, 137.0, 135.3, 134.6, 132.3, 132.2, 131.1, 130.8, 129.6, 125.6, 121.1, 120.6, 114.9, and 114.8 (ArC), 21.1, 20.3, and 19.1 (ArCH₃).

EI-MS (m/z): 714 (3, [M]⁺), 541 (100, [2.8-Me]⁺).

Anal. Calcd. for C₃₈H₃₉N₂Cl₂PZr: C, 63.67; H, 5.48; N, 3.91; Found: C, 63.65; H, 5.80; N, 3.98.

[NPN]¹ZrCl₂(THF) (2.11). THF (1-2 drops) was added to an NMR tube with 2.10 (20 mg, 28 µmol) in C₆D₆ (0.8 mL) to produce a bright red-orange solution. Attempts to isolate 2.11 by precipitation (from toluene/THF solutions layered with pentane at -35 °C) or by concentrating solutions under vacuum gave 2.10. Two sharp resonances due to free THF were observed by ¹H NMR spectroscopy, but signals due to coordinated THF could not be distinguished.
$^1$H NMR ($C_6D_6$, 300 MHz): $\delta = 7.75$ (t, 2H, 8 Hz), 7.38 (d, 2H, 8 Hz), 7.07 (m, 3H), 6.91 (s, 2H), 6.83 (s, 2H), 6.82 (d, 2H, 8 Hz), and 6.04 (dd, 2H, $J_{HH} = 7$ Hz, $J_{HP} = 6$ Hz) (ArH), 2.46 (s, 6H), 2.30 (s, 6H), 2.12 (s, 6H), and 1.95 (s, 6H) (ArCH$_3$).

$^{31}$P{$^1$H} NMR ($C_6D_6$, 121 MHz): $\delta = 2.7$ (s).

$[^{NPN}]^1ZrCl_2$($^{PMe_3}$) (2.12). $^{PMe_3}$ (1-2 drops) was added to an NMR tube with 2.10 (20 mg, 28 µmol) in $C_6D_6$ (0.8 mL) to produce a bright red solution. Attempts to isolate 2.12 by precipitation (from toluene/$^{PMe_3}$ solutions layered with pentane at $-35$ °C) or by concentrating solutions under vacuum gave 2.10. A broad singlet due to free $^{PMe_3}$ was observed by $^1$H and $^{31}$P{$^1$H} NMR spectroscopy, but a separate peak due to coordinated $^{PMe_3}$ could not be distinguished.

$^1$H NMR ($C_6D_6$, 500 MHz): $\delta = 7.78$ (t, 2H, 8 Hz), 7.35 (d, 2H, 8 Hz), 7.12 (m, 3H), 6.88 (s, 2H), 6.84 (s, 2H), 6.78 (d, 2H, 8 Hz), and 5.97 (dd, 2H, $J_{HH} = 8$ Hz, $J_{HP} = 5$ Hz) (ArH), 2.42 (s, 6H), 2.19 (s, 6H), 2.16 (s, 6H), and 1.99 (s, 6H) (ArCH$_3$).

$^{31}$P{$^1$H} NMR ($C_6D_6$, 202 MHz): $\delta = 3.4$ (s).

$[^{NPN}]^1ZrCl_2$(Py) (2.13). Pyridine (0.49 g, 0.50 mL, 6.2 mmol) was added dropwise to a stirred yellow solution of 2.10 (0.400 g, 0.558 mmol) in toluene (5 mL). The solution turned red-orange instantly and was stirred for 30 min. The reaction mixture was taken to dryness to obtain a red-orange powder that was collected on a frit, rinsed with hexanes (5 mL), and dried (0.434 g, 0.545 mmol, 98%). Red single crystals of 2.13 suitable for X-ray diffraction were grown by slow evaporation of a benzene solution of the compound.
$^1$H NMR (C$_6$D$_6$, 400 MHz): $\delta$ = 8.38 (d, 2H, 4 Hz, C$_6$H$_2$N), 7.96 (t, 2H, 8 Hz), 7.34 (d, 2H, 8 Hz), 7.13 (m, 3H), 6.95 (s, 2H), 6.78 (d, 2H, 7 Hz), 6.73 (s, 2H), 6.60 (t, 1H, 7 Hz, $p$-C$_6$H$_3$N), 6.18 (t, 2H, 7 Hz, C$_6$H$_2$N), and 6.04 (dd, 2H, $J_{HH} = 8$ Hz, $J_{HP} = 6$ Hz) (ArH), 2.30 (s, 6H), 2.18 (s, 6H), 2.05 (bs, 6H), and 1.95 (s, 6H) (ArCH$_3$).

$^{31}$P$^{1}$H NMR (C$_6$D$_6$, 162 MHz): $\delta$ = 2.7 (s).

$^{13}$C$^{1}$H NMR (C$_6$D$_6$, 101 MHz): $\delta$ = 151.6, 140.9, 139.2, 139.0, 137.7, 136.3, 134.1, 133.4, 132.9, 132.8, 130.6, 130.5, 130.0, 129.9, 129.7, 129.6, 125.6, 123.2, and 115.7 (d, 9 Hz) (ArC), 21.0, 20.5, 20.1, and 19.6 (ArCH$_3$).


Anal. Calcd. for C$_{43}$H$_{63}$N$_3$Cl$_2$PZr: C, 64.89; H, 5.57; N, 5.28; Found: C, 65.20; H, 5.89; N, 5.35.

[NPN]$^+$Hf(NMe$_2$)$_2$ (2.14). Hf(NMe$_2$)$_4$ (2.85 g, 8.03 mmol) and 2.8 (4.48 g, 8.05 mmol) were mixed together and toluene (50 mL) was added. The lemon yellow solution was stirred for 2 h, and the reaction mixture was taken to dryness. The pale yellow residue so obtained was dissolved in pentane (25 mL), and after about 30 s a pale yellow precipitate formed that was collected on a frit, washed with pentane (5 mL), and dried under vacuum (5.81 g, 7.07 mmol, 88%). X-ray quality crystals of 2.14 were grown by slow evaporation of a benzene solution of the compound.

$^1$H NMR (C$_6$D$_6$, 500 MHz): $\delta$ = 7.50 (t, 2H, 8 Hz), 7.44 (d, 2H, 8 Hz), 7.06 (m, 2H), 7.01 (m, 1H), 6.96 (s, 2H), 6.92 (s, 2H), 6.88 (d, 2H, 8 Hz), and 6.15 (dd, 2H, $J_{HH} = 8$ Hz, $J_{HP} = 6$ Hz)
[NPN]*HfCl₃ (2.15). To a stirred toluene solution (50 mL) of 2.14 (5.10 g, 6.94 mmol) was added chlorotrimethylsilane (2.55 g, 23.5 mmol) dropwise. The clear yellow solution was stirred overnight, whereupon a pale yellow precipitate formed. The reaction mixture was taken to dryness and the pale yellow solid so obtained was suspended in pentane (25 mL). The solid was collected on a frit, washed with pentane (3 × 5 mL), and dried under vacuum to obtain a pale yellow powder (4.97 g, 6.87 mmol, 99%). X-ray quality crystals were grown by slow evaporation of a benzene solution of 2.15.

1H NMR (CD₂Cl₂, 300 MHz): δ = 7.59 (dd, 2H, J₁H₂ = 8 Hz, J₁H₁ = 10 Hz), 7.42 (d, 2H, 8 Hz), 7.03 (m, 3H), 6.92 (s, 2H), 6.86 (d, 2H, 8 Hz), 6.82 (s, 2H), and 6.10 (dd, 2H, J₁H₁ = 8 Hz, J₁H₂ = 6 Hz) (ArH), 2.48 (s, 6H), 2.41 (s, 6H), 2.10 (s, 6H), and 1.96 (s, 6H) (ArCH₃).

31P{1H} NMR (CD₂Cl₂, 121 MHz): δ = 0.1 (s).

13C{1H} NMR (CD₂Cl₂, 75 MHz): δ = 160.9 (d, 30 Hz), 139.0 (d, 5 Hz), 138.3, 137.4, 136.5, 135.5, 134.6, 132.3 (d, 12 Hz), 131.0 (d, 5 Hz), 130.9, 130.8, 130.4 (d, 2 Hz), 129.2 (d, 10 Hz), 120.1, 119.5, and 116.2 (d, 10 Hz) (ArC), 21.1, 20.2, 19.14, and 19.12 (ArCH₃)
EI-MS (m/z): 804 (100, [M]+), 541 (40, [2.8 – Me]+).

Anal. Calcd. for C_{38}H_{39}N_{2}Cl_{2}Pf: C, 56.76; H, 4.89; N, 3.48; Found: C, 57.10; H, 5.00; N, 3.68.

\[ \text{[NPN]}^{1} \text{HfCl}_{2} (\text{Py}) \ (2.16). \] Pyridine (0.49 g, 0.50 mL, 6.2 mmol) was added dropwise to a stirred solution of \( 2.15 \) (0.400 g, 0.498 mmol) in toluene (10 mL). The light yellow solution turned yellow-orange instantly and was stirred for 30 min. at rt. The reaction mixture was taken to dryness to obtain a pale orange powder that was collected on a frit, rinsed with hexanes, and dried (0.420 g, 0.476 mmol, 95%).

\(^1\)H NMR \((\text{C}_{6}\text{D}_{6}, 400 \text{MHz,} 300 \text{K})\): \( \delta = 8.31 \) (d, 2H, 5 Hz), 7.97 (m, 2H), 7.32 (dd, 2H, 8 Hz, 1 Hz), 7.14 (m, 3H), 6.96 (s, 2H), 6.82 (d, 2H, 8 Hz), 6.73 (bs, 2H), 6.60 (t, 1H, 7 Hz), 6.15 (t, 2H, 7 Hz), and 6.10 (dd, 2H, \( J_{\text{HH}} = 8 \) Hz, \( J_{\text{HP}} = 6 \) Hz) (ArH), 2.31 (bs, 12H), 2.20 (s, 6H), and 1.97 (s, 6H) (ArCH\(_3\)).

\(^1\)H NMR \((\text{C}_{7}\text{D}_{8}, 400 \text{MHz,} 220 \text{K})\): \( \delta = 8.47 \) (bs, 2H), 7.89 (bs, 2H), 7.38 (d, 1H, 8 Hz), 7.32 (d, 1H, 8 Hz), 7.14 (s, 3H), 7.03 (s, 1H), 6.95 (s, 1H), 6.92 (s, 1H), 6.77 (d, 1H, 8 Hz), 6.74 (d, 1H, 8 Hz), 6.50 (bt, 1H, 7 Hz), 6.36 (s, 1H), 6.12 (bs, 2H), and 6.01 (bs, 2H) (ArH), 3.15 (s, 3H), 2.62 (s, 3H), 2.26 (s, 3H), 2.17 (s, 3H), 2.08 (s, 3H), 2.02 (s, 3H), 1.88 (s, 3H), and 0.84 (s, 3H) (ArCH\(_3\)).

\(^1\)H NMR \((\text{C}_{7}\text{D}_{8}, 400 \text{MHz,} 360 \text{K})\): \( \delta = 8.46 \) (bs, 2H), 7.73 (dd, 2H, \( J_{\text{HH}} = 8 \) Hz, \( J_{\text{HP}} = 8 \) Hz), 7.29 (d, 2H, 8 Hz), 7.14 (m, 3H), 6.91 (bs, 1H), 6.88 (s, 2H), 6.79 (d, 2H, 8 Hz), 6.68 (s, 2H), 6.53 (bs, 2H), and 5.97 (dd, 2H, \( J_{\text{HH}} = 8 \) Hz, \( J_{\text{HP}} = 6 \) Hz) (ArH), 2.22 (s, 6H), 2.14 (s, 12H), 2.00 (s, 6H) (ArCH\(_3\)).

\(^{31}\)P\(^{1}\)H NMR \((\text{C}_{6}\text{D}_{6}, 162 \text{MHz})\): \( \delta = 3.2 \) (s).
[NPN]$^+\text{HfI}_2$ (2.17). To a stirred toluene solution (15 mL) of 2.15 (1.75 g, 2.18 mmol) was added iodotrimethylsilane (3.0 mL, 2.6 g, 24 mmol) dropwise. The clear yellow solution was stirred overnight, whereupon a bright yellow precipitate formed. The reaction mixture was taken to dryness to obtain a yellow solid that was suspended in pentane (25 mL), collected on a frit, washed with pentane (3 × 5 mL), and dried under vacuum to obtain a yellow powder (2.13 g, 2.15 mmol, 99%). Single crystals of 2.17 were grown by slow evaporation of a benzene solution of the compound.

$^1\text{H}$ NMR (C$_6$D$_6$, 500 MHz): δ = 7.55 (dd, 2H, $J_{HH} = 8$ Hz, $J_{PH} = 10$ Hz), 7.36 (d, 2H, 8 Hz), 7.11 (t, 2H, 8 Hz), 7.05 (t, 1H, 8 Hz), 6.89 (s, 2H), 6.84 (d, 2H, 7 Hz), 6.84 (s, 2H), and 6.09 (dd, 2H, $J_{HH} = 8$ Hz, $J_{HP} = 6$ Hz) (ArH), 2.56 (s, 6H), 2.30 (s, 6H), 2.10 (s, 6H), and 1.92 (s, 6H) (ArCH$_3$).

$^{31}\text{P}$($^1\text{H}$) NMR (C$_6$D$_6$, 202 MHz): δ = 3.9 (s).

$^{13}\text{C}$($^1\text{H}$) NMR (C$_6$D$_6$, 126 MHz): δ = 160.3 (d, 29 Hz), 138.6, 138.3, 137.8, 135.8, 135.4, 134.6, 133.0 (d, 11 Hz), 131.4, 131.2, 131.1, 130.5, 129.0 (d, 10 Hz), 121.3, 121.0, and 116.3 (d, 10 Hz) (ArC), 21.4, 20.7, 20.2, and 20.1 (ArCH$_3$).

EI-MS (m/z): 988 (100, [M]$^+$), 861 (100, [M − I]$^+$).
Anal. Calcd. for C_{38}H_{39}N_{2}I_{2}PPh: C, 46.24; H, 3.98; N, 2.84; Found: C, 46.58; H, 4.23; N, 2.81.

2.5 References.


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Chapter Three

Zirconium and Hafnium Organometallic Complexes

3.1 Introduction.

Since Ziegler and Natta discovered that mixtures of Ti or Zr halides and organoaluminum reagents catalyze olefin polymerization, interest in group 4 chemistry has continued unabated. A major development in the organometallic chemistry of group 4 has been the creation of homogeneous olefin polymerization catalysts based on titano- and zirconocenes, which have been found to be highly active in the presence of co-catalysts such as boranes or methylaluminoxane (MAO). Metalocene catalysts have not only allowed chemists to probe the mechanism of olefin polymerization, but they have also been tailored to yield polymers with narrow molecular weight distributions, to polymerize prochiral olefins stereospecifically, and to give polyolefin products with new structures for advanced applications. In addition, non-metalocene group 4 complexes are being investigated for olefin polymerization. In 1995, Ziegler-Natta catalysis was estimated to provide over 35 million tonnes of polyolefins per year. Recent estimates include the production of over 80 million tonnes of polyethylene and 65 million tonnes of polypropylene per year.

In addition to olefin polymerization, metalocene and non-metalocene organotitanium, -zirconium, and -hafnium complexes have been investigated as hydrogenation, hydroamination, C–C cross-coupling, silane dehydropolymerization, enantioselective organic synthesis, and hydrosilylation catalysts. Small molecule activation, C–F bond activation, C–H bond activation and migratory insertion reactions to yield new organic compounds are other areas of interest to early transition-metal chemists.
A new reaction for early transition-metal alkyl complexes emerged in the late 1990s when a group 4 organometallic complex was reacted with H₂ gas, followed by N₂ gas; a dinitrogen complex, methane, and hydrogen are the major products of this reaction. The synthesis of N₂ complexes by the hydrogenolysis of early transition-metal alkyl complexes is attractive because H₂ is the only reagent besides N₂ that is added to the reaction. There are many examples of early transition-metal complexes that bind and activate N₂ following reduction by an alkali metal reagent, such as potassium graphite (KC₈) or sodium amalgam. The use of strong reductants to activate N₂ is one of the major barriers to the development of homogeneous catalytic or industrial processes for nitrogen fixation. Among other problems, reducing agents such as KC₈ or Na/Hg amalgam are difficult to work with because they are pyrophoric, are generally incompatible with other reagents required to functionalize N₂ (such as electrophiles), and are difficult to introduce into a catalytic or large-scale reaction.

The reaction of (η⁵-C₅Me₄H)₂TiR (R = Me, Ph) with H₂ gives the red-brown Ti(III) hydride, (η⁵-C₅Me₄H)₂TiH, that instantly forms a blue Ti-N₂ complex, [(η⁵-C₅Me₄H)₂Ti]₂(μ-η¹:η¹-N₂), upon exposure to N₂ (Scheme 3.1). Dinitrogen is weakly activated in this end-on dinuclear complex: the N–N bond length is 1.170(4) Å. Overall, this reaction represents the formation of an N₂ complex from an organometallic complex, H₂, and N₂.

Scheme 3.1.
A Zr-N₂ complex is also prepared by hydrogenolysis of an alkylzirconium complex.²⁴ When solutions of (rac-Bp)ZrMe₂ (rac-Bp = [Me₂Si(-2-Me₃Si-4'-Bu-η⁵-C₅H₂)₂]²⁻) are exposed to H₂ gas, (rac-Bp)ZrH₂ forms. Exposure of the dihydride to N₂ gas yields [(rac-Bp)Zr]₂(µ-η²:η²-N₂) with loss of H₂ (Scheme 3.2). Again, a group 4 organometallic complex has activated N₂ without the use of harsh reductants. The N–N bond length of 1.241(3) Å suggests a diazenide, or N₂²⁻, unit is present in the complex.

Scheme 3.2.

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The preceding examples illustrate a rare, but appealing method of synthesizing early transition-metal N₂ complexes: the addition of N₂ to a metal hydride. The reverse reaction,
however, is well known; some early transition-metal complexes react with H₂ to liberate N₂, even if the N–N bond is activated in the starting complex. The addition of H₂ to [Cp₂Zr(η¹⁻N₂)]₂(μ-η¹⁻N₂) gives Cp₂ZrH₂, which cannot be induced to coordinate N₂.²⁷ It should be noted that there are many reports of late transition-metal N₂ complexes synthesized by the elimination of H₂ from a metal hydride, but N₂ is only weakly activated in the products.²⁸

The use of H₂ in the synthesis of N₂ complexes has two main advantages: it can be readily added to a reaction mixture under a variety of conditions, and it is compatible with a range of reagents that functionalize coordinated N₂, such as silanes, boranes, alanes, and some organic electrophiles. The use of hydrogen as a reductant may someday facilitate the development of catalytic N–E bond-forming reactions. The incompatibility of reductants and electrophiles has been overcome recently in a different manner under carefully designed experimental conditions.²⁹ Eight equivalents of ammonia are obtained from N₂ in the presence of a bulky Mo catalyst, a weak organic acid ([2,6-Me₂C₅H₅NH][3,5-(CF₃)₂C₆H₃]₄B], and a relatively mild reducing agent (Cp₄Cr). In this system, the electrophile and reducing agent do not react with each other to give H₂. The choice of electrophile, reductant, and solvent (heptane), and the use of an automated syringe pump proved crucial in this regard.

To determine if group 4 organometallic complexes with the [NPN]⁺ ancillary ligand react with H₂ to give metal hydride complexes, the M(IV) dialkyl complexes, [NPN]⁺MR₂ (M = Zr, Hf; R = Me, CH₂Ph, CH₂SiMe₃), have been prepared and characterized. The reactivity of [NPN]⁺MMe₂ with H₂ gas, as well as the thermal decomposition of the Zr complexes are described in this chapter.
3.2 Results and Discussion.

3.2.1 Synthesis of [NPN]*MMe₂ (M = Zr, Hf).

[NPN]*ZrMe₂, 3.1, can be prepared as a light- and heat-sensitive hexanes-soluble yellow powder in high yield from [NPN]*ZrCl₂ (2.10) and 2.2 equivalents of MeMgCl in Et₂O (Equation 3.1). There is a singlet at δ -14.1 in the ³¹P{¹H} NMR spectrum of 3.1 in C₆D₆. By ¹H and ¹³C{¹H} NMR spectroscopy, there are four distinct ArCH₃ groups, which is suggestive of a Cₙ symmetric complex, and the peaks in the aromatic regions of both spectra are also consistent with the proposed structure. In the ¹H NMR spectrum (Figure 3.1), the doublet at δ 0.93 (2JHP = 5 Hz) is assigned to one Zr–CH₃ group (Me₆), and the singlet at δ -0.11 is assigned to the second Zr–CH₃ group (Me₅). Me₆ and Me₅ do not interconvert on the NMR timescale. By HMQC spectroscopy, Me₆ is assigned to a doublet at δ 45.1 (2JCₚ = 6 Hz), and Me₅ is assigned to a doublet at δ 41.8 (2JCₚ = 29 Hz) in the ¹³C{¹H} NMR spectrum. Unfortunately, NOE difference spectroscopy could not distinguish whether Me₆ or Me₅ is trans to P.
Figure 3.1. 300 MHz $^1$H NMR spectrum of 3.1 in C$_6$D$_6$.

The NMR spectra of 3.1 resemble those of methylzirconium complexes of another diamidophosphine ligand. In the $^1$H NMR spectrum of [Ar$_2$NPN]ZrMe$_2$ ([Ar$_2$NPN] = [(2,6-Me$_2$C$_6$H$_3$NSiMe$_2$CH$_2$)$_2$PPh]) there are two doublets due to the Zr—CH$_3$ groups at $\delta$ 0.88 ($^3$J$_{HP}$ = 6.6 Hz) and $\delta$ −0.24 ($^3$J$_{HP}$ = 1.5 Hz). The $^{13}$C($^1$H) NMR spectrum also has two doublets for the Zr—CH$_3$ groups at $\delta$ 46.4 ($^2$J$_{CP}$ = 30.1 Hz) and 45.0 ($^2$J$_{CP}$ = 6.2 Hz). The Zr—CH$_3$ groups in [Ar$_2$NPN]ZrMe$_2$ were assigned as cis ($^1$H: $\delta$ 0.88, $J_{HP}$ = 6.6 Hz; $^{13}$C: $\delta$ 45.0, $J_{CP}$ = 6.2 Hz) and trans ($^1$H: $\delta$ −0.24, $J_{HP}$ = 1.5 Hz; $^{13}$C: $\delta$ 46.4, $J_{CP}$ = 30.1) to phosphorus. Schrock et al. illuminated the solution- and solid-state structures of alkylzirconium complexes further by preparing monosubstituted [Ar$_2$NPN]ZrMe(Cl). The solid-state molecular structure shows that the Me group is equatorial (cis to P), whereas the Cl substituent is apical and trans to P. The Zr—CH$_3$ group gives rise to a doublet at $\delta$ 0.54 ($^3$J$_{HP}$ = 8.8 Hz) in the $^1$H
NMR spectrum of the complex. Although at first glance the apparent mismatch in the magnitude of $J_{CP}$ and $J_{HP}$ for two methyl substituents coordinated to Zr on $\text{[Ar}_2\text{NPN]}\text{ZrMe}_2$ may seem unusual, it is not inconsistent with the Karplus relationship. In particular, the sign and magnitude of heteronuclear coupling constants in some organometallic complexes have been rationalized in terms of torsion angles and stereochemistry at the metal centre.\(^{32}\)

Complex 3.1 decomposes in $\text{C}_6\text{D}_6$ solution over several days to give a red-brown solution that shows several peaks in its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. If a solution of 3.1 is stored at 298 K in a sealed J. Young NMR tube, a singlet attributable to methane is observed by $^1\text{H}$ NMR spectroscopy.\(^{33}\) Although small crystals of 3.1 grow in pentane in the dark at $-35^\circ\text{C}$, rapid desolvation and decomposition prevent them from being analyzed by X-ray diffraction. Since Hf alkyl complexes are often less thermally sensitive than their Zr congeners,\(^{34}\) the preparation of $\text{[NPN]}^*\text{HfMe}_2$ has been undertaken.

$\text{[NPN]}^*\text{HfMe}_2$, 3.2, can be prepared as a pale yellow powder in high yield from 2.15 and 2.2 equivalents of MeMgCl in Et$_2$O (see Equation 3.1). The $^{31}\text{P}\{^1\text{H}\}$, $^1\text{H}$ and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra are very similar to those observed for 3.1, and are consistent with a complex that is a $C_1$ symmetric monomer in solution with two inequivalent Hf–CH$_3$ groups that do not interconvert on the NMR timescale. The $^1\text{H}$ NMR spectrum of 3.2 in $\text{C}_6\text{D}_6$ displays two Hf–CH$_3$ resonances: a doublet at $\delta$ 0.67 ($^3J_{HP} = 5$ Hz) (Me$_A$), and a singlet at $\delta$ –0.21 (Me$_B$).

By $^{13}\text{C}\{^1\text{H}\}$ NMR and HMQC spectroscopy, 3.2 has two doublets: Me$_A$ is at $\delta$ 55.1 ($^2J_{CP} = 8$ Hz), and Me$_B$ is at 54.8 ($^2J_{CP} = 24$ Hz). Again NOE difference spectroscopy is unable to establish whether Me$_A$ is cis or trans to P. Although it is likely that Me$_A$ is cis to P, and Me$_B$ is trans to P in 3.1 and 3.2,\(^{30}\) it may be necessary to characterize 3.1 and 3.2 further, or to prepare complexes such as $\text{[NPN]}^*\text{MMe(Cl)}$, to obtain additional support for this assignment.
The ORTEP representation of the solid-state molecular structure of 3.2 is shown in Figure 3.2. The five-coordinate complex is distorted trigonal bipyramidal at Hf, and the Me groups are axial and equatorial. The Hf–C (C39, C40) bond lengths to methyl groups cis and trans to P are the same, within error, at ~2.22 Å. Again, the [NPN]⁺ ligand appears to hinge the amide donors out of the equatorial plane with P–Hf–N1 and P–Hf–N2 angles of 70.10(12)° and 72.09(13)°, respectively. The Hf–N, Hf–P, Hf–C bond lengths are similar to others reported in the literature.35

Figure 3.2. ORTEP drawing of the solid-state molecular structure of [NPN]⁺HfMe₂ 3.2 (ellipsoids drawn at the 50% probability level). All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Hf1–P1 2.7861(14), Hf1–N1 2.092(4), Hf1–N2 2.075(4), Hf1–C39 2.211(6), Hf1–C40 2.232(6), P1–Hf1–N1 70.10(12), P1–Hf1–N2 72.09(13), P1–Hf1–C39 86.79(19), P1–Hf1–C40 178.01(18), N1–Hf1–N2 116.35(17), C39–Hf1–C40 95.2(3).
3.2.2 Synthesis and reactivity of [NPN]*M(CH\(_2\)Ph)\(_2\).

[NPN]*Zr(CH\(_3\)C\(_6\)H\(_5\))\(_2\), 3.3, can be prepared from [NPN]*ZrCl\(_2\) (2.10) and 2.2 equivalents of C\(_6\)H\(_5\)CH\(_2\)MgCl in Et\(_2\)O, and is isolated as a heat- and light-sensitive yellow powder in high yield (Scheme 3.3). When [NPN]*H\(_2\) (2.8) and Zr(CH\(_2\)Ph)\(_4\)\(_36\) are mixed together in C\(_6\)D\(_6\) solution, no new signals appear in the \(^{31}\)P\{'H\} NMR spectrum. Thus, this route to benzylzirconium complexes cannot be used as an alternative to the Grignard reaction described above.\(^{37}\)

Scheme 3.3.

The \(^{31}\)P\{'H\} NMR spectrum of 3.3 in C\(_6\)D\(_6\) shows a singlet at \(\delta = -7.2\). The \(^1\)H NMR spectrum is consistent with the assignment of 3.3 as a five-coordinate C\(_5\) symmetric complex in solution. Once again, restricted rotation about N–C\(_\text{ar}\) gives rise to four inequivalent ArCH\(_3\) groups, but singlets due to two of the four ArCH\(_3\) groups overlap. There are two different benzyl groups that do not exchange on the NMR timescale. The benzylic protons appear as a doublet (\(\delta 2.92, J_{\text{HP}} = 9\) Hz), assigned to CH\(_{\text{ar}(A)}\), and a singlet (\(\delta 1.81\)), assigned to CH\(_{\text{ar}(B)}\), in the \(^1\)H NMR spectrum. By HMQC spectroscopy, CH\(_{\text{ar}(B)}\) appears as a singlet (\(\delta 74.6\)) and CH\(_{\text{ar}(A)}\) appears as a doublet (\(\delta 73.0, J_{\text{CP}} = 22\) Hz) in the \(^{13}\)C\{'H\} NMR spectrum.
Although 3.3 has not been characterized in the solid state, crystals of a derivative of this complex suitable for X-ray diffraction were obtained from C₆D₆ solutions of 3.3 at room temperature over one week. This derivative can also be prepared on a preparative scale when a toluene solution of 3.3 is stirred in the dark at ambient temperature for two days (see Scheme 3.3). The red-orange product, 3.4, displays a singlet at δ -5.2 in the $^{31}$P{¹H} NMR spectrum acquired in C₆D₆. The absence of C₄ symmetry in the product is apparent in its ¹H NMR spectrum.

The ¹H and $^{13}$C{¹H} NMR spectra of 3.4 in C₆D₆ are consistent with the formulation of the complex as a C₄ symmetric monomer with one CH₂Ph ligand and a cyclometalated [NPN]*. There are two doublets, each integrating to 1H, at δ 2.28 ($J_{HH} = 7$ Hz) and 1.75 ($J_{HH} = 7$ Hz) in the ¹H NMR spectrum (Figure 3.3). These resonances are assigned to diastereotopic benzylic protons. The doublet at δ 2.28 overlaps with two ArCH₃ singlets and can be located using ¹H-¹H COSY. A second set of diastereotopic benzylic resonances is observed: a doublet of doublets integrating to 1H at δ 2.70 ($J_{HH} = 9$ Hz, $J_{HP} = 1$ Hz) and a broad doublet integrating to 1H at δ 1.85 ($J_{HH} = 9$ Hz). These signals are assigned to the Zr(-2-CH₂-4,6-Me₂C₆H₂N) protons of the ortho-methyl metalated [NPN]* ligand. The observation of seven ArCH₃ singlets in the ¹H and $^{13}$C{¹H} NMR spectra, and two benzylic CH₂ resonances in the $^{13}$C{¹H} NMR spectrum supports the proposed structure for 3.4. The ortho-methyl metalated [NPN]* ligand will be denoted [NPNC]* because it coordinates to N, P, N, and C atoms on [NPN]* ([NPNC]* = [(2-MesN-5-MeC₆H₂)P(Ph)(2-(N-C₆H₂-2,4-CH₃-6-CH₂)-5-MeC₆H₂)]³). The proposed structure of 3.4, [NPNC]*Zr(CH₂Ph), has been confirmed by single-crystal X-ray diffraction analysis.
Figure 3.3. 400 MHz $^1$H NMR spectrum of 3.4 in C$_6$D$_6$.

The ORTEP representation of the solid-state molecular structure of 3.4 is shown in Figure 3.4. Complex 3.4 features one $\eta^2$-CH$_2$Ph substituent bound to Zr with a Zr–C$_{39}$–C$_{40}$ angle of 85.74(11)$^\circ$. This compares well to other $\eta^2$-benzyl Zr complexes that have Zr–C–C angles in the range of 85 to 100$^\circ$. The Zr–C bond lengths and interatomic distances are also typical: the Zr–C$_{39}$ bond length is 2.3027(19) Å, and there is a distance of 2.6346(17) Å between Zr and C$_{40}$. The C$_{39}$–C$_{40}$ bond is 1.462(3) Å. In addition, the Zr–C$_{41}$, Zr–C$_{45}$ distances (Zr–C$_{41}$ and Zr–C$_{45}$), at 2.96 and 3.48 Å, respectively, are too long to be considered bonding interactions. The two Zr–C bond lengths differ because the benzyl ligand is tilted to one side of the complex; the non-cyclometalated MesN substituent of [NPN]$^+$ is effectively blocking the other side of 3.4. The C$_{40}$–C$_{41}$ and C$_{40}$–C$_{45}$ bond lengths (1.410(3), 1.424(3) Å) that are slightly longer than the remaining four C–C bond lengths in the phenyl ring, and the similarity of these four remaining C–C bond lengths to
each other, are all consistent with $\eta^2$-coordination of the benzyl ligand to Zr. One (2-CH$_2$-4,6-Me$_2$C$_6$H$_2$N) group is coordinated through N2 and C38 to Zr with bond lengths of 2.1230(14) and 2.2807(19) Å, respectively. The Zr–C38–C35 angle is 93.34(11)$^\circ$. The geometry at Zr is best described as distorted square pyramidal with C39 apical and P1, N1, N2, and C38 basal. It appears that complex 3.3 has lost one equivalent of toluene to yield 3.4. The mechanism of toluene elimination is discussed in the following section.

**Figure 3.4.** ORTEP drawing of the solid-state molecular structure of [NPNC]$^+$Zr($\eta^2$-CH$_2$Ph) (3.4) (ellipsoids drawn at the 50% probability level). Hydrogen atoms and carbon atoms of the distal Mes substituent (except C$_{\phi}$) have been omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Zr1–P1 2.7646(5), Zr1–N1 2.1132(14), Zr1–N2 2.1230(14), Zr1–C38 2.2807(19), Zr1–C39 2.3027(19), Zr1–C40 2.6346(17), C39–C40 1.462(3), P1–Zr1–N1 71.65(4), P1–Zr1–N2 70.21(4), P1–Zr1–C39 133.09(5), Zr1–C39–C40 85.74(11), Zr1–C38–C35 93.34(11), N1–Zr1–N2 127.13(5).
To characterize dibenzyl complexes of group 4 in the solid state, the Hf analogue of 3.3 has been prepared. As with 3.1 and 3.2, the Hf dibenzyl complex is more heat- and light-stable than 3.3, and could be characterized crystallographically. \([\text{NPN}^*\text{Hf(CH}_2\text{C}_6\text{H}_2)_2, \, 3.5\], is prepared from 2.15 and 2.2 equivalents of \(\text{C}_6\text{H}_5\text{CH}_2\text{MgCl}\) in \(\text{Et}_2\text{O}\), and is isolated as a pale yellow powder in quantitative yield (Equation 3.2). In \(\text{C}_6\text{D}_6\) solution, the benzylic resonances appear as doublets at \(\delta 2.59 \, (\hat{J}_{\text{HP}} = 7.6 \, \text{Hz})\) and 1.59 \(\, (\hat{J}_{\text{HP}} = 2 \, \text{Hz})\) (Figure 3.5) in the \(^1\text{H}\) NMR spectrum. In the \(^{13}\text{C}\{^1\text{H}\}\) NMR spectrum, the two \(\text{CH}_2\text{Ph}\) resonances appear as doublets at \(\delta 72.3 \, (\hat{J}_{\text{CP}} = 6 \, \text{Hz})\) and 66.0 \(\, (\hat{J}_{\text{CP}} = 20 \, \text{Hz})\). Thus, the structure of 3.5 in solution is proposed to be five-coordinate and \(\text{C}_s\) symmetric with two distinct \(\text{CH}_2\text{Ph}\) substituents, one trans and one cis to \(\text{P}\).
Figure 3.5. 500 MHz $^1$H NMR spectrum of 3.5 in C$_6$D$_6$.

The ORTEP representation of the solid-state molecular structure of 3.5 is shown in Figure 3.6. The complex is distorted trigonal bipyramidal at Hf, and has typical Hf–P and Hf–N bond lengths. In the equatorial plane, the Hf–C39 bond length is 2.263(3) Å, and the Hf–C39–C40 bond angle is 120.32(18)°. For the axial benzyl ligand trans to P, the Hf–C46 bond is 2.298(3) Å, slightly longer than for Hf–C39, and the Hf1–C46–C47 angle is 118.74(18)°. The solid-state molecular structure is consistent with the solution data in that it shows two distinct $\eta^1$-CH$_2$Ph groups coordinated to Hf.
Figure 3.6. ORTEP drawing of the solid-state molecular structure of \([\text{NPN}]^+\text{Hf}(\eta^1-\text{CH}_2\text{Ph})_2\), 3.5 (ellipsoids drawn at the 50% probability level). Hydrogen atoms and carbon atoms of the proximal \text{Mes} (except \text{C}_{\text{ph}}) have been omitted for clarity. Selected bond lengths (Å) and angles (°): Hf1–P1 2.8228(7), Hf1–N1 2.079(2), Hf1–N2 2.1250(19), Hf1–C39 2.263(3), Hf1–C46 2.298(3), C39–C40 1.495(4), C46–C47 1.514(4), N1–C1 1.462(3), P1–Hf1–N1 69.96(6), P1–Hf1–N2 71.12(5), P1–Hf1–C39 87.78(7), P1–Hf1–C46 175.67(8), N1–Hf1–N2 115.36(8), C39–Hf1–C46 96.49(10), Hf1–C39–C40 120.32(18)°, Hf1–C46–C47 118.74(18)°.

Benzyl ligands are known to coordinate to metals in the $\eta^1$, $\eta^2$, or $\eta^3$-bonding mode. The $\eta^1$-bonding mode is $sp^3$ hybridized at the benzylic C, and the M–C$_\alpha$–C$_{\text{ph}}$ angle is close to the 109.5° predicted for tetrahedral C. A good example of the $\eta^1$-bonding mode of benzyl is Sn(CH$_2$Ph)$_4$. The Sn–C$_\alpha$–C$_{\text{ph}}$ angles in tetrabenzyl tin are all nearly 111° (110, 110, 112
and 114°), and the bonding is analogous to a simple organic compound without any unusual intra- or intermolecular interactions. If there is an interaction between M and C_{\phi\psi} of CH_{2}Ph, then the \( \eta^2 \)-coordination mode may be present. For the \( \eta^2 \)-bonding mode, M–C_{\alpha}–C_{\phi\psi} angles of about 90°, and a shortened M–C_{\phi\psi} distance are typically observed, although a range of bond lengths and angles has been reported. For example, the solid-state molecular structure of \([N_2P]Zr(CH_3)(CH_2Ph)\) (\([N_2P] = [[(Me_3SiNCH_2CH_2)PPh_2]_2\) determined by X-ray crystallography indicates that an \( \eta^2 \)-CH_{2}Ph group is present with a Zr–C_{\alpha}–C_{\phi\psi} angle of 95.4(2)° and a Zr–C_{\phi\psi} distance of 2.835(4) Å. In comparison, Hf(CH_{2}Ph)_{4} has at least three \( \eta^2 \)-benzyl groups, and the Hf–C_{\alpha}–C_{\phi\psi} angles are 88, 92, 93, and 101°. Thus, there is some variety in the degree of \( \eta^2 \)-bonding observed for the benzyl ligand. Although other bonding modes have been proposed for transition-metal bound benzyl ligands, they are not usually cited in discussions of group 4 benzyl complexes.

In 3.5, the Hf–C_{\alpha}–C_{\phi\psi} angles (120.32(18)° and 118.74(18)°) are larger than those observed for Hf(CH_{2}Ph)_{4} in the solid state. The Hf–C_{\alpha}–C_{\phi\psi} angles are also larger than would be predicted for an sp^{3} hybridized C_{\alpha} of \( \eta^1 \)-benzyl, although a range of angles has also been reported for the \( \eta^1 \)-bonding mode. For example, in \([Cp^*Cr(CH_2Ph)(\mu-Cl)]_2\) (M–C_{\alpha}–C_{\phi\psi} 121.4(3)°), and in \( C_{p^*}Cr(CH_2Ph)_2(Py)\) (M–C_{\alpha}–C_{\phi\psi} 124.0(6)°, M–C_{\alpha}–C_{\phi\psi} 119.5(5)°), the large M–C_{\alpha}–C_{\phi\psi} angles may be explained by the steric influence of the bulky Cp^{*} ligand. One benzyl ligand in the complex \([O_2NN'Me]Zr(CH_2Ph)_2\) \([O_2NN'Me] = [[(2-C_5H_4N)CH_2N(CH_2-2-O-3,5-C_6H_2Me_2)_2]^2\) also features a large M–C_{\alpha}–C_{\phi\psi} angle (118.9(2)°). Although the bis(aminophenolate) ligand is not very bulky, the coordination sphere of the octahedral complex is quite crowded. Thus, the Hf–C_{\alpha}–C_{\phi\psi} angles observed in 3.5 are within the range of literature values for \( \eta^1 \)-benzyl complexes, and may be slightly larger than
111° (found for Sn(CH₂Ph)₄) because of the steric influence of the bulky mesitylamido substituents on [NPN]⁺ or because of crystal packing.

3.2.3 Kinetics of [NPN]⁺Zr(CH₂Ph)₂ decomposition.

The formation of red-orange [NPNC]⁺Zr(η²-CH₂Ph) (3.4) and one equivalent of toluene from yellow [NPN]⁺Zr(CH₂Ph)₂ (3.3) in C₆D₆ solution occurs over about two days with no detectable intermediates (see Scheme 3.3). The reverse of this reaction, formation of 3.3 from 3.4 in the presence of excess toluene is not observed. By monitoring the decomposition of three samples with different concentrations (25.9, 41.4, and 56.9 ± 2 mM) at 298 K over two days by NMR spectroscopy, the reaction was determined to be first order in 3.3. The decomposition of five 43.1 ± 0.8 mM concentration samples in toluene-d₈ has been followed by ¹H NMR spectroscopy at 328 K, 338 K, 348 K or 358 K in a pre-heated NMR probe, or at 298 K by periodically acquiring a ¹H NMR spectrum. The combination of integrals used to calculate the fraction of 3.3 is outlined in appendix two, as is a sample plot of ln[3.3] vs. time (at 338 K) used to determine k₀bh, and a discussion of the estimation of errors. The Eyring plot of ln(k/₁) vs. 1/₁ is shown in Figure 3.7. From the Eyring plot, the activation parameters for the reaction are ΔH° = 20.8 ± 0.4 kcal mol⁻¹, and ΔS° = −10.3 ± 1.3 cal K⁻¹ mol⁻¹. The negative value for the entropy of activation is consistent with the formation of an ordered transition state for the intramolecular reaction.
Figure 3.7. Eyring plot for the thermal decomposition of \([\text{NPN}^*\text{Zr(CH}_2\text{Ph)}]_2\), 3.3.

Two possible mechanisms for the decomposition of 3.3 are illustrated in Scheme 3.4.\textsuperscript{47} In Path A, direct \(\sigma\)-bond metathesis via a four-centre–four-electron transition state allows concerted bond forming (C–H of toluene, and Zr–C to [NPNC]\textsuperscript{*}) and breaking (C–H of NMes, and Zr–C of CH\textsubscript{2}Ph) to yield 3.4. The second benzyl ligand is not directly involved in Path A. In Path B, toluene is lost via intramolecular \(\alpha\)-H abstraction from one Zr–CH\textsubscript{2}Ph group to give [NPN]\textsuperscript{*}Zr=CHPh, a benzylidene intermediate. [NPN]\textsuperscript{*}Zr=CHPh accepts a proton from the ortho-CH\textsubscript{3} group on NMes to give cyclometalated 3.4.
There are several examples of transition-metal benzyl complexes that form cyclometalated products with loss of toluene. The decomposition may go through a benzylic intermediate, whereas in other cases a σ-bond metathesis mechanism is invoked. Sigma-bond metathesis is usually accompanied by a negative entropy of activation ($\Delta S^\dagger = -10$ to $-24$ cal mol$^{-1}$ K$^{-1}$), since the ancillary ligand and benzyl ligand have to adopt an ordered geometry in the transition state for bond making and breaking to
occur. Of course, ligand cyclometalation reactions are also known for complexes without benzyl substituents. If C–H activation occurs via a benzylidene or alkylidene intermediate, the entropy of activation is usually near zero, typical for α-hydrogen abstraction processes.

It should be noted, however, that there are many exceptions to this pattern. For example, \([\text{NPYCH}_2\text{Ph}] (\text{NP} = \text{[N(SiMe}_2\text{CH}_2\text{PMe}_2])}) produces cyclometalated \([\text{NPY}]^+ (\text{NP} = \text{[Me}_2\text{PCH}_2\text{SiMe}_2\text{NSiMe}_2\text{(CH)}\text{PMe}_2])^2\) and toluene via σ-bond metathesis since the formation of an alkylidene to C in the backbone of \([\text{NP}]\) is unlikely. The \(\Delta S^\ddagger\) for the reaction is \(-3 \pm 3\) cal mol\(^{-1}\) K\(^{-1}\), which is atypically close to zero for a reaction that proceeds via σ-bond metathesis. The authors speculate that dissociation of a phosphine donor of \([\text{NP}]\) from the metal centre in the transition state might offset the negative entropy of activation expected for this process.

The negative entropy of activation for the decomposition of 3.3 is consistent with the reaction occurring via σ-bond metathesis (Path A). To test this proposed mechanism, an isotopic labelling experiment has been performed. Complex 3.3 with perdeuterated benzyl groups can be prepared by the reaction of 2.2 equivalents of KCD\(_2\)C\(_6\)D\(_5\) and 2.10 in Et\(_2\)O. When \([\text{NP}]^+\text{Zr(}\text{CD}_2\text{C}_6\text{D}_5)\)\(_2\), 3.3-\(\text{d}_{10}\) is dissolved in C\(_6\)D\(_8\), transferred to an NMR tube, and heated at 55 °C for 3 h, a clear red-orange solution is observed. Toluene-\(d_7\) (C\(_4\)D\(_6\)CD\(_2\)H) gives rise to a quintet at δ 2.09 in the \(^1\)H NMR spectrum, which is consistent with the decomposition of 3.3-\(\text{d}_{14}\) occurring by Path A, since the \(^1\)H is transferred directly from NMe\(_3\) to the leaving toluene. In addition, there is no evidence for \([\text{NPNC}]^+\text{Zr(}\text{H}_2\text{-CHD(C}_6\text{D}_5)\)\(_2\)), or 3.4-\(\text{d}_{10}\) in the \(^1\)H NMR spectrum of the product. Thus, the presence of a perdeuterated \(\eta^2\)-benzyl on 3.4-\(\text{d}_7\) is confirmed. If decomposition of 3.3-\(\text{d}_{14}\) occurs by Path B, then 3.4-\(\text{d}_6\) would be the expected product because of \(^1\)H transfer from MesN to
Zr=C(D)Ph. A fraction of the reaction mixture can be separated from the solvent by GC, and the highest molecular weight peak of this fraction is at \( m/z = 99 \) in the mass spectrum. Thus, the results of GC-MS are consistent with the presence of toluene-\( d_7 \). The decomposition of 3.3-\( d_{14} \) to 3.4-\( d_7 \) and toluene-\( d_7 \) lends further support to the \( \sigma \)-bond metathesis mechanism proposed for this reaction.

### 3.2.4 Synthesis and reactivity of [NPN]\(^*\)M(CH\(_2\)SiMe\(_3\))\(_2\).

The decomposition of [NPN]\(^*\)ZrMe\(_2\) yields a mixture of products that includes methane, as determined by \(^1\)H NMR spectroscopy. Similarly, the evolution of toluene is observed by \(^1\)H NMR spectroscopy when 3.3 decomposes in C\(_6\)D\(_6\) solution. To determine if the cyclometalated [NPNC]\(^*\) ligand can form via elimination of other alkanes from [NPN]\(^*\)ZrR\(_2\), pale yellow [NPN]\(^*\)Zr(CH\(_2\)SiMe\(_3\))\(_2\), 3.6, has been prepared and characterized. Complex 3.6 can be prepared in high yield from 2.10 and 2.2 equivalents of LiCH\(_2\)SiMe\(_3\) in Et\(_2\)O (Scheme 3.5). The \(^1\)H NMR spectrum of C\(_6\) symmetric 3.6 in C\(_6\)D\(_6\) features resonances assigned to two distinct CH\(_2\)SiMe\(_3\) groups: a doublet at \( \delta \) 1.39 (\( J_{CH} = 7 \) Hz) and a singlet at \( \delta \) 0.04, and singlets due to two Si(CH\(_3\))\(_3\) groups at \( \delta \) 0.10 and -0.08, as well as the expected ArH and ArCH\(_3\) resonances. The \(^{31}\)P{\(^1\)H} NMR spectrum of 3.6 shows a singlet at \( \delta \) -15.3. The \(^1\)H NMR spectrum compares well to other Zr–CH\(_2\)SiMe\(_3\) complexes.\(^{54}\)
Upon stirring a toluene solution of 3.6 at ambient temperature in the dark for three
days, a yellow to red-orange colour change occurs. Red-orange 3.7 is obtained in high yield
(see Scheme 3.5). The singlet observed in the $^{31}$P{$^1$H} NMR spectrum of 3.6 shifts to $\delta$ -8.5
for 3.7, and the $^1$H NMR spectrum is indicative of a loss of $C_4$ symmetry in the complex. In
particular, the $^1$H NMR spectrum features seven ArCH$_3$ singlets and one singlet integrating
to 9H at $\delta$ -0.32 attributable to Si(CH$_3$)$_3$. Four diastereotopic CH$_2$ resonances are also
observed. By analogy with the assignment of 3.4, 3.7 contains the cyclometalated [NPNC]$^*$
ligand. Assigned to the Mes–CH$_2$–Zr group are a doublet at $\delta$ 2.36 ($^{1}J_{HH} = 11.8$ Hz) and a
doublet of doublets at $\delta$ 1.56 ($^{1}J_{HH} = 11.8$ Hz, $^{3}J_{HP} = 4$ Hz), each integrating to 1H. Assigned
to the Me$_3$Si–CH$_2$–Zr group are two doublets at $\delta$ 0.56 and -0.13, each integrating to 1H with $^{1}J_{HH} = 11.4$ Hz. In the $^{13}$C{$^1$H} NMR spectrum, the two CH$_2$ groups appear as a singlet
at $\delta$ 65.6 and a doublet at $\delta$ 64.1 ($^{2}J_{CP} = 8$ Hz). In addition to the expected ArC and ArCH$_3$
resonances, a singlet at $\delta$ 2.38 due to Si(CH$_3$)$_3$ is observed in the $^{13}$C{$^1$H} NMR spectrum.

The ORTEP representation of the solid-state molecular structure of 3.7 is shown in
Figure 3.8, and it bears a strong resemblance to [NPNC]$^*$Zr($\eta^2$-CH$_2$Ph) (3.4). The $C_4$
symmetric structure of 3.7 features the cyclometalated [NPNC]$^*$ ligand and one CH$_2$SiMe$_3$
ligand bound to Zr. The geometry about Zr is distorted square pyramidal. The Zr–N, Zr–P,
and Zr–C bond lengths are similar to those in 3.4, although the Zr–C39 (2.218(2) Å) bond is slightly shorter in 3.7 (Zr–C39 is about 2.30 Å in 3.4). The Zr–C39–Si angle is 124.7(1)°. The Zr–C bond and the Zr–C–Si angle are similar to those observed for other group 4 trimethylsilylmethyl complexes. The P–Zr–N angles are also both acute at about 70°, as is observed for the other [NPN]*Zr complexes reported here.

As expected, tetramethylsilane forms in C₆D₆ solutions of 3.6 over several days at room temperature. Also, the formation of 3.7 from 3.6 appears to proceed without intermediates by ³¹P{'H} NMR spectroscopy. The decomposition of [NPN]*ZrR₂ to [NPNC]*ZrR may be a general mode of decomposition for these complexes, provided R does not contain β-hydrogens. An investigation into the mechanism of formation of 3.6 has not been performed.
Figure 3.8. ORTEP drawing of the solid-state molecular structure of 

\([\text{NPNC}]^+\text{Zr(CH}_2\text{SiMe}_3)\), 3.7, (ellipsoids drawn at the 50% probability level). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Zr1–P1 2.7349(5), Zr1–N1 2.1237(15), Zr1–N2 2.1022(15), Zr1–C36 2.270(2), Zr1–C39 2.218(2), C39–Si1 1.864(2), C35–C36 1.487(3), P1–Zr1–N1 71.77(4), P1–Zr1–N2 69.19(4), P1–Zr1–C39 118.37(6), P1–Zr1–C36 127.41(6), N1–Zr1–N2 131.71(6), Zr1–C39–Si1 124.79(11), Zr1–C36–C35 92.05(13).

\([\text{NPN}]^+\text{Hf(CH}_2\text{SiMe}_3)\), 3.8, can be prepared from 2.15 and 2.2 equivalents of LiCH$_2$SiMe$_3$ in Et$_2$O, in the same fashion as 3.6 (Equation 3.3). $^1$H NMR spectroscopy of 3.8 in C$_6$D$_6$ indicates that the pale yellow complex has two Hf–CH$_2$SiMe$_3$ environments: a doublet at δ 0.80 ($J_{\text{HP}} = 6$ Hz), and a singlet at δ –0.30 are assigned to the Hf–CH$_2$TMS protons, and two singlets are assigned to two distinct Si(CH$_3$)$_3$ groups at δ 0.10 and –0.10. The $^{31}$P{$^1$H} and $^{13}$C{$^1$H} NMR spectra are also consistent with 3.8 being a five-coordinate C$_5$ symmetric complex with inequivalent CH$_2$SiMe$_3$ groups that do not exchange on the
NMR timescale. Although EI-MS was helpful in assigning the structure of 3.4, only peaks due to [NPN]*H₂ are seen in the mass spectra of 3.6, 3.7 and 3.8.

\[ \text{[NPN]*HfCl₂ (3.3)} \]

2.15

3.2.5 Attempted hydrogenolysis of [NPN]*MMe₂.

When C₆D₆ solutions of 3.2 are stored under 1 atm of H₂ in a sealed J. Young NMR tube for one month, there is no change in the colour of the solution, and no new signals appear in the ³¹P{¹H} or ¹H NMR spectra of the sample. When a toluene solution of 3.1 or 3.2 is stirred under 4 atm of H₂, the reaction mixture becomes brown immediately. However, the solution reverts to yellow after about 5 min., and no further colour changes are observed. There is also no reaction by ³¹P{¹H} or ¹H NMR spectroscopy, since the yellow product obtained upon work-up contains only peaks that can be attributed to starting material in its NMR spectra. The brown species has not been isolated or identified.

The reaction of an organometallic complex with hydrogen gas to liberate an alkane and yield a metal hydride is also called hydrogenolysis. The hydrogenolysis of late transition-metal alkyl complexes is exothermic since the bond dissociation enthalpy of M–H is greater than for M–C. The reaction of early transition-metal alkyl complexes with H₂ to yield metal hydrides is typically less exothermic, but can be spontaneous. In addition, the hydrogenolysis of late transition-metal alkyl complexes often occurs by oxidative addition, a route that is not invoked for Zr(IV) or Hf(IV) complexes. Instead, for early transition-metal
alkyl complexes, a σ-bond metathesis mechanism in which H₂ adds across the M—C bond via a four-centred transition state may be invoked. This is a preferable explanation for the reactivity of a Zr(IV) alkyl complex because it requires a vacant orbital on the metal centre, but does not require d electrons. If a Zr(IV) alkyl complex does not react with H₂, it may be because there is no readily accessible orbital for H₂ to interact with the metal. The inaccessibility itself may be due to electronic or steric factors, or a combination of the two. For example, the presence of π-donating ligands, or bulky ancillary ligands, may prevent H₂ from approaching the M—C bond.

The reaction of 3.2 with 4 atm of H₂ gas does not yield a metal hydride complex. In a related system, the hydrogenolysis of [P₂N₂]HfMe₂ ([P₂N₂] = [PhP(CH₂SiMe₂NSiMe₂CH₂)₂PPh]₂) yields ([P₂N₂]Hf)₂(μ-H)₄, while a zirconium hydride is not obtained from the reaction of [P₂N₂]ZrMe₂ with H₂. However, since Hf-N₂ complexes are rare, and have only been prepared from Hf diiodides in the presence of strong reducing agents, it is unlikely that one would be obtained from the reaction of a Hf hydride with N₂ gas. The formation of hydride complexes from 3.1 or 3.2 may be possible by a two-step route: the synthesis of complexes of the type {[NPN]*M(CH₃)}⁺ (M = Zr, Hf), followed by reaction with H₂ in the absence of coordinating solvents or counterions. Although the reactions of 3.3, 3.5, 3.6 or 3.8 with H₂ have not been attempted, the presence of benzyl or trimethylsilylmethyl ligands is not likely to increase the reactivity of the complex since the steric crowding at the metal centre should be even greater.

Although a Zr or Hf hydride complex has not been prepared by hydrogenolysis of 3.1 or 3.2, there are many other routes to early transition-metal hydrides that have not been attempted. Since the synthesis of metal-hydride precursors for N₂ activation from H₂ under mild conditions is a major goal outlined in this chapter, the use of metal hydride reagents
such as lithium aluminum hydride, or other strong reducing agents\textsuperscript{64} to obtain Zr or Hf hydrides holds limited appeal.

3.3 Conclusions.

Zr and Hf alkyl complexes with the [NPN]\textsuperscript{*} ancillary ligand are synthesized as yellow powders in high yield from [NPN]\textsuperscript{*}MCl\textsubscript{2} (M = Zr, Hf). By NMR spectroscopy, [NPN]\textsuperscript{*}MR\textsubscript{2} complexes (M = Zr, Hf; R = Me, CH\textsubscript{2}Ph, CH\textsubscript{2}SiMe\textsubscript{3}) are monomeric C\textsubscript{s} symmetric 5-coordinate species with two distinct alkyl groups that do not interconvert on the NMR timescale. In addition, the solid-state molecular structures of [NPN]\textsuperscript{*}HfMe\textsubscript{2} and [NPN]\textsuperscript{*}Hf(CH\textsubscript{2}Ph)\textsubscript{2} confirm the solution structures.

Whereas the Hf alkyl complexes are thermally stable and can be analyzed by X-ray diffraction, [NPN]\textsuperscript{*}ZrR\textsubscript{2} complexes decompose over several hours to give either a mixture of products (R = Me), or cyclometalated [NPNC]\textsuperscript{*}ZrR (R = CH\textsubscript{2}Ph, or CH\textsubscript{2}SiMe\textsubscript{3}) by C–H activation of the ancillary ligand. The two [NPNC]\textsuperscript{*}ZrR complexes have been characterized in solution and in the solid state as C\textsubscript{1} symmetric five-coordinate complexes. The decomposition of [NPN]\textsuperscript{*}Zr(CH\textsubscript{2}Ph)\textsubscript{2} to give [NPNC]\textsuperscript{*}Zr(\eta\textsuperscript{2}-CH\textsubscript{2}Ph) and toluene is first order in [NPN]\textsuperscript{*}Zr(CH\textsubscript{2}Ph)\textsubscript{2}, and occurs with $\Delta H^\ddagger = 20.8 \pm 0.4$ kcal mol\textsuperscript{-1}, and $\Delta S^\ddagger = -10.3 \pm 1.3$ cal K\textsuperscript{-1} mol\textsuperscript{-1}. The negative value for the entropy of activation, and the fact that decomposition of [NPN]\textsuperscript{*}Zr(CD\textsubscript{2}C\textsubscript{6}D\textsubscript{5})\textsubscript{2} yields toluene-d\textsubscript{7} and [NPNC]\textsuperscript{*}Zr(CD\textsubscript{2}C\textsubscript{6}D\textsubscript{5}) indicate that the reaction proceeds via $\sigma$-bond metathesis.

Hydrogenolysis of [NPN]\textsuperscript{*}MM\textsubscript{3} (M = Zr, Hf) does not yield hydride complexes under the conditions employed here. In the absence of a hydrogenolysis route to Zr-N\textsubscript{2} complexes, a more direct route to dinitrogen complexes from [NPN]\textsuperscript{*}ZrCl\textsubscript{2} (2.10) and alkali metal
reducing agents is described in chapter four. The synthesis, characterization, and reactivity of a Zr-N₂ complex are presented in chapters four and five.

3.4 Experimental.

3.4.1 General experimental.

Except where noted, experimental procedures follow those outlined in chapter two. GC-MS spectra were recorded on an Agilent series 6890 GC system with a 5973 mass selective detector.

3.4.2 Starting materials and reagents.

Hydrogen gas was purchased from Praxair and used as received. LiCH₂SiMe₃ was purchased from Aldrich as a 1M solution in pentane that was taken to dryness, and recrystallized from pentane prior to use. Deuterated benzyl potassium was prepared from toluene-d₄, freshly sublimed KO'Bu, and "BuLi in hexanes solution according to the literature.⁶⁵ All other compounds were purchased from commercial sources and were used as received.

\[[\text{NPN}]^*\text{ZrMe}_2 \text{ (3.1)}\]. To a stirred suspension of 2.10 (0.300 g, 0.419 mmol) in Et₂O (10 mL) at −35 °C in the dark was added methylmagnesium chloride (3.0 M in THF, 0.31 mL, 0.92 mmol) dropwise. The yellow suspension became translucent pale yellow as it warmed to rt, whereupon 1,4-dioxane (0.1 mL) was added. The reaction mixture was taken to dryness, and hexanes (10 mL) and toluene (5 mL) were added to the yellow solid. The yellow suspension was filtered through Celite, and the filtrate was taken to dryness to obtain a pale yellow
powder. The pale yellow powder was collected on a frit, washed with pentane (5 mL), dried under vacuum, and stored in the dark at —35 °C (0.225 g, 0.332 mmol, 80%).

$^1$H NMR (C$_6$D$_6$, 500 MHz): $\delta = 7.54$ (m, 4H), 7.07 (m, 2H), 7.02 (m, 1H), 6.93 (s, 2H), 6.90 (d, 2H, 2 Hz), 6.88 (s, 2H), and 6.12 (t, 2H, $J_{HP} = J_{HH} = 7$ Hz) (ArH), 2.51 (s, 6H), 2.14 (s, 6H), 2.09 (s, 6H), and 2.00 (s, 6H) (ArCH$_3$), 0.93 (d, 3H, $J_{HP} = 5$ Hz), and $-0.11$ (s, 3H) (ZrCH$_3$).

$^{31}$P{'H} NMR (C$_6$D$_6$, 202 MHz): $\delta = -14.1$ (s).

$^{13}$C{'H} NMR (C$_6$D$_6$, 126 MHz): $\delta = 159.4$ (d, 33 Hz), 139.4, 138.6, 137.5, 135.3 (d, 5 Hz), 135.1 (d, 3 Hz), 134.4, 132.1 (d, 13 Hz), 130.9, 130.4, 129.2 (d, 4 Hz), 129.1, 129.0, 128.3, 121.1 (d, 25 Hz), and 114.3 (d, 9 Hz) (ArC), 45.1 (d, 6 Hz), and 41.8 (d, 29 Hz) (ZrCH$_3$), 21.1, 20.3, 19.1, and 18.9 (ArCH$_3$).

Anal. Calcd. for C$_{45}$H$_{45}$N$_2$PZr: C, 71.07; H, 6.71; N, 4.14; Found: C, 71.35; H, 7.06; N, 4.08.

[NPN]*HfMe$_2$ (3.2). In the dark at −35 °C, MeMgCl (3.0 M in THF, 0.78 mL, 2.34 mmol) was added to a stirred suspension of 2.15 (0.840 g, 1.04 mmol) in Et$_2$O (10 mL). The mixture was translucent pale yellow after 30 min. at rt. 1,4-Dioxane (0.5 mL) was added to the reaction mixture and it was taken to dryness to obtain yellow solids that were extracted with hexanes (30 mL), followed by toluene (10 mL). The extracts were filtered through Celite, and the filtrate was taken to dryness to obtain a pale yellow powder (0.770 g, 1.01 mmol, 96%).

$^1$H NMR (C$_6$D$_6$, 500 MHz): $\delta = 7.53$ (m, 4H), 7.06 (m, 2H), 7.00 (t, 1H, 7 Hz), 6.93 (s, 2H), 6.91 (d, 2H, 7 Hz), 6.90 (s, 2H), and 6.15 (dd, 2H, $J_{HP} = 6$ Hz, $J_{HH} = 8$ Hz) (ArH), 2.52 (s, 6H), 2.19 (s, 6H), 2.14 (s, 6H), and 2.00 (s, 6H) (ArCH$_3$), 0.67 (d, 3H, $J_{HP} = 5$ Hz), and $-0.21$ (s, 3H) (HfCH$_3$).
$^{31}$P {$^1$H} NMR (C$_6$D$_6$, 202 MHz): $\delta = -8.9$ (s).

$^{13}$C {$^1$H} NMR (C$_6$D$_6$, 126 MHz): $\delta = 161.1$ (d, 32 Hz), 139.1, 137.6, 137.0 (d, 5 Hz), 136.7, 135.1, 134.8, 132.0 (d, 13 Hz), 130.8, 130.4, 129.1, 129.0, 128.3, 120.1, 119.9, and 115.4 (d, 10 Hz) (ArC), 55.1 (d, 8 Hz), and 54.8 (d, 24 Hz) (HfCH$_3$), 21.1, 20.2, 19.0, and 18.9 (ArCH$_3$).


Anal. Calcd. for C$_{45}$H$_{45}$N$_2$PHf: C, 62.94; H, 5.94; N, 3.67; Found: C, 62.83; H, 6.26; N, 4.00.

$[\text{NPNI}^*\text{Zr(CH}_2\text{Ph})_2]$ (3.3). To a stirred suspension of 2.10 (0.770 g, 1.07 mmol) in Et$_2$O (15 mL) at –35 °C in the dark was added benzylmagnesium chloride (1.0 M in Et$_2$O, 2.40 mL, 2.40 mmol) dropwise. The yellow suspension became translucent pale yellow as it warmed to rt, whereupon 1,4-dioxane (0.1 mL) was added. The reaction mixture was taken to dryness to obtain a yellow solid that was extracted with hexanes (10 mL) and toluene (5 mL). The extracts were filtered through Celite, and the filtrate was taken to dryness to obtain a yellow powder that was collected on a frit, washed with pentane (5 mL), dried under vacuum, and stored in the dark at –35 °C (0.795 g, 0.960 mmol, 89%).

$^1$H NMR (C$_6$D$_6$, 300 MHz): $\delta = 7.60$ (t, 2H, 8 Hz), 7.53 (d, 2H, 7 Hz), 7.07 (m, 5H), 6.95 (m, 4H), 6.80 (m, 6H), 6.36 (d, 2H, 7 Hz), 6.33 (d, 2H, 7 Hz), and 6.02 (dd, 2H, $J_{HH} = 5$ Hz, $J_{HP} = 8$ Hz) (ArH), 2.92 (d, 2H, $J_{HP} = 9$ Hz, ZrCH$_2$), 2.17 (s, 12H), 2.03 (s, 6H), and 1.96 (s, 6H) (ArCH$_3$), 1.81 (s, 2H, ZrCH$_2$).

$^{31}$P {$^1$H} NMR (C$_6$D$_6$, 121 MHz): $\delta = -7.2$ (s).

\[113\]
$^{13}$C $^1$H NMR (C$_6$D$_6$, 75 MHz): $\delta = 159.1$ (d, 31 Hz), 150.4, 146.0, 139.5, 138.9, 138.0, 136.2 (d, 4 Hz), 134.5, 134.3, 132.7, 132.6, 131.3, 131.1, 130.8, 130.4, 129.9 (d, 4 Hz), 129.3, 128.2, 127.2, 126.1, 122.0 (d, 5 Hz), 121.6, 120.6, and 114.3 (d, 9 Hz) (ArC), 74.6, and 73.0 (d, 22 Hz) (ZrCH$_2$), 21.1, 20.3, 19.0, and 18.5 (ArCH$_3$).

Anal. Calcd. for C$_{52}$H$_{53}$N$_2$PZr: C, 75.41; H, 6.45; N, 3.38; Found: C, 75.06; H, 6.65; N, 3.68.

$[\text{NPN}]^+\text{Zr}(\eta^1\text{-CD$_2$C$_6$D$_5$})_2$ (3.3–d$_{14}$). KCD$_2$C$_6$D$_5$ (62 mg, 0.45 mmol) suspended in Et$_2$O (3 mL) was added dropwise to a stirred suspension of 2.10 (0.145 g, 0.202 mmol) in Et$_2$O (5 mL) at $-35^\circ$C in the dark. The red-orange mixture was stirred at rt for 30 min., and 1,4-dioxane (0.1 mL) was added. The mixture was taken to dryness to obtain a yellow powder. The yellow powder was extracted with C$_6$D$_6$ (1.0 mL), and the yellow extracts were filtered through Celite into an NMR tube.

$^1$H NMR (C$_6$D$_6$, 400 MHz): $\delta = 7.60$ (t, 2H, 8 Hz), 7.53 (d, 2H, 7 Hz), 7.10 (m, 1H), 7.08 (d, 2H, 7 Hz), 6.96 (s, 2H), 6.82 (d, 2H, 8 Hz), 6.80 (s, 2H), and 6.02 (dd, 2H, $J_{HP} = 5$ Hz, $J_{HH} = 8$ Hz) (ArH), 2.17 (s, 12H), 2.03 (s, 6H), and 1.96 (s, 6H) (ArCH$_3$).

$^{31}$P $^1$H NMR (C$_6$D$_6$, 162 MHz): $\delta = -6.8$ (s).

$[\text{NPNC}]^+\text{Zr}(\eta^2\text{-CH$_2$Ph})$ (3.4). Compound 3.3 (0.450 g, 0.540 mmol) was dissolved in toluene (15 mL) and stirred in the dark at rt for 2 d to obtain a clear, red-orange solution. The reaction mixture was taken to dryness to obtain a red solid that was collected on a frit, rinsed with pentane (5 mL), and dried under vacuum (0.390 g, 0.530 mmol, 98%). Crystals of 3.4 suitable for X-ray analysis were grown by slow evaporation of a benzene solution of 3.3.
\(^1H\) NMR (C\(_6\)D\(_6\), 400 MHz): \(\delta = 7.61\) (dd, 1H, 8 Hz, 2 Hz), 7.49 (dd, 1H, 8 Hz, 2 Hz), 7.15 (m, 2H), 7.00 (m, 4H), 6.91 (d, 1H, 8 Hz), 6.90 (s, 3H), 6.81 (d, 1H, 8 Hz), 6.48 (t, 2H, 8 Hz), 6.22 (dd, 2H, \(J_{HH} = 8\) Hz, \(J_{HP} = 6\) Hz), 6.22 (dd, 1H, \(J_{HH} = 8\) Hz, \(J_{HP} = 6\) Hz), and 5.98 (d, 2H, 8 Hz) (ArH), 2.70 (dd, 1H, \(J_{HH} = 9\) Hz, \(J_{HP} = 1\) Hz, ZrCH\(_2\)H\(_5\)Mes), 2.29 (s, 3H), 2.28 (d, 1H, 7 Hz, ZrCH\(_2\)H\(_5\)Ph), 2.27 (s, 3H), 2.26 (s, 3H), 2.21 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), and 1.95 (s, 3H) (ArCH\(_3\)), 1.85 (bd, 1H, 9 Hz, ZrCH\(_2\)H\(_5\)Mes), 1.75 (d, 1H, 7 Hz, ZrCH\(_2\)H\(_5\)Ph).

\(^{31}\)P\(^{1H}\) NMR (C\(_6\)D\(_6\), 162 MHz): \(\delta = -5.2\) (s).

\(^13\)C\(^{1H}\) NMR (C\(_6\)D\(_6\), 101 MHz): \(\delta = 160.5\) (d, 32 Hz), 157.0 (d, 27 Hz), 139.8, 137.8 (d, 4 Hz), 137.0, 136.6, 136.2, 136.0, 135.6, 134.6, 134.5 (d, 3 Hz), 134.37, 134.31 (d, 2 Hz), 134.0 (d, 5 Hz), 133.7, 133.3, 133.0, 132.4, 132.3, 131.3, 130.4, 130.1, 128.9, 128.6, 128.5, 128.1, 124.8, 124.7, 123.3, 118.4, 115.0 (d, 10 Hz), and 112.7 (d, 9 Hz) (ArC), 66.5, and 63.8 (d, 8 Hz) (ZrCH\(_2\)Ar), 21.5, 21.1, 20.4, 20.3, 20.1, 19.7, and 19.3 (ArCH\(_3\)).

EI-MS (m/z): 734 (2, [M]+), 643 (2, [M – Bn]+), 541 (10, [2.8 – Me]'), 91 (100, [Bn]+).

Anal. Calcd. for C\(_{45}\)H\(_{45}\)N\(_2\)PZr: C, 73.43; H, 6.16; N, 3.81; Found: C, 73.15; H, 6.30; N, 4.04.

[NPNC]\(^+\)Zr(\(\eta^2\)-CD\(_2\)C\(_6\)H\(_5\)) (3.4-d). Approximately 0.8 mL of a C\(_6\)D\(_6\) solution of 3.3-d as prepared above was heated in an NMR tube at 55 °C for 2 h to obtain a bright red-orange solution. After analyzing the sample by NMR spectroscopy, the NMR tube was opened to air, and MeOH (0.1 mL) was added. The white suspension was filtered through Celite, and the clear, colourless filtrate was analyzed by GC-MS.

\(^1H\) NMR (C\(_6\)D\(_6\), 400 MHz): \(\delta = 7.61\) (d, 1H, 8 Hz), 7.52 (d, 1H, 8 Hz), 7.15-7.00 (m, 4H), 6.95-6.8 (m, 7H), 6.22 (m, 1H), and 5.98 (dd, 1H, \(J_{HH} = 8\) Hz, \(J_{HP} = 6\) Hz) (ArH), 2.70 (dd,
1H, 9 Hz, 1 Hz, ZrCH$_{14}$H$_{16}$Mes), 2.29 (s, 3H), 2.27 (s, 3H), 2.26 (s, 3H), 2.21 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), and 1.96 (s, 3H) (ArCH$_3$), 1.85 (bd, 1H, 9 Hz, ZrCH$_{14}$H$_{16}$Mes).

$^3$P{'H} NMR (C$_6$D$_6$, 162 MHz): $\delta = -5.3$ (s).

GC-MS: 3.48 – 3.59 min. ($m$/z): 99 (15, [C$_7$D$_7$H]$	extsuperscript{+}$).

[NPN]'Hf(CH$_2$Ph)$_2$ (3.5). In the dark at –35 °C, benzylmagnesium chloride (1.0 M in Et$_2$O, 2.0 mL, 2.0 mmol) was added to a stirred suspension of 2.15 (0.721 g, 0.900 mmol) in Et$_2$O (10 mL). The solution was translucent pale yellow after 30 min. at rt, whereupon 1,4-dioxane (0.5 mL) was added. The pale yellow suspension was taken to dryness to obtain a yellow solid that was extracted with hexanes (20 mL), followed by toluene (10 mL). The yellow extracts were filtered through Celite, and the filtrate was taken to dryness to obtain a pale yellow powder (0.805 g, 0.880 mmol, 98%). X-ray quality crystals were grown by slow evaporation of a benzene solution of the compound.

$^1$H NMR (C$_6$D$_6$, 500 MHz): $\delta = 7.52$ (m, 2H, 8 Hz), 7.13 (t, 1H, 7 Hz), 7.07 (m, 4H, 8 Hz), 7.02 (t, 2H, 7 Hz), 6.97 (s, 2H), 6.94 (t, 2H, 8 Hz), 6.85 (d, 2H, 7 Hz), 6.82 (s, 2H), 6.76 (t, 1H, 7 Hz), 6.73 (t, 1H, 7 Hz), 6.49 (d, 2H, 7 Hz), 6.28 (d, 2H, 7 Hz), and 6.06 (dd, 2H, $J_{HP} = 8$ Hz, $J_{HH} = 8$ Hz) (ArH), 2.59 (d, 2H, $J_{HP} = 7.6$ Hz, CH$_2$Ph), 2.19 (s, 6H), 2.17 (s, 6H), 2.13 (s, 6H), and 1.96 (s, 6H) (ArCH$_3$), and 1.59 (d, 2H, $J_{HP} = 2$ Hz, CH$_2$Ph).

$^3$P{'H} NMR (C$_6$D$_6$, 121 MHz): $\delta = -5.8$ (s).

$^{13}$C{'H} NMR (C$_6$D$_6$, 75 MHz): $\delta = 160.3$ (d, 31 Hz), 150.2, 146.4, 138.9, 138.7, 137.4, 134.7, 134.6, 133.8, 133.6, 132.6 (d, 12 Hz), 131.1, 130.8, 129.7 (d, 4 Hz), 129.4, 129.1, 129.0, 128.5, 127.3, 126.9, 122.1, 121.0, 120.8, and 115.6 (d, 10 Hz) (ArC), 83.2 (d, 6 Hz), and 81.5 (d, 21 Hz) (HfCH$_3$), 21.1, 20.2, 19.1, and 18.5 (ArCH$_3$).

Anal. Calcd. for C$_{52}$H$_{53}$N$_2$PHf: C, 68.22; H, 5.84; N, 3.06; Found: C, 67.98; H, 5.93; N, 3.44.
[NPN$^+$]Zr(CH$_2$SiMe$_3$)$_2$ (3.6). To a stirred suspension of 2.10 (0.750 g, 1.05 mmol) in Et$_2$O (5 mL) at -35 °C in the dark was added LiCH$_2$SiMe$_3$ (0.217 g, 2.30 mmol) in Et$_2$O (2 mL) dropwise. The solution became clear pale yellow instantly and was stirred at rt for 30 min. 1,4-Dioxane (0.5 mL) was added to obtain a pale yellow suspension that was taken to dryness. Toluene (10 mL) was added to the yellow solid, and the suspension was filtered through Celite. The yellow filtrate was taken to dryness to obtain a pale yellow powder. The powder was collected on a frit, washed with pentane (5 mL), and dried under vacuum (0.815 g, 0.994 mmol, 95%).

$^1$H NMR (C$_6$D$_6$, 500 MHz): $\delta$ = 7.60 (t, 2H, 8 Hz), 7.53 (d, 2H, 7 Hz), 7.10 (t, 2H, 7 Hz), 7.03 (t, 1H, 7 Hz), 6.97 (s, 2H), 6.85 (s, 2H), 6.84 (d, 2H, 7 Hz), and 6.06 (dd, 2H, $J_{HH} = 8$ Hz, $J_{HP} = 6$ Hz) (ArH), 2.57 (s, 6H), 2.17 (s, 6H), 2.11 (s, 6H), and 1.96 (s, 6H) (ArCH$_3$), 1.39 (d, 2H, $J_{HP} = 7$ Hz, CH$_2$SiMe$_3$), 0.10 (s, 9H, Si(CH$_3$)$_3$), 0.04 (s, 2H, CH$_2$SiMe$_3$), and -0.08 (s, 9H, Si(CH$_3$)$_3$).

$^{31}$P{$^1$H} NMR (C$_6$D$_6$, 202 MHz): $\delta$ = -15.3 (s).

[NPNC]$^*$Zr(CH$_2$SiMe$_3$) (3.7). A yellow solution of 3.6 (0.350 g, 0.427 mmol) in toluene (10 mL) was stirred for 3 d at rt until the reaction mixture was clear, bright red-orange. The reaction mixture was taken to dryness to obtain an orange powder that was recrystallized from benzene. The red-orange crystals were collected on a frit, rinsed with pentane (5 mL), and dried under vacuum (0.273 g, 0.373 mmol, 87%). Red single crystals of 3.7 were grown by slow evaporation of a benzene solution of the compound.

$^1$H NMR (C$_6$D$_6$, 500 MHz): $\delta$ = 7.59 (d, 1H, 8 Hz), 7.56 (d, 1H, 8 Hz), 7.49 (dd, 2H, 11 Hz, 7 Hz), 7.05 (m, 3H), 7.02 (d, 1H, 8 Hz), 7.01 (s, 1H), 6.98 (bs, 1H), 6.96 (s, 1H), 6.94 (d, 1H,
8 Hz), 6.88 (s, 1H), 6.44 (dd, 1H, $J_{HH} = 8$ Hz, $J_{HP} = 6$ Hz), and 6.28 (dd, 1H, $J_{HH} = 8$ Hz, $J_{HP} = 6$ Hz) (ArH), 2.53 (s, 3H), 2.51 (s, 3H), 2.36 (d, 1H, 11.8 Hz, ZrCH$_2$H$_6$Ar), 2.25 (s, 3H), 2.21 (s, 3H), 2.18 (s, 3H), 2.04 (s, 3H), and 1.99 (s, 3H) (ArCH$_3$), 1.56 (bdd, 1H, $J = 11.8$ Hz, $J = 4$ Hz, ZrCH$_a$H$_b$Ar), 0.56 (d, 1H, 11.4 Hz, ZrCH$_3$H$_4$TMS), −0.13 (d, 1H, 11.4 Hz, ZrCH$_2$H$_2$TMS), −0.32 (s, 9H, Si(CH$_3$)$_3$).

$^{31}$P{$_1^H$} NMR (C$_6$D$_6$, 202 MHz): $\delta = -8.5$ (s).

$^{13}$C{$_1^H$} NMR (C$_6$D$_6$, 126 MHz): $\delta =$ 160.9 (d, 32 Hz), 157.0 (d, 27 Hz), 140.3, 138.3, 137.8, 137.7, 136.6, 136.1, 135.8, 135.2, 135.0, 134.7, 133.8, 133.5, 131.8, 131.7, 130.5, 130.4, 130.2, 129.6, 129.2, 127.7, 116.5, 116.2, 115.5, 115.2, 114.4 (d, 10 Hz), and 113.4 (d, 10 Hz) (ArC), 65.6, and 64.1 (d, 8 Hz) (ZrCH$_2$R), 21.3, 21.1, 20.4, 20.3, 20.0, 19.6, and 18.7 (ArCH$_3$), 2.38 (Si(CH$_3$)$_3$).

Anal. Calcd. for C$_{51}$H$_{58}$N$_2$PSiZr: C, 72.12; H, 6.88; N, 3.30; Found: C, 72.38; H, 6.84; N, 3.51.

$[^{[PNN]}]^*_{Hf(CH_2SiMe_3)_2}$ (3.8). To a stirred suspension of 2.15 (0.385 g, 0.479 mmol) in Et$_2$O (5 mL) at −35 °C in the dark was added LiCH$_2$SiMe$_3$ (0.099 g, 1.05 mmol) in Et$_2$O (2 mL) dropwise. The reaction mixture became clear yellow instantly and was stirred at rt for 30 min. 1,4-Dioxane (0.5 mL) was added, and the reaction mixture was taken to dryness to obtain a yellow solid that was suspended in toluene (10 mL). The suspension was filtered through Celite, and the filtrate was taken to dryness to obtain a light yellow powder (0.370 g, 0.408 mmol, 86%).

$^1$H NMR (C$_6$D$_6$, 500 MHz): $\delta =$ 7.58 (t, 2H, 8 Hz), 7.51 (d, 2H, 7 Hz), 7.09 (m, 2H), 7.01 (t, 1H, 7 Hz), 6.97 (s, 2H), 6.87 (bs, 4H), and 6.10 (dd, 2H, $J_{HH} = 8$ Hz, $J_{HP} = 6$ Hz) (ArH), 2.58
(s, 6H), 2.19 (s, 6H), 2.17 (s, 6H), and 1.97 (s, 6H) (ArCH₃), 0.80 (d, 2H, J₁H₂ = 6 Hz, CH₂SiMe₃), 0.10 (s, 9H, Si(CH₃)₃), −0.10 (s, 9H, Si(CH₃)₃), −0.30 (s, 2H, CH₂SiMe₃).

³¹P{¹H} NMR (C₆D₆, 202 MHz): δ = −7.5 (s).

¹³C{¹H} NMR (C₆D₆, 126 MHz): δ = 160.7 (d, 31 Hz), 140.1, 138.2, 137.4, 136.6, 134.6, 133.1, 133.0, 130.8, 129.3, 129.1, 128.9, 128.8, 120.4, 120.2, and 115.6 (d, 10 Hz) (ArC), 72.3 (d, 6 Hz), and 66.0 (d, 20 Hz) (CH₂SiMe₃), 20.9, 20.2, 19.9, and 19.3 (ArCH₃), 3.74, and 2.86 (Si(CH₃)₃).

Anal. Calcd. for C₄₆H₆₁N₂PSi₂Hf: C, 60.87; H, 6.77; N, 3.09; Found: C, 61.00; H, 6.81; N, 3.10.

Thermal Decomposition Studies. The rt decomposition of 3.3 was monitored by NMR spectroscopy to determine the order of the reaction. Complex 3.3 (15.0, 24.0 or 33.0 mg) was weighed into a 3-mL vial and 0.70 mL of C₆D₆ was transferred to the vial by syringe. The yellow solution was transferred to an NMR tube and the sample was analyzed periodically over 2 d by ¹H NMR spectroscopy. To determine the rate constant for the reaction at each of five different temperatures, 3.3 (25.0 mg) was weighed into a 3-mL vial and dissolved in 0.70 mL toluene-d₈. The solution was transferred to an NMR tube and immediately frozen at −10 °C until it could be analyzed. Each sample was placed in the NMR probe heated to 328, 338, 348, or 358 K, and the reaction was followed by ¹H NMR spectroscopy. The first ¹H NMR spectrum was measured two min. after the sample was inserted into the probe. From the plot of ln[3.3] vs. time, no further time appeared necessary for the sample to reach thermal equilibrium before the first ¹H NMR spectrum was collected. One sample was stored at rt, and monitored periodically over 2 d.
Reaction of [NPN]₇MMe₂ with 4 atm H₂ (M = Zr or Hf). In a typical experiment, yellow 3.1 (0.300 g, 0.444 mmol) was dissolved in toluene (10 mL) in a 200-mL Teflon-sealed thick-walled bomb. The solution was degassed by three freeze-pump-thaw cycles and filled with H₂ at 77 K. The flask was warmed to rt (4 atm H₂) behind a blast shield. The solution became pale brown after the solvent thawed, but after about 5 min. the reaction mixture was clear yellow again. The yellow solution was stirred in the dark for 4 h. (For 3.2, the reaction mixture was stirred for 3 d since starting material decomposition was not a concern.) After venting the pressure of H₂, an aliquot of the yellow reaction mixture was analyzed by ³¹P{¹H} NMR spectroscopy, and a second aliquot was concentrated under vacuum to obtain a yellow powder that was analyzed by NMR spectroscopy. Visually, and by NMR spectroscopy, only starting material was present.

Reaction of [NPN]₇HfMe₂ with 1 atm H₂. Pale yellow 3.2 (50 mg, 66 µmol) was dissolved in C₆D₆ (~ 1 mL), filtered, and transferred to a J. Young NMR tube. The solution was degassed by three freeze-pump-thaw cycles (frozen at −10 °C, thawed under flow of H₂ gas) and sealed (1 atm H₂) at rt. The solution was monitored over 4 weeks. There was no colour change and no new peaks were observed in the ³¹P{¹H} or ¹H NMR spectra.

3.5 References.


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Chapter Four

Synthesis and Structure of Zirconium Dinitrogen Complexes

4.1 Introduction.

Molecular nitrogen is unreactive, in part because it has a strong triple bond (945 kJ mol⁻¹), a large HOMO-LUMO gap, and it lacks a dipole.¹ In 1965, however, the first dinitrogen complex, \([\text{Ru(NH}_3)_5(\eta^1-N_2)]^{2+}\), was reported.² Initially prepared serendipitously from \(N_2H_4\cdot H_2O\) and \(\text{RuCl}_3\cdot xH_2O\), the complex was later intentionally synthesized from \(N_2\) gas, \(\text{Ru(NH}_3)_5\text{Cl}_3\), and \(\text{Zn}\).³ Today, \(N_2\) complexes of most of the transition elements and the lanthanides are known.⁴ Dinitrogen coordinated to a transition metal from groups 7 to 10 (late transition metals for the purpose of this discussion) is usually unactivated or only weakly activated, with an \(N-N\) bond length similar to that of \(N_2\) gas (1.0975 Å).⁵ Transition metals from groups 4 to 6 (termed early transition metals here) can activate \(N_2\) strongly because they are more reducing. The \(N-N\) bond in \([\text{PNP}]\text{ZrCl}_2(\mu-\eta^2:N_2)\) is 1.548(7) Å, longer than the \(N-N\) single bond in hydrazine (1.47 Å).⁶

Most late transition-metal dinitrogen complexes are electronically saturated species prepared without strong reducing agents or harsh conditions. For example, \([\text{Re(PMe}_3)_5(\eta^1-N_2)]^{+}\text{Cl}\) forms when \(\text{Re(PMe}_3)_3\text{Cl}\) is dissolved in EtOH in the presence of \(N_2\).⁷ In contrast, early transition-metal dinitrogen complexes are usually synthesized by reducing a metal halide complex with a strong alkali metal reducing agent. Reduction of \([\text{PNP}]\text{ZrCl}_3\) with \(\text{Na/Hg amalgam provides } ([\text{PNP}]\text{ZrCl}_2(\mu-\eta^2:N_2))\), whereas potassium graphite (\(\text{KC}_6\)) reduction of \([\text{P}_2\text{N}_2]\text{ZrCl}_2\) provides \([\text{P}_2\text{N}_2]\text{Zr}(\mu-\eta^2:N_2)\) (\(N-N\) bond: 1.43(1) Å) (Figure
Recently, the reduction of $[\text{NPN}]\text{ZrCl}_4(\text{THF})$ with KC$_8$ to give $\{[\text{NPN}]\text{Zr(THF)}\}_2(\mu-$
$\eta^2: \eta^2-\text{N}_2\}$ (N–N bond: 1.503(3) Å) has been reported.\(^9\)

![Zirconium dinitrogen complexes](image)

**Figure 4.1.** Zirconium dinitrogen complexes (silyl methyl substituents of $[\text{P}_2\text{N}_2]$ omitted).

Early transition-metal $\text{N}_2$ complexes can be synthesized directly from low-valent metal complexes and $\text{N}_2$. The Nb(III) complex, $[\text{P}_2\text{N}_2]\text{NbCH}_3$, reacts with $\text{N}_2$ to give diamagnetic $\{[\text{P}_2\text{N}_2]\text{Nb(CH}_3\}_2(\mu-$
$\eta^1: \eta^1-\text{N}_2\}$, with an N–N bond length of 1.280(7) Å (Figure 4.2).\(^10\)

Complete cleavage of the N–N triple bond is also achieved from the direct reaction of $\text{N}_2$
with a reduced metal complex; two equivalents of [Ar(R)N]_3Mo(III) (Ar = 3,5-Me_2C_6H_3, R = C(CD_3)_2CH_3) reduce N_2 by six electrons to yield two equivalents of [Ar(R)N]_3Mo≡N (Figure 4.2). Early transition-metal hydrides can also activate N_2. (Cp''_2Zr)(μ-η^2:η^2-N_2) (Cp'' = 1,3-(SiMe_3)_2-η^5-C_5H_5) forms when two equivalents of 'BuLi are allowed to react with Cp''_2ZrCl_2 (Scheme 4.1). The initial product of the reaction, Cp''_2Zr(H)(CH_2CH(CH_3)_2), decomposes to give a cyclometalated Zr hydride, Cp''(1-SiMe_3-3-(SiMe_2CH_2-)η^5-C_5H_5)ZrH, that activates N_2.

\[
\begin{align*}
2 \text{Ph}_2\text{P} & \text{N}_2 \rightarrow \text{Ph}_2\text{P} \text{N}_2 \\
\Delta, -\text{N}_2 & \rightarrow \\
\text{R} & \text{N}_2 \rightarrow \text{R} \text{N}_2
\end{align*}
\]

\[
\text{Ar} = 3,5-\text{Me}_2\text{C}_6\text{H}_3, \ \text{R} = \text{C(CH}_3\text{)(CD}_3\text{)}_2
\]

**Figure 4.2.** Reactions of low-valent early transition-metal complexes with N_2 (silyl methyl substituents of [P_2N_2] omitted).
Although many N\textsubscript{2} complexes are known, predicting the conditions that will lead to their formation is a challenge. Ancillary ligand, metal, solvent, and \( \text{N}_2 \) pressure are important factors in determining whether \( \text{N}_2 \) activation occurs rather than activation of the solvent\textsuperscript{13}, or the ancillary ligand\textsuperscript{14}, formation of a reduced product that does not contain \( \text{N}_2 \)\textsuperscript{15}, or formation of a mixture of products. Chelating \( \pi \)-acceptor ligands can facilitate synthesis of early transition-metal \( \text{N}_2 \) complexes because they stabilize reduced species.

It is an exciting time in \( \text{N}_2 \) research since ancillary ligand design is at the core of several recent major breakthroughs\textsuperscript{16}. In 1974, the synthesis of \([\text{Cp}^*\text{Zr} (\eta^1-\text{N}_2) ]_2 (\mu-\eta^1: \eta^1-\text{N}_2) \) from \( \text{Cp}^*\text{ZrCl}_2 \) and Na/Hg amalgam was reported\textsuperscript{17}. The bridging end-on bound \( \text{N}_2 \) is slightly activated (N--N bond: 1.182(5) \( \text{Å} \)), and hydrazine is produced in high yield upon addition of HCl to the complex. The addition of \( \text{H}_2 \) to the complex provides \( \text{Cp}^*\text{ZrH}_2 \) and free \( \text{N}_2 \)\textsuperscript{18}. In 2004, the synthesis of \([\eta^5-C_5\text{Me}_5 \text{H}_2\text{Zr}]_2 (\mu-\eta^2: \eta^2-\text{N}_2) \) from \( (\eta^5-C_5\text{Me}_5 \text{H})_2\text{ZrCl}_2 \) and Na/Hg amalgam was reported\textsuperscript{19}. \( \text{N}_2 \) in this complex is strongly activated (N--N bond: 1.377(3) \( \text{Å} \)), and it reacts with \( \text{H}_2 \) to yield \([\eta^5-C_5\text{Me}_5 \text{H}_2\text{Zr}(\text{H})]_2 (\mu-\eta^2: \eta^2-\text{N}_2\text{H}_2) \) with two new N--H
bonds. Thus, the use of tetramethylcyclopentadiene rather than pentamethylcyclopentadiene changed the coordination mode, bond length and reactivity of $N_2$.

In this chapter, the synthesis of a dinuclear Zr-$N_2$ complex by KC$_8$ reduction of [NPN]$^\ast$ZrCl$_2$ is described. $N_2$ is coordinated side-on to the two Zr atoms, as revealed by single crystal X-ray analysis. Coordinated THF can be replaced with Py, PMe$_3$, and PMe$_2$Ph, and these adducts are characterized in the solid state (Py and PMe$_2$Ph) and in solution. An attempt to synthesize a Hf-$N_2$ complex is also presented.

4.2 Results and Discussion.

4.2.1 Synthesis and structure of $\{[\text{NPN}]^\ast\text{Zr(THF)}\}_2(\mu-\eta^2:\eta^2-N_2)$.

Deep blue-green $\{[\text{NPN}]^\ast\text{Zr(THF)}\}_2(\mu-\eta^2:\eta^2-N_2)$, 4.1, can be prepared from [NPN]$^\ast$ZrCl$_2$ (2.10) and 2.2 equivalents of KC$_8$ in THF under 4 atm of $N_2$ (Equation 4.1). Black crystals of 4.1 are obtained upon work-up in 79\% yield. Initially, a Zr-$N_2$ complex could not be isolated using this method, although there were signs that an $N_2$ complex formed: the reaction mixture turned bright green and a peak attributable to a dimeric [NPN]$^\ast$Zr species was apparent in the mass spectrum. There is also evidence that a Zr-$N_2$ complex forms under other conditions (i.e., 2.2 equivalents KC$_8$, THF, 1 atm $N_2$, or five equivalents Na/Hg, THF, 4 atm $N_2$), but in all cases, the green reaction mixture transforms to a beige powder during work-up.
The isolation of a Zr-N₂ complex is possible if the THF used for the reaction is rigorously H₂O- and O₂-free, if the reaction mixture warms slowly to room temperature (EtOH/liquid-N₂ bath: −116 °C), and if the mixture is vigorously stirred and the flask periodically inverted over the course of the reaction. If a deep purple or blue-green colour is observed during the first hour after the flask is charged with N₂, then a high yield of 4.1 is generally obtained. It is unclear why 4.1 can be isolated under these conditions, whereas decomposition is observed otherwise. It is known that Zr-N₂ complexes are extremely air and moisture sensitive, and that vigorous stirring will increase the concentration of N₂ in the reaction mixture.

Another factor that may have complicated the isolation of 4.1 is its apparent decomposition in the absence of THF. Crystalline samples are dried under vacuum briefly (~15 min.) prior to analysis because 4.1 becomes an off-white powder when it is stored under vacuum for prolonged periods. The powder contains a benzene-soluble fraction, and a fraction that is insoluble in benzene, water, THF or DMSO. The benzene-soluble fraction is [NPN]¹H₂ (2.8), as determined by ¹H and ³¹P{¹H} NMR spectroscopy, EI-MS and microanalysis. The insoluble white fraction has not been characterized. The mechanism of the decomposition of 4.1 under vacuum remains a mystery.
There is a singlet at δ 5.0 in the $^{31}\text{P}^1\text{H}$ NMR spectrum of 4.1 in THF-$d_8$. Both phosphines in the proposed dimeric structure are equivalent. The $^1\text{H}$ NMR spectrum (Figure 4.3) shows four singlets between δ 2.2 and 1.7 due to four distinct $\text{ArCH}_3$ groups in the $C_{2h}$ symmetric complex, as well as the expected $\text{ArH}$ resonances. Singlets due to coordinated THF appear at δ 3.54 and 1.69, and partially overlap with resonances due to free THF in the $^1\text{H}$ NMR spectrum. In the $^{13}\text{C}^1\text{H}$ NMR spectrum, the expected arylmethyl and aromatic carbon signals, as well as resonances attributable to free and coordinated THF, are observed. There are two equivalents of THF in the crystal lattice of 4.1 as revealed by $^1\text{H}$ NMR spectroscopy of 4.1 in $C_6D_6$. The results of combustion analysis are also consistent with the formulation 4.1·2THF. Crystalline samples of 4.1·2THF are stable, and can be stored for months at −35 °C. Prior to use, crystalline samples can be dissolved in THF and dried (with careful monitoring) to obtain a green powder that does not contain solvent of crystallization, which is convenient for determining stoichiometry. In the mass spectrum of 4.1, there is a peak at $m/\zeta = 1320$ that is assigned to \([M − 2\text{THF}]^+\)

![Figure 4.3. 500 MHz $^1\text{H}$ NMR spectrum of 4.1 in THF-$d_8$.](image-url)
Little is known about the mechanism of formation of early transition-metal dinitrogen complexes, although some relevant information can be gleaned from the literature. Potassium graphite (KC₈) has a reduction potential similar to potassium metal, although its power decreases as electrons are transferred to the substrate.²⁰ Like elemental potassium, reduction by KC₈ occurs via one-electron transfer steps. KC₈ has become a widely used reducing agent for metal complexes because it is easy to work with on a multi-gram scale, and graphite is the only by-product, in addition to KCl, for example, if metal chlorides are reduced. Cyclic voltammetry of (η⁵-C₅H₄R)₂ZrCl₂ (R = Me, Et, SiMe₃, H) shows that a reversible one-electron reduction at E₁/₂ ≈ −1.7 V occurs to yield the Zr(III) species [(η⁵-C₅H₄R)₂ZrCl₂]²⁺.²¹ Chemical reduction of Cp₂TiCl₂ produces the Ti(III) species, [Na(THF)₄][Cp₂TiCl₂], which is observed by ESR spectroscopy.²² Although some Zr(III) and Hf(III) complexes are stable and have been structurally characterized,²³ others disproportionate to give a mixture of M(II) and M(IV) species.²⁴ A Ti(II) dinitrogen complex, (η⁵-C₅H₄(SiMe₂Ph))₂Ti(η¹-N₂), has been characterized crystallographically,²⁵ whereas discrete mononuclear Zr(II) N₂ complexes are unknown, likely due to the stronger reduction potential of Zr compared to Ti.

One proposed route to 4.1 involves the one-electron reduction of [NPN]⁺ZrCl₂ to produce a species like [K(THF)₄][NPN]⁺ZrCl₂. Disproportionation of this Zr(III) anion is expected to give [NPN]⁺ZrCl₂ and a solvated [NPN]⁺Zr(II) intermediate, such as [NPN]⁺Zr(THF)₂, along with two equivalents of KCl. Although N₂ is a weaker donor than most solvents or Lewis bases, the formation of strong hard-hard bonding interactions between Zr and N₂ is a thermodynamic driving force for Zr-N₂ complex formation. Since the first step in the reduction of N₂ (i.e., N₂ to N₂²⁻) occurs at a higher potential than the
subsequent reduction steps (e.g., N$_2$\textsuperscript{2-} to N$_2$\textsuperscript{4-}), the formation of a formally Zr\textsuperscript{4+}(N$_2$\textsuperscript{4-})Zr\textsuperscript{4+} dimer may be facile compared to the initial formation of a Zr\textsuperscript{2+}(N$_2$\textsuperscript{2-}) species. This is one possible explanation for the prevalence of dinuclear N$_2$ complexes of the early transition metals.\textsuperscript{23A} In addition, a species such as Zr(N$_2$\textsuperscript{2-}) is expected to be much more Lewis basic than N$_2$, which may allow the formation of a dinuclear complex. The mechanism of dinitrogen activation by reduced Zr species is still unclear, probably because the conditions required for the synthesis of most Zr-N$_2$ complexes are somewhat incompatible with characterizing intermediates spectroscopically, or monitoring reactions over time.

When 2.10 is reduced with 2.2 equivalents of KC$_8$ under identical conditions used to obtain 4.1, but in the absence of N$_2$, blue-green 4.1 does not form. Instead, the reaction mixture turns brown. When an aliquot of the reaction mixture is analyzed by $^3$P\{$^1$H\} NMR spectroscopy, singlets at $\delta$ -14.6 and -15.4 are observed due to the major diamagnetic P-containing products, along with minor products such as 2.8, and other unidentified species. No peaks at $m/z > 556$ (2.8) are observed by EI-MS. The major products could not be separated from each other for further characterization.

Reduction of early transition-metal halide complexes in the absence of N$_2$ can lead to solvent activation, ancillary ligand activation, or formation of a reduced complex that does not contain N$_2$. Solvent activation by reduced species is exemplified by C–O cleavage of THF,\textsuperscript{26} or C–H activation of toluene to give an $\eta^6$-benzyl complex,\textsuperscript{27} whereas ancillary ligand activation is exemplified by the formation of dimeric $\eta^6$-phenyl-bridged ([P$_2$N$_2$]Zr)$_2$ from [P$_2$N$_2$]ZrCl$_2$.\textsuperscript{14} The reduction of ZrCl$_4$/PEt$_3$ mixtures with sodium amalgam gives [ZrCl$_3$(PEt$_3$)$_2$]$_2$ as a forest green Zr(III) compound with bridging chlorides.\textsuperscript{15} Likewise, sodium amalgam reduction of [PCP]ZrCl$_3$ ([PCP] = [1,3-(P$_2$Z$_2$PCH$_2$SiMe$_2$)$_2$-$\eta^5$-C$_5$H$_3$]) under
Ar yields [PCP]ZrCl₂. There is insufficient evidence to determine if any of these reactions has occurred for the reduction of 2.10.

When 2.10 is reduced under \(^{15}\text{N}_2\), blue-green 4.1-\(^{15}\text{N}_2\) is obtained. It should be noted that \(^{15}\text{N}_2\)-labelled 4.1 cannot be isolated if a glass bulb of \(^{15}\text{N}_2\) gas is used, possibly because a pressure of 4 atm of \(\text{N}_2\) is not attained in the flask at room temperature. When \(^{15}\text{N}_2\) from a small lecture bottle is used, 4.1-\(^{15}\text{N}_2\) is isolated in high yield as a black crystalline solid. There is a doublet (\(\mathcal{J}_{\text{PN}} = 6.7\) Hz) at \(\delta = 5.0\) in the \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum of 4.1-\(^{15}\text{N}_2\), where a singlet was observed for 4.1. There is also a doublet at \(\delta = 116.6\) (relative to MeNO₂ at \(\delta = 0\)) in the \(^{15}\text{N}\{^1\text{H}\}\) NMR spectrum (Figure 4.4). The \(^{31}\text{P}\{^1\text{H}\}\) and \(^{15}\text{N}\{^1\text{H}\}\) NMR spectra indicate that an AA'XX' spin system is present in 4.1-\(^{15}\text{N}_2\) although \(^{15}\text{N}\) can only be observed to couple to one \(^{31}\text{P}\) nucleus (\(\mathcal{J}_{\text{PN}} \neq 0\)). Since the two \(^{15}\text{N}\) and \(^{31}\text{P}\) nuclei are magnetically inequivalent, \(\text{N}_2\) evidently does not rotate about the Zr---Zr axis in 4.1.

![NMR Spectrum](image)

**Figure 4.4.** 40 MHz \(^{15}\text{N}\{^1\text{H}\}\) NMR spectrum of 4.1-\(^{15}\text{N}_2\) in THF-\(d_8\).

The presence of a signal in the \(^{15}\text{N}\{^1\text{H}\}\) NMR spectrum of 4.1-\(^{15}\text{N}_2\) confirms that the source of \(\text{N}_2\) in the complex is \(^{15}\text{N}_2\) gas. At this time, it is difficult to correlate the \(^{15}\text{N}\) chemical shift in dinitrogen complexes with the coordination mode or extent of \(\text{N}_2\)
activation. A wide range of such chemical shifts is known for \( N_2 \) complexes.\(^2\) The majority of side-on \( N_2 \) complexes listed in Table 1.2 have \( ^{15}N \) chemical shifts between \( \delta \) 495 and 621, and the chemical shift of hydrazine is \( \delta \) 690. The \( ^{15}N \) chemical shifts of \( ([NPNI_Ta)_2(\mu-H)_2(\mu-\eta^1:\eta^2-N_2) \) are \( \delta \) –20.4 and 163.6. The 6.7 Hz P-N coupling is similar to other \( ^2J_{NP} \) values observed for \( ^{15}N_2 \) complexes with phosphine ligands,\(^3\) although the reported values of \( ^2J_{NP} \) cover a wide range,\(^4\) and in many cases P-N coupling in \( ^{15}N_2 \) complexes is unreported or unobserved.

The ORTEP representation of the solid-state molecular structure of 4.1 is shown in Figure 4.5, and the arrangement of P, N, and O about Zr is illustrated in Figure 4.6. The dinuclear complex features one THF molecule, and one facially coordinated \([NPNI^*\] per Zr. \( N_2 \) is bound side-on to both zirconium centres with a slight butterfly or hinge distortion; the angle between the two ZrN\(_2\) planes is 166°. The two halves of the molecule are related by a two-fold rotation axis that bisects the N–N bond; 4.1 is \( C_2 \) symmetric in the solid state. The N–N bond length is 1.503(6) Å, which corresponds to reduction to \( N_2^4 \), or hydrazide. The Zr–N bond lengths to \( N_2 \) are slightly different: Zr1–N3 is 2.023(3) Å, and Zr1–N3' is 2.089(3) Å. The Zr–N1 and Zr–N2 bonds are 2.184(3) Å and 2.224(3) Å, respectively. The Zr–P1 bond is 2.6777(10) Å, and the Zr–O bond is 2.371(2) Å. The geometry around Zr is best described as distorted trigonal bipyramidal with O and P donors apical and N1, N2 and the dinitrogen fragment equatorial. As with other complexes of \([NPNI^*\), the P–Zr–N1 and P–Zr–N2 angles are acute at 71.84(8), and 73.42(8)°, respectively.
Figure 4.5. ORTEP drawing of the solid-state molecular structure of \([\{\text{NPN}\}^+\text{Zr}(\text{THF})_2(\mu-\eta^2:\eta^2-\text{N}_2)]\), 4.1 (ellipsoids drawn at the 50% probability level). Carbon atoms of the proximal Mes substituents (except for C) and all hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Zr1–P1 2.6777(10), Zr1–N1 2.184(3), Zr1–N2 2.224(3), Zr1–O1 2.371(2), Zr1–N3 2.023(3), Zr1–N3’ 2.089(3), N3–N3’ 1.503(6), P1–Zr1–N1 71.84(8), P1–Zr1–N2 73.42(8), N3–Zr1–N3’ 42.85(15), Zr1–N3’–Zr1’ 135.02(15), O1–Zr1–P1 154.14(7), P1–Zr1–N3 82.00(8).
Complex 4.1 is $C_2$ symmetric in the solid state, but $C_{2v}$ symmetric in solution. The mirror plane of symmetry in the solution structure encompasses the Zr$_2$N$_2$ core that is butterfly-distorted in the solid state. Thus, if Zr$_2$N$_2$ is butterfly-distorted in solution, a fluxional process that flips N$_2$ from one side of the Zr---Zr axis to the other may be responsible for the apparent mirror plane on the NMR timescale. DFT calculations on a model compound of ([P$_2$N$_2$]Zr)$_2$(µ-η$^2$:η$^2$-N$_2$) show that a butterfly-distorted structure (147.8° between ZrN$_2$ planes) is 11.2 kcal mol$^{-1}$ more stable than the planar structure found in the solid state, and Raman spectroscopy provides evidence that a butterfly-distorted conformation of the compound exists in solution. Like 4.1, ([PNP]Zr(O-2,6-Me$_2$C$_6$H$_3$)$_2$(µ-η$^2$:η$^2$-N$_2$) ([PNP] = [(Pr$_2$PCH$_2$SiMe$_2$)$_2$N]) is butterfly-distorted (152.6° between ZrN$_2$ planes) (Figure 4.7), with two halves of the dinuclear complex equivalent, and N$_2$ bonds to Zr with two different Zr--N bond lengths (2.034(4) and 2.082(4) Å). Also, a singlet is apparent in the $^{31}$P{¹H} NMR spectrum of the complex, implying that if the butterfly...
distortion exists in solution, a fluxional process lets \( \text{N}_2 \) experience both sides of the Zr---Zr axis.

**Figure 4.7.** Structure of \{[PNP]Zr(O-2,6-Me_2C_6H_3)}_2(\mu-\eta^2:\eta^2-N_2).\]

Complex 4.1 resembles \{[NPN]Zr(THF)}_2(\mu-\eta^2:\eta^2-N_2), reported by the Fryzuk group in 2005.\(^9\) This dark purple complex forms in high yield from the reaction of 2.2 equivalents of KC\(_8\) with [NPN]ZrCl\(_2\)(THF) under 1 or 4 atm of \( \text{N}_2 \). Like 4.1, there is a singlet in the \(^{31}\text{P}\{^1\text{H}\} \) NMR spectrum (\( \delta \) —5.6) and the complex appears to have \( \text{C}_{2h} \) symmetry in solution. In the solid state, one [NPN] and one THF ligand coordinate to each Zr, and \( \text{N}_2 \) is bound side-on to two Zr centres. The N—N bond is 1.503(3) Å, identical to that of 4.1, and the other bond lengths and angles are similar between the two structures. The Zr-N\(_2\)-Zr core is planar, not butterfly-distorted, in \{[NPN]Zr(THF)}_2(\mu-\eta^2:\eta^2-N_2).\]

Compared to other side-on bound Zr-N\(_2\) complexes, 4.1 and \{[NPN]Zr(THF)}_2(\mu-\eta^2:\eta^2-N_2) have long N—N bonds, although neither are as long as the N—N bond in \{[PNP]ZrCl\}_2(\mu-\eta^2:\eta^2-N_2) (1.548(7) Å), which contains the longest intact N—N bond observed for a metal complex.\(^{34}\) (Cp''\(_2\)Zr)}\_2(\mu-\eta^2:\eta^2-N_2) (Cp'' = 1,3-(SiMe\(_3\))\_2-\eta^2-C_5H_4) has a similar N—N bond length to 4.1, within error, at 1.47(3) Å.\(^{12}\) Other side-on bound Zr-N\(_2\)
complexes contain somewhat shorter N–N bonds: \([\{[\text{P}_2\text{N}_2]\text{Zr}\}_2(\mu-\eta^2:\eta^2-\text{N}_2)\)}\) (1.43(1) \(\text{Å}\))^8, \([\{\text{η}^5-\text{C}_3\text{Me}_3\text{H}\text{Zr}\}_2(\mu-\eta^2:\eta^2-\text{N}_2)\} (1.377(3) \text{Å})\]^9, and \([\text{rac-BpZr}_2(\mu-\eta^2:\eta^2-\text{N}_2)\]) (1.241(3) \text{Å})^{10} and are discussed in detail in chapter one.

4.2.2 Synthesis and structure of \([^\{\text{NPN}\}^*\text{Zr(Py)}\}_2(\mu-\eta^2:\eta^2-\text{N}_2)\].

The pyridine adduct of the \(\text{Zr}_2\text{N}_2\) complex, \([^\{\text{NPN}\}^*\text{Zr(Py)}\}_2(\mu-\eta^2:\eta^2-\text{N}_2)\], 4.2, can be prepared from 4.1 and excess Py in \(\text{C}_6\text{H}_6\) solution (Equation 4.2). The dark evergreen complex appears to form instantly, and is isolated in high yield as a dark green powder upon work-up. In contrast to 4.1, complex 4.2 can be stored under vacuum for several hours without any noticeable decomposition, possibly because Py is bound more tightly to Zr than THF is. The results of combustion analysis of 4.2 are consistent with the formula given, and a peak corresponding to \([\text{M} – \text{Py}]^+\) is apparent in the mass spectrum.

There is a singlet in the \(^{31}\text{P}\{^1\text{H}\}\} \text{NMR spectrum of 4.2 in } \text{C}_6\text{D}_6 \text{at } \delta 6.0, \text{and the } ^1\text{H} \text{ and } ^{13}\text{C}\{^1\text{H}\}\) NMR spectra are also consistent with the \(\text{C}_{2\text{h}}\) symmetric structure proposed. In the \(^1\text{H}\) NMR spectrum (Figure 4.8), there are three singlets at \(\sim \delta 2.0\) assigned to \(\text{ArCH}_3\) groups; although four singlets should appear based on the symmetry of the complex, the singlet at \(\delta 2.03\) integrates to 24H, indicating that two of the \(\text{ArCH}_3\) groups have accidental
magnetic equivalence. In the $^{13}$C($^1$H) NMR spectrum, the expected four distinct ArCH$_3$ resonances are apparent. The aromatic regions of the $^1$H and $^{13}$C($^1$H) NMR spectra contain the expected peaks for Py and [NPN]$^\ast$.

Figure 4.8. 500 MHz $^1$H NMR spectrum of 4.2 in C$_6$D$_6$.

$$\text{ArCH}_3$$

ArH and PyH

--- ArH and PyH ---

7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0

Figure 4.8. 500 MHz $^1$H NMR spectrum of 4.2 in C$_6$D$_6$.

$$\{[\text{NPN}]^\ast\text{Zr(Py-$d_5$)}\}_2(\mu-\eta^2:\eta^2-\text{N}_2), \text{4.2-$d_{10}$}$$ can be prepared from 4.1 and Py-$d_5$ by the same method used to prepare 4.2. The singlet in the $^{31}$P($^1$H) NMR spectrum is at $\delta$ 6.0, not shifted from that of 4.2. The $^1$H NMR spectrum of 4.2-$d_{10}$ in C$_6$D$_6$ is nearly identical to that of 4.2, except that the multiplet at $\delta$ 7.12 and the triplet at $\delta$ 6.55 are absent, and the multiplet at $\delta$ 6.01 integrates to only 4H. Thus, these resonances are assigned to coordinated Py in 4.2. There is a peak assigned to [M – Py-$d_5$]$^+$ in the mass spectrum. $^{15}$N-labelled $$\{[\text{NPN}]^\ast\text{Zr(Py)}\}_2(\mu-\eta^2:\eta^2-^{15}\text{N}_2), \text{4.2-$^{15}$N}_2$$, can be prepared from 4.1-$^{15}$N$_2$ and Py in C$_6$H$_6$.
solution. There is a 1:3:1 triplet at δ 6.0 in the $^{31}$P{1H} NMR spectrum of 4.2-$^{15}$N$_2$ that corresponds to an AXX' (each $^{31}$P nucleus couples to two magnetically inequivalent $^{15}$N nuclei) spin system with $^2J_{PN} = 7$ Hz, and $^2J_{PN'} = 3$ Hz. A multiplet appears at δ 118.2 in the $^{15}$N{1H} NMR spectrum that corresponds to an AA'XX' spin system with $^2J_{NP} = 7$ Hz, $^2J_{NP'} = 3$ Hz, and $^1J_{NN'} = 2$ Hz. As for 4.1, the magnetic inequivalence of the two $^{31}$P and two $^{15}$N nuclei indicates that N$_2$ does not freely rotate about the Zr---Zr axis in 4.2.

The ORTEP representation of the solid-state molecular structure of 4.2 is shown in Figure 4.9, along with selected bond lengths and angles. Two views of the arrangement of N and P donors around Zr are shown in Figure 4.10. The dinuclear structure is similar to that observed for 4.1. The N–N bond length is 1.481(5) Å, about the same as the N–N bond length observed for 4.1, within error. Similar to 4.1, there are two sets of similar length Zr–N bonds: the Zr1–N5 and Zr2–N6 bond lengths average to 2.00 Å, and the Zr1–N6 and Zr2–N5 bond lengths average to 2.09 Å. Thus, the N$_2$ unit is slightly canted: the N–N bond is not exactly perpendicular to the Zr---Zr axis. One Py is coordinated to each Zr, and the Zr1–N7 and Zr2–N8 bonds to Py are the same within error at about 2.44 Å. These are within the expected range, but are slightly longer than the Zr–N bond to Py in [NPN]$^*$ZrCl$_2$(Py) 2.13, which is 2.3889(16) Å, and may be due to the trans influence of the P donor in 4.2. The bond lengths and angles between [NPN]$^*$ and Zr are similar to those in 4.1 and the other [NPN]$^*$Zr complexes reported here. There is a butterfly distortion in the Zr$_2$N$_2$ core: the two ZrN$_2$ planes meet at a 168° angle.
Figure 4.9. ORTEP drawing of the solid-state molecular structure of $\{[\text{NPN}]^+\text{Zr(Py)}\}_2(\mu-\eta^2:\eta^2-\text{N}_2)$, 4.2 (ellipsoids drawn at the 50% probability level). Carbon atoms of the proximal Mes substituents (except C$_{\text{Mes}}$) and all hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Zr1–P1 2.6699(12), Zr1–N1 2.203(4), Zr1–N2 2.166(4), Zr1–N5 2.002(4), Zr1–N6 2.092(4), Zr1–N7 2.448(4), Zr2–P2 2.6725(12), Zr2–N3 2.172(4), Zr2–N4 2.218(4), Zr2–N5 2.097(4), Zr2–N6 2.011(4), Zr2–N7 2.441(4), N5–N6 1.481(5), N5–Zr1–N6 42.33(14), N6–Zr2–N5 42.19(14), P1–Zr1–N7 156.80(9), N1–Zr1–N2 109.51(14), N7–Zr1–N5 119.68(13).
Complex 4.2 resembles $\{[\text{NPN}]\text{Zr(Py)}\}_2(\mu-\eta^2:\eta^2-\text{N}_2)$, previously prepared in the Fryzuk group.\textsuperscript{36} This dark green complex is synthesized from the bright purple THF adduct $\{[\text{NPN}]\text{Zr(THF)}\}_2(\mu-\eta^2:\eta^2-\text{N}_2)$, and appears $C_{2v}$ symmetric in solution and in the solid state. The solid-state molecular structure of the complex confirms that one Py is coordinated to each Zr and that N\textsubscript{2} is coordinated side-on to two Zr atoms, as is observed for the THF adduct. The two Py molecules adopt a trans configuration about the Zr---Zr axis. The N---N bond length is 1.503(2) Å, and the N\textsubscript{2} unit is also canted with respect to the Zr---Zr axis: Each Zr atom has a 2.0453(14) Å and a 2.0819(13) Å bond to N of coordinated N\textsubscript{2}. As with the THF adduct of this complex, the Zr\textsubscript{2}N\textsubscript{2} core is planar. The other bond lengths are similar to those of 4.2.

Py is a stronger Lewis base than THF,\textsuperscript{37} so it is likely to displace THF from 4.1 in C\textsubscript{6}H\textsubscript{6} solution spontaneously. Although both 4.1 and 4.2 are intensely coloured green compounds, an instant blue-green to dark evergreen colour change is apparent when excess Py is added.

\textbf{Figure 4.10.} Two views of the stereochemistry around Zr in 4.2.
to a benzene solution of 4.1. In addition to the donor strength of Py, the synthesis of 4.2 is facilitated by the low volatility of Py: upon work-up, THF and even the solvent will be removed before Py. No evidence for an asymmetric complex such as \{[NPN]^*Zr(Py)]\}(\mu-\eta^2:\eta^2-N_2)\{Zr[NPN]^*(THF)\} is observed, although [NPN]-supported \{[NPN]Zr(Py)]\}(\mu-\eta^2:\eta^2-N_2)\{Zr[NPN](THF)\} is known.\(^3^6\) This asymmetric adduct forms along with the bis-Py and bis-THF adducts upon dissolving the bis-Py adduct in THF.

Complex 4.2 and \{[NPN]Zr(Py)]\}(\mu-\eta^2:\eta^2-N_2) have another thing in common: they can be readily prepared by the addition of Py to an \(N_2\) complex. In contrast, \{[PNP]Zr(OAr)]\}(\mu-\eta^2:\eta^2-N_2) and \{[PNP]ZrCp\}(\mu-\eta^1:\eta^1-N_2) cannot be prepared directly from \{[PNP]ZrCl]2(\mu-\eta^1:\eta^2-N_2).\(^3^3\) Instead, these complexes must be prepared by the alkali metal reduction of separately prepared precursors, such as [PNP]ZrCl2(OAr). Thus, the [NPN] and [NPN]^* ligated Zr-\(N_2\) complexes can be tuned electronically and sterically by the simple addition of a donor molecule to a solution of \{[NPN]Zr(THF)]\}(\mu-\eta^2:\eta^2-N_2) and 4.1, respectively. In addition, \{[NPN]Zr(PhCN)]\}(\mu-\eta^2:\eta^2-N_2) has been prepared and characterized in solution,\(^3^6\) and other adducts of the [NPN]-supported \(N_2\) complex, as well as many other adducts of the [NPN]^*-supported \(N_2\) complex are waiting to be synthesized.

If tuning the \{[NPN]^*Zr\}(\mu-\eta^2:\eta^2-N_2) core of 4.1 by replacing THF with other donor ligands is a major goal of this chapter, it should be determined what effect, if any, Py has on the structure of the Zr-\(N_2\) complex. In addition to comparing 4.1 to 4.2, \{[NPN]Zr(THF)]\}(\mu-\eta^2:\eta^2-N_2) (A) will be compared to \{[NPN]Zr(Py)]\}(\mu-\eta^2:\eta^2-N_2) (B). The singlets observed in the \(3^1P^\\{^1H\}\) NMR spectra of 4.1 and A shift upfield by 1 ppm for Py adducts 4.2 and B. The \(N-N\) bond lengths for all four compounds are the same, within error. The Zr–P and Zr–N (to \(N_2\)) bonds are slightly shorter (\(~0.02\ \AA\)) in A than in B,
whereas these bonds are essentially the same for 4.1 and 4.2. So far, no major differences exist among these four complexes, except for the identity of the donor itself. Thus, a comparison between 4.1 and 4.2 will not be complete until vibrational analysis and supporting DFT calculations are performed. The UV-Visible absorption spectra of 4.1 and 4.2 are provided in section 4.2.4.

4.2.3 Phosphine adducts of \(\{\text{NPN}\}^\ddagger\text{Zr}\}_2(\mu-\eta^2:\eta^2-\text{N}_2)\).

In addition to THF and Py adducts of \(\{\text{NPN}\}^\ddagger\text{Zr}\}_2(\mu-\eta^2:\eta^2-\text{N}_2)\), phosphine adducts of the \(\text{Zr}_2\text{N}_2\) complex can be readily prepared. \(\{\text{NPN}\}^\ddagger\text{Zr(PMe}_3\}_2(\mu-\eta^2:\eta^2-\text{N}_2)\{\text{Zr[NPN]}^\ddagger\), 4.3, can be prepared from 4.1 and excess PMe₃ in Et₂O solution (Equation 4.3). Upon addition of excess PMe₃ to a solution of 4.1 in Et₂O, a colour change from deep blue-green to bright emerald green is observed. Complex 4.3 is isolated as a hexanes-soluble green powder in quantitative yield upon taking the reaction mixture to dryness. As occurs with 4.1, complex 4.3 decomposes under prolonged exposure to vacuum to a beige powder that contains 2.8 and a white insoluble solid. In contrast to 4.1, 4.3 is also unstable in the solid state and can decompose spontaneously at ambient temperature or at −35 °C. Samples of 4.3 are synthesized immediately before use, or are stored for a few days in hexanes solutions with a small amount of added PMe₃ at −35 °C. Small crystals of 4.3 can be obtained from toluene/HMDSO in the presence of PMe₃ at −35 °C overnight. Unfortunately, single crystals suitable for X-ray analysis could not be obtained, due in part to the solubility of the complex in non-polar solvents, and to its tendency to decompose.
Complexes 4.1 and 4.2 are $C_{2v}$ symmetric in solution and each Zr atom is coordinated to one [NPN]* and one THF or Py molecule. In contrast, complex 4.3 appears to be asymmetric in C$_6$D$_6$ by $^{31}$P{$^1$H} NMR spectroscopy. Two doublets at $\delta$ 5.1 and $-33.1$ ($^{2}J_{PP} = 44$ Hz) and a singlet at $\delta$ 2.5, each integrating to 1P, are apparent (Figure 4.11). The downfield signals are due to coordinated [NPN]* and the signal at $-33.1$ is due to coordinated PMe$_3$. The 44 Hz coupling is consistent with two-bond P-P coupling of trans-disposed phosphines on an early transition-metal complex. Thus, the $^{31}$P{$^1$H} NMR spectrum suggests that one Zr is coordinated to [NPN]*, and the other Zr is coordinated to [NPN]* and PMe$_3$. In the $^1$H NMR spectrum, there are eight singlets due to ArCH$_3$ groups, a doublet at $\delta$ 0.27 ($^{3}J_{PH} = 6$ Hz, 9H) attributable to coordinated PMe$_3$, and ArH resonances consistent with 4.3 being a $C_s$ symmetric dimer. The absence of resonances for free or coordinated THF in the $^1$H and $^{13}$C{$^1$H} NMR spectra also supports the proposed structure.
As with Py adduct 4.2, complex 4.3 appears to form instantly in Et₂O solution because there is a blue-green to emerald green colour change upon addition of the phosphine. The choice of solvent for this reaction is critical because PMe₃ is volatile. If the reaction is carried out in toluene, 4.1 is isolated upon work-up.

Isotopically labelled 4.3-¹⁵N₂ can be readily prepared from 4.1-¹⁵N₂ and PMe₃ in Et₂O by the method used to prepare 4.3. At room temperature, the ³¹P{¹H} and ¹H NMR spectra of 4.3-¹⁵N₂ in C₆D₆ are identical to those of 4.3, whereas the ¹⁵N{¹H} NMR spectrum shows two broad singlets at δ 119.3 and 117.9. Since attempts to grow single crystals of 4.3 were hindered by its high solubility and its tendency to decompose, a different phosphine was chosen to prepare an asymmetric adduct of {[NPN]⁺Zr}₂(N₂). Benzene-soluble {[NPN]⁺Zr(PMe₂Ph)}(μ-η²:η²-N₂){Zr[NPN]⁺}, 4.4, can be prepared from 4.1 and excess PMe₂Ph in toluene solution (Equation 4.4). The complex is obtained as an emerald green
powder in 82% yield upon work-up. Complex 4.4 can be placed under vacuum for several hours without decomposition, which is necessary for the complete removal of excess PMe₂Ph.

Similar to 4.3, there are two doublets at δ 7.3 and −22.5 ($J_{PP} = 46$ Hz), and a singlet at δ 1.9 in the $^{31}$P{¹H} NMR spectrum of 4.4 in C₆D₆ (Figure 4.12). Again, the doublet at δ −22.5 is assigned to PMe₂Ph coordinated to Zr, and the downfield resonances are due to coordinated [NPN]⁺. In the ¹H NMR spectrum there are eight ArCH₃ singlets, a doublet at δ 0.80 ($J_{HP} = 6$ Hz) due to coordinated P(CH₃)₂Ph, and peaks in the ArH region consistent with the $C_s$ symmetric structure proposed for 4.4.
Figure 4.12. 162 MHz $^3$P{$^1$H} NMR spectrum of 4.4 in C$_6$D$_6$.

Isotopically labelled 4.4-$^{15}$N$_2$ can be prepared from 4.1-$^{15}$N$_2$ and PMe$_2$Ph by the same method used to prepare 4.4. The $^3$P{$^1$H} NMR spectrum of 4.4-$^{15}$N$_2$ in C$_6$D$_6$ is similar to that of 4.4, but with additional P-N coupling apparent at 253 K in toluene-$d_6$. There is a doublet of doublets of doublets at $\delta$ 7.3 ($^2$J$_{PP}$ = 46 Hz, $^2$J$_{PN}$ = 4 Hz, $^2$J$_{PN}$ = 7 Hz), a singlet at $\delta$ -1.9, and a doublet of doublets at $\delta$ -22.5 ($^2$J$_{PP}$ = 46 Hz, $^2$J$_{PN}$ = 7 Hz). It is unclear why the singlet at $\delta$ -1.9 is not split by $^{15}$N. There are two AA'XX' multiplets ($^2$J$_{NN}$ = 8 Hz, $^2$J$_{PN}$ = 4 Hz, $^2$J$_{PN}$ = 7 Hz) in the $^{15}$N{$^1$H} NMR spectrum in toluene-$d_6$ at 253 K at $\delta$ 119.0 and 118.0, each integrating to 1N.

The ORTEP representation of the solid-state molecular structure of 4.4 is shown in Figure 4.13, along with selected bond lengths and angles. Two views of the arrangement of N and P donors around Zr$^+$ are shown in Figure 4.14. As expected from the NMR spectra of the complex, 4.4 is asymmetric; there is one [NPN]$^+$ coordinated to each Zr, but Zr2 also
has a coordinated PMe₂Ph. The N–N bond length is 1.488(2) Å, the same as that in 4.1, within error. The Zr–P bond lengths to [NPN]⁺ (Zr₁–P₁ 2.6967(6), Zr₂–P₂ 2.6445(6) Å) are similar to those of 4.1 and 4.2, but the Zr₂–P₃ bond length to PMe₂Ph is much longer at 2.9139(6) Å. The Zr₂–P₃ bond length is similar to other long Zr–P bonds to tertiary phosphines reported in the literature. Unlike in 4.1 and 4.2, three of the Zr–N bond lengths to N₂ are similar (Zr₁–N₃, Zr₁–N₄, and Zr₂–N₃ average to ~2.04 Å) and the Zr₂–N₄ bond is longer (2.1153(17) Å), possibly due to the steric influence of PMe₂Ph. As with 4.1 and 4.2, there is a butterfly distortion between the two ZrN₂ planes of 165° in the C₁ symmetric solid-state structure. P₁ and P₂ are staggered across the Zr---Zr axis (P₁–Zr₁–Zr₂–P₂ torsion angle is 179.9°), whereas P₁ and P₃ are nearly eclipsed (P₁–Zr₁–Zr₂–P₃ torsion angle is 7.8°). Since 4.4 is C₁ symmetric in solution, the Zr₂N₂ core is either planar, or there is a fluxional process that allows N₂ to sample both sides of the Zr---Zr axis on the NMR timescale.
Figure 4.13. ORTEP drawing of the solid-state molecular structure of 
{[NPN]^+Zr(PMe2Ph)}\(\mu\cdot\eta^2:\eta^2\cdot\text{N}_2\)__4.4 (ellipsoids drawn at the 50% probability level). Carbon atoms of the proximal Mes substituents (except C\(_{\phi\psi}\)) and all hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Zr1–P1 2.6967(6), Zr2–P2 2.6445(6), Zr1–N1 2.1370(18), Zr1–N2 2.1689(18), Zr2–N5 2.1818(18), Zr2–N6 2.1747(17), Zr1–N3 2.0450(17), Zr1–N4 2.0315(17), Zr2–N3 2.0371(18), Zr2–N4 2.1153(17), Zr2–P3 2.9139(6), N3–N4 1.488(2), N3–Zr1–N4 42.83(7), Zr1–N3–Zr2 137.18(9), P2–Zr2–P3 166.605(19), P1–Zr1–N4 94.18(5), P1–Zr1–N3 136.91(5), P1–Zr1–N1 71.28(5), P1–Zr1–N2 75.25(5), N1–Zr1–N3 118.84(7), N1–Zr1–N4 115.84(7).
The solid-state molecular structure of 4.4 provides some clue as to why only one phosphine donor is coordinated in 4.3 and 4.4. From Figure 4.14, it appears as though the coordination of PMe₂Ph to Zr₂ pushes the [NPN]⁺ ligand on Zr₁ away. The new position of the NMes substituents of [NPN]⁺ on Zr₁, and the PPh substituent of [NPN]⁺ on Zr₂ effectively block a second equivalent of PMe₂Ph from coordinating to Zr₁. Complex 4.4 appears to be the first dinuclear Zr-N₂ complex characterized in the solid state with different coordination environments at each Zr.

4.2.4 UV-Visible spectroscopy of zirconium dinitrogen complexes.

Complexes 4.1, 4.2, and 4.4 are intensely green coloured compounds in solution and in the solid state. The UV-visible absorption spectrum of blue-green 4.1 in toluene is shown in Figure 4.15. There is one peak at 652 nm (ε = 6.1 × 10³ L mol⁻¹ cm⁻¹) and a second peak at 358 nm (ε = 1.0 × 10⁴ L mol⁻¹ cm⁻¹). It should be noted that ε values are approximate for
these complexes because the dilute solutions become less intensely coloured over several
hours under N₂ in Teflon-sealed cuvettes as they react with trace O₂ and H₂O in the solvent.
By analogy with the UV-visible absorption spectrum of ([P₂N₂]Zr)₂(μ-η²:η²-N₂),³² the peak at
652 nm is tentatively assigned to a charge-transfer (CT) transition from the π* MO of N₂⁺ to
a d orbital of Zr(IV), and the peak at 358 nm is assigned to a CT from the π* MO of N₂⁺ to
a higher energy d orbital of Zr(IV). Similarly, absorption maxima in the UV-visible
absorption spectrum of evergreen-coloured 4.2 in toluene solution (Figure 4.16) at 736 nm
(ε = 6.1 × 10³ L mol⁻¹ cm⁻¹) and 366 nm (ε = 1.0 × 10⁴ L mol⁻¹ cm⁻¹) are assigned to N₂ π*
→ Zr(IV) d CT transitions. There is also a shoulder on the high energy CT band at 401 nm
(ε = 6.6 × 10³ L mol⁻¹ cm⁻¹), as well as a smaller peak at 504 nm (ε = 2.2 × 10³ L mol⁻¹ cm⁻¹)
that have not been assigned, but are similar to features observed in the spectrum of
([P₂N₂]Zr)₂(μ-η²:η²-N₂). There are two peaks in the UV-visible absorption spectrum of green
4.4 in toluene solution (Figure 4.17) at 699 nm (ε = 9.7 × 10³ L mol⁻¹ cm⁻¹), and 363 nm (ε =
1.1 × 10⁴ L mol⁻¹ cm⁻¹) also tentatively assigned to N₂ → Zr CT transitions. The UV-visible
absorption spectra of 4.1, 4.2, and 4.4 are similar to other group 4 dinitrogen complexes
(Table 4.1).
Figure 4.15. UV-visible absorption spectrum of 4.1 in toluene.

Figure 4.16. UV-visible absorption spectrum of 4.2 in toluene.
Figure 4.17. UV-visible absorption spectrum of 4.4 in toluene.

Table 4.1. UV-visible absorption maxima of some Group 4 N₂ complexes in toluene.

<table>
<thead>
<tr>
<th>N₂ complex</th>
<th>λₘₐₓ (nm)</th>
<th>ε (× 10³ L mol⁻¹ cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>652, 358</td>
<td>6.1, 10</td>
</tr>
<tr>
<td>4.2</td>
<td>736, 401, 366</td>
<td>6.1, 6.6, 10</td>
</tr>
<tr>
<td>4.4</td>
<td>699, 363</td>
<td>9.7, 11</td>
</tr>
<tr>
<td>[(P₃N₅)₂Zr]₂(µ-η²:η²-N₂)ₗ</td>
<td>670, 455, 390</td>
<td>c</td>
</tr>
<tr>
<td>[(rac-Bp)Zr]₂(µ-η²:η²-N₂)ₗ</td>
<td>612, 392</td>
<td>c</td>
</tr>
<tr>
<td>[(η°-C₅Me₅)ₗ₂Zr]ₗ(µ-η²:η²-N₂)ₗ</td>
<td>648, 351</td>
<td>c, 3.7</td>
</tr>
<tr>
<td>[(η°-C₅Me₅)ₗ₂Hf]ₗ(µ-η²:η²-N₂)ₗ</td>
<td>886, 553</td>
<td>6.5, 0.38</td>
</tr>
</tbody>
</table>

a: Ref. 31; b: (rac-Bp = Me₂Si(-2-Me₃Si-4'-Bu-C₅H₅)₂) Ref. 34; c: not reported; d: Ref. 19; e: Ref. 16B.

4.2.5 Attempted synthesis of a hafnium dinitrogen complex.

When the conditions used to prepare 4.1 are replicated in an attempt to prepare a hafnium-dinitrogen compound from [NPN]⁺HfI₂ (2.15) and KC₆, the formation of a toluene-soluble brown solid is observed. The brown solid has not been characterized, as it
could not be separated from \([\text{NPN}]^+\text{H}_2 (2.8)\). Only peaks due to 2.8 are apparent by NMR spectroscopy and EI-MS. The brown product may be paramagnetic, and higher molecular weight peaks may not be apparent by EI-MS because any Hf complexes that are present are thermally sensitive, or not volatile enough for this technique. When 2.15 is stirred with Na/Hg amalgam in toluene solution under 1 atm of \(\text{N}_2\) at ambient temperature, a deep red-brown colour forms over four weeks. After one week, signals attributable to multiple products can be seen in the \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum, including a small peak at \(\delta 3.5\). After four weeks, the peak at \(\delta 3.5\) and a peak due to 2.8 represent the major products of the reaction. Unfortunately, 2.8 could not be removed completely from the red-brown solids.

If 2.15 is stirred over Na/Hg amalgam in THF under 4 atm of \(\text{N}_2\), a slow colour change from orange to yellow-green is observed over three weeks. According to \(^{31}\text{P}\{^1\text{H}\}\) NMR spectroscopy, the major product is characterized by a singlet at \(\delta -10.6 (62\%)\). There are also minor products at \(\delta -3.1 (16\%), -6.9 (10\%),\) and \(-10.5 (12\%).\) Attempts to purify the major product are currently ongoing, however, there is no evidence that the mixture contains a Hf-\(\text{N}_2\) complex.

While there are quite a few examples of Zr-\(\text{N}_2\) complexes, the synthesis of Hf-\(\text{N}_2\) complexes remains a challenge. In 1985, the first Hf dinitrogen complex, \([\text{Cp}^*\text{Hf} (\text{N}_2)]_2 (\mu-\text{N}_2)\), was prepared from \(\text{Cp}^*\text{HfI}_2\) and Na/K alloy in 20% yield. Unfortunately, the product has not been crystallographically characterized. Although the reduction of \([\text{P}_2\text{N}_2]\text{HfI}_2\) with \(\text{KC}_8\) yields \(\{[\text{P}_2\text{N}_2]\text{Hf}\}_2 (\text{N}_2)\) by EI-MS, and hydrazine is obtained upon addition of HCl to the product, the complex could not be purified or characterized in the solid state. The reduction of \(\{\eta^5-\text{C}_5\text{Me}_4\text{H}\}_2\text{HfI}_2\) with Na/Hg amalgam yields \(\{\eta^5-\text{C}_5\text{Me}_4\text{H}\}_2\{\mu-\eta^2:\eta^2-\text{N}_2\}\), in which \(\text{N}_2\) is bound side-on to two Hf centres with an N-N bond length of 1.423(11) Å.
This complex reacts with H₂ to give \{((\eta^5-C_5Me_4H)_2Hf(H))_2(\mu-\eta^2:\eta^2-N_2H_2)\}, as was observed for the Zr congener. Hafnium diiodides have been used as starting materials for Hf-N₂ complexes because the analogous hafnium dichloride complexes contain strong Hf-Cl bonds that are unreactive in the presence of strong reducing agents. Hf-I and Zr-I bonds have similar bond dissociation enthalpies, but Zr(IV) complexes are easier to reduce than corresponding Hf(IV) complexes.

4.3 Conclusions.

In this chapter, the synthesis of a new arene-bridged zirconium dinitrogen complex, \{[NPN]^*Zr(THF)\}_2(\mu-\eta^2:\eta^2-N_2)\}, is reported. The deep blue-green compound has been characterized in solution and in the solid state. By $^{31}$P{\textsuperscript{1}H}, $^1$H, and $^{13}$C{\textsuperscript{1}H} NMR spectroscopies, the dinuclear complex is $C_{2v}$ symmetric with one THF and one [NPN]^* coordinated to each Zr. The solid-state molecular structure of the complex shows that N₂ is coordinated side-on to two Zr atoms with an N–N bond length of 1.503(6) Å. N₂ is formally N₂⁺, or hydrazide, in the complex.

Adducts of the Zr-N₂ complex can be prepared easily by adding Py, PMe₃, or PMe₂Ph to a solution of \{[NPN]^*Zr(THF)\}_2(\mu-\eta^2:\eta^2-N_2)\}. The addition of excess Py to this complex provides \{[NPN]^*Zr(Py)\}_2(\mu-\eta^2:\eta^2-N_2)\} in high yield as a dark green powder. The complex is $C_{2v}$ symmetric in solution by $^{31}$P{\textsuperscript{1}H}, $^1$H and $^{13}$C{\textsuperscript{1}H} NMR spectroscopies. The solid-state molecular structure shows that N₂ is coordinated side-on to two Zr atoms, as expected. In fact, the only major difference between the structure of the THF adduct and that of the Py adduct is the identity of the donor. The N–N bond lengths are the same within error, and both structures show a similar butterfly distortion between the ZrN₂ planes.
The addition of excess PMe$_3$ or PMe$_2$Ph to $\{[\text{NPN}]^\ast\text{Zr(THF)}\}_2(\mu-\eta^2:\eta^2-N_2)$ provides $\{[\text{NPN}]^\ast\text{Zr}(\text{PMe}_2\text{R})\}(\mu-\eta^2:\eta^2-N_2)\{\text{Zr}[\text{NPN}]^\ast\}$ (R = Me, Ph) as a bright green powder in high yield. In solution, the PMe$_2$R adducts are C$_s$ symmetric with one Zr atom coordinated to N$_2$, [NPN]$^\ast$ and PMe$_2$Ph, and the other coordinated to N$_2$ and [NPN]$^\ast$. The solid-state molecular structure of the PMe$_2$Ph adduct confirms that only one PMe$_2$Ph is coordinated to the dimeric species, and that N$_2$ is side-on bound to two Zr atoms. As with the THF and Py adducts, the N–N bond length indicates that an N–N single bond is present, and the N$_2$ unit is butterfly-distorted relative to the Zr–Zr axis. The synthesis of $\{[\text{NPN}]^\ast\text{Zr(Py)}\}_2(\mu-\eta^2:\eta^2-N_2)$ and $\{[\text{NPN}]^\ast\text{Zr(PMe}_2\text{Ph})\}(\mu-\eta^2:\eta^2-N_2)\{\text{Zr}[\text{NPN}]^\ast\}$ from $\{[\text{NPN}]^\ast\text{Zr(THF)}\}_2(\mu-\eta^2:\eta^2-N_2)$ represents a simple, high-yield route to side-on N$_2$ complexes with new donor groups.

4.4 Experimental.

4.4.1 General experimental.

General experimental conditions are as given in chapter two. Flasks sealed under N$_2$ gas at liquid-nitrogen temperature reach a pressure of 4 atm at rt. Only thick-walled Teflon-sealed Kontes glassware should be used for these procedures. Reaction mixtures should be thawed completely behind a blast shield and handled with great care whenever the flask must be removed from behind the shield. Warming solutions slowly to rt in a liquid-N$_2$/EtOH slurry may minimize shock to the flask upon thawing. $^{15}$N{$^1$H} NMR spectra were recorded on a Bruker AV-400 direct detect spectrometer operating at 400.1 MHz for $^1$H NMR spectra and were referenced externally to MeNO$_2$ at $\delta$ 0. $^{15}$N-labelled complexes were isolated and handled under unlabelled N$_2$. UV-visible spectra were recorded on a Varian/Cary 5000 UV-Vis spectrometer using a 1 cm cuvette. For UV-vis spectra, the compound was dissolved in
toluene (dried according to the procedure outlined in chapter two, then stirred over sodium sand for one hour in an N₂-filled glovebox, and filtered through Celite), and the solution was transferred to a Teflon-sealed Kontes UV-Vis cuvette.

4.4.2 Starting materials and reagents.

Tetrahydrofuran was purified as usual, stored over purple sodium benzophenone ketyl indicator and degassed by three freeze-pump-thaw cycles prior to use. Pyridine was dried over CaH₂ and distilled under N₂ prior to use. Potassium graphite (KC₈) was prepared according to literature methods. Trimethylphosphine and dimethylphenylphosphine were purchased from Strem Chemical Ltd. and used without further purification. ¹⁵N₂ gas (isotopic purity 98+%, 1 or 2 litres) was purchased from Cambridge Isotopes Ltd. in a small carbon steel lecture bottle and used as received. Mercury was purified according to literature methods. Sodium amalgam was prepared immediately before use in a nitrogen atmosphere, and was washed with toluene until the washings were clear and colourless.

\([\text{[NPN]}^+\text{Zr(THF)}]_2(\mu-\eta^2:\eta^2-\text{N}_2)\) (4.1). Compound 2.10 (1.00 g, 1.40 mmol) and KC₈ (0.414 g, 3.07 mmol) were added to a 400-mL thick-walled bomb and shaken to mix thoroughly. THF (10 mL) was vacuum-transferred to the mixture at 77 K. The flask was filled with N₂ gas at 77 K, sealed, and warmed slowly to rt in a liquid-N₂/EtOH slurry behind a blast shield. As soon as the mixture had melted, it was stirred vigorously. The flask was periodically inverted to coat the walls of the flask with the concentrated reaction mixture. The solution turned purple after 2 h, and bright blue-green after 5 h, and was stirred overnight. The suspension was diluted with THF (10 mL), and filtered through Celite. The Celite was washed with additional THF (~10 – 20 mL). The filtrate was concentrated under
vacuum to about 5 – 10 mL. The deep blue-green solution was layered with pentane (50 mL) and chilled to −35 °C. The black crystals that formed were collected on a frit, washed with pentane (5 mL), and dried under vacuum for 15 min. (0.802 g, 0.548 mmol, 79%). Storing crystals of 4.1 under vacuum overnight gave a white powder that contained benzene-soluble and -insoluble fractions. Crystals of 4.1 suitable for X-ray analysis were grown in a large Teflon-sealed bomb by vapour diffusion of hexanes into a concentrated benzene/THF solution of the compound in an NMR tube over 3 weeks.

$^1$H NMR (THF-$d_8$, 500 MHz): $\delta = 7.42$ (t, 4H, 7.5 Hz), 7.22 (m, 6H), 7.08 (d, 4H, 7.5 Hz), 6.82 (s, 4H), 6.73 (s, 4H), 6.64 (d, 4H, 8.5 Hz), and 5.43 (dd, 4H, $J_{HH} = 8$ Hz, $J_{HP} = 6$ Hz) (ArH), 3.54 (bs, THF), 2.18 (s, 12H), 2.07 (s, 12H), 1.94 (s, 12H), and 1.74 (s, 12H) (ArCH$_3$), 1.69 (bs, THF).

$^{31}$P{^1}H NMR (THF-$d_8$, 202 MHz): $\delta = 5.0$ (s).

$^{13}$C{^1}H NMR (THF-$d_3$, 126 MHz): $\delta = 163.1$ (d, 11 Hz), 144.7, 137.9, 136.7, 136.4, 134.9, 134.1, 133.8, 130.0, 129.9, 128.9, 128.8, 125.1, 118.2, 117.9, and 113.7 (d, 10 Hz) (ArC), 68.2, and 26.4 (THF), 20.9, 20.4, 20.3, and 19.2 (ArCH$_3$).

EI-MS (m/z): 1432 (1, [M – N$_2$]$^+$), 1320 (2, [M – 2THF]$^+$), 541 (100, [2.8 – Me]$^+$).

Anal. Calcd. for 4.1·2THF: C$_{92}$H$_{110}$N$_6$O$_4$P$_2$Zr$_2$: C, 68.71; H, 6.89; N, 5.23; Found: C, 68.34; H, 7.24; N, 4.90.

UV-Vis (toluene) $\lambda_{\text{max}}$ (ε) = 358 (1.0 × 10$^4$), 652 (6.1 × 10$^3$) nm (L mol$^{-1}$ cm$^{-1}$).

**Reduction of [NPN]$^+$ZrCl$_2$ in the absence of N$_2$.** Using the procedure outlined for the synthesis of 4.1, THF (10 mL) was transferred to a mixture of [NPN]$^+$ZrCl$_2$ (0.350 g, 0.488 mmol) and KC$_8$ (0.145 g, 1.07 mmol) at 77 K, and the flask was evacuated and sealed. The
reaction mixture was a brown suspension while warming to rt. The mixture was stirred overnight, the pressure was vented, and an aliquot of the reaction mixture was analyzed by $^{31}$P{$^1$H} NMR spectroscopy. The reaction mixture was filtered, and the filtrate was concentrated and layered with pentane, but no crystals were obtained. After 2 d, the brown solution was taken to dryness to obtain a brown powder. $^{31}$P{$^1$H} NMR spectroscopy indicated the reaction mixture and solid obtained upon work-up had the same composition.

$^{31}$P{$^1$H} NMR (C$_6$D$_6$, 202 MHz): $\delta = 20.3$ (s, ~5%), 17.9 (s, ~5%), −14.6 (s, ~30%), −15.4 (s, ~40%), −31.4 (s, ~20%).

$[^{31}P]^{1}\text{Zr(THF)}_2(\mu-\eta^2:\eta^2-^{15}\text{N}_2)$ (4.1-^{15}\text{N}_2). Complex 4.1-^{15}\text{N}_2 (0.254 g, 0.173 mmol, 83%) was prepared from 2.10 (0.321 g, 0.448 mmol) and KC$_8$ (0.133 g, 0.985 mmol) in a 200-mL Teflon-sealed bomb by the same general method used to prepare 4.1. After vacuum-transferring THF (5 mL) to the flask at 77 K, the sealed, frozen flask was connected to a lecture bottle of $^{15}\text{N}_2$ gas (1 L, 1 – 2 atm pressure) via a small transfer bridge. The apparatus was evacuated and backfilled three times, the flask containing the frozen solution was opened, and the entire apparatus was evacuated and then closed to the Schlenk line. The lecture bottle was slowly opened in the closed system. The flask was warmed to rt in a liquid-$\text{N}_2$/EtOH slurry (4 atm $\text{N}_2$) behind a blast shield with vigorous stirring. The $^1$H NMR spectrum was the same as for 4.1.

$^{31}$P{$^1$H} NMR (THF-d$_6$, 162 MHz): $\delta = 5.0$ (d, $^2J_{PN} = 6.7$ Hz).

$^{15}$N{$^1$H} NMR (THF-d$_6$, 40 MHz): $\delta = 116.6$ (d, $^2J_{PN} = 6.7$ Hz).

EI-MS (m/z): 1432 (8, [M − $\text{N}_2$]$^+$), 1322 (6, [M − 2THF]$^+$), 541 (100, [2.8 − Me]$^+$).

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\text{[\{NPN\}^+Zr(Py)\}_2(\mu-\eta^2:\eta^2-N_2)\ (4.2). To a stirred blue-green suspension of 4.1 (0.815 \text{ g}, 0.557 \text{ mmol}) in C_6H_6 (15 \text{ mL}) was added Py (0.98 \text{ g}, 1.0 \text{ mL}, 12 \text{ mmol}) dropwise. The solution turned dark evergreen instantly. After 15 min. the reaction mixture was taken to dryness to obtain a dark green powder that was suspended in hexanes, collected on a frit, rinsed with hexanes (5 \text{ mL}), and dried (0.723 \text{ g}, 0.489 \text{ mmol}, 88\%). Large black crystals suitable for X-ray analysis were grown by slow evaporation of a benzene solution of the compound in an NMR tube.

^1H NMR (C_6D_6, 500 MHz): \delta = 7.55 \text{ (bm, 4H), 7.45 (d, 4H, 6 Hz), 7.12 (m, 4H, Py), 6.84 (d, 4H, 8 Hz), 6.77 (s, 4H), 6.65 (bs, 6H), 6.55 (t, 2H, 8 Hz, Py), and 6.47 (s, 4H) (ArH), 6.00 (m, 8H, ArH and Py), 2.23 (s, 12H), 2.11 (s, 12H), and 2.03 (s, 24H) (ArCH_3).

^31P{^1H} NMR (C_6D_6, 202 MHz): \delta = 6.0 \text{ (s)}.

^13C{^1H} NMR (C_6D_6, 126 MHz): \delta = 162.7 \text{ (d, 33 Hz), 149.9, 143.9, 137.3, 136.8, 136.0, 134.6, 133.7, 133.2, 133.0, 129.6, 129.5, 128.3, 127.6 (d, 8 Hz), 127.5, 125.6, 125.1, 121.9, and 114.0 (d, 10 Hz) (ArC), 20.8, 20.4, 20.1, and 19.3 (ArCH_3).

EI-MS (m/\chi): 1399 (30, [M – Py]^{+}), 1320 (30, [M – 2Py]^{+}), 541 (100, [2.8 – Me]^{+}).

Anal. Calcd. for C_{86}H_{88}N_8P_2Zr_2: C, 69.88; H, 6.00; N, 7.58; Found: C, 70.20; H, 6.31; N, 7.20.

UV-Vis (toluene) \lambda_{max} (\epsilon) = 366 (1.0 \times 10^4), 401 (6.6 \times 10^3), 504 (2.2 \times 10^3), 736 (6.1 \times 10^3) \text{ nm (L mol}^{-1} \text{ cm}^{-1}).

\text{[\{NPN\}^+Zr(Py-d_5)\}_2(\mu-\eta^2:\eta^2-N_2)\ (4.2-d_5). Complex 4.2-d_5 was prepared in the same manner as 4.2 from 4.1 (0.290 g, 0.198 mmol) and Py-d_5 (0.53 g, 0.50 mL, 6.3 mmol) in C_6H_6 (5 \text{ mL}), and was isolated as a moss green powder (0.270 g, 0.181 mmol, 91\%). The ^31P{^1H} and ^13C{^1H} NMR spectra are the same as those of 4.2.
\(^1\text{H} \text{NMR (C}_6\text{D}_6, 500 \text{ MHz):} \delta = 7.55 (m, 4\text{H}), 7.45 (d, 4\text{H}, 7 \text{ Hz}), 6.84 (d, 4\text{H}, 8 \text{ Hz}), 6.77 (s, 4\text{H}), 6.65 (bs, 6\text{H}), 6.46 (s, 4\text{H}), \text{and } 6.01 (dd, 4\text{H}, J_{\text{HP}} = 6 \text{ Hz}, J_{\text{HH}} = 8 \text{ Hz}) (\text{ArH}), 2.23 (s, 12\text{H}), 2.11 (s, 12\text{H}), \text{and } 2.03 (s, 24\text{H}) (\text{ArCH}_3).

EI-MS (m/\chi): 1404 (10, [M – (Py-d\text{5})]^+) , 1320 (15, [M – 2(Py-d\text{5})]^+), 541 (100, [2.8 – Me]^+).

\{[\text{NPN}]^*\text{Zr(Py)}\}_2(\mu-\eta^2:\eta^2-\text{N}_2) \ (4.2-\text{N}_2). \text{ Complex 4.2-\text{N}_2 was prepared in the same manner as 4.2 from 4.1-\text{N}_2 (0.150 g, 0.102 mmol) and Py (0.24 g, 0.25 mL, 3.0 mmol) in C}_6\text{H}_6 (3 \text{ mL}), \text{ and was isolated as a dark green powder (0.129 g, 0.087 mmol, 85\%). The} \ ^1\text{H} \text{ NMR spectrum was the same as that of 4.2.}

\(^{31}\text{P}\{^1\text{H}\} \text{NMR (C}_6\text{D}_6, 161 \text{ MHz):} \delta = 6.0 (\text{AXX’ triplet } 2J_{\text{PP}} = 6 \text{ Hz}, 2J_{\text{PN}} = 3 \text{ Hz}).

\(^{15}\text{N}\{^1\text{H}\} \text{NMR (C}_6\text{D}_6, 40 \text{ MHz):} \delta = 118.2 (\text{AA’XX’ multiplet, } 2J_{\text{NP}} = 7 \text{ Hz}, 2J_{\text{NP’}} = 3 \text{ Hz, } 1J_{\text{NN’}} = 2 \text{ Hz}).

EI-MS (m/\chi): 1322 (10, [M – 2Py]^+), 541 (100, [2.8 – Me]^+).

\{[\text{NPN}]^*\text{Zr(PMe}_3\text{)}\}_2(\mu-\eta^2:\eta^2-\text{N}_2)\{\text{Zr[NPN]}^*\} \ (4.3). \text{ Et}_2\text{O (5 mL) and 4.1 (0.320 g, 0.221 mmol) were mixed and chilled to –35 °C. To the stirred solution was added PMe}_3\ (0.52 g, 0.60 mL, 6.9 mmol) in Et}_2\text{O (3 mL), and the mixture turned clear bright green instantly. After 30 min, the reaction mixture was taken to dryness to obtain a green powder (0.306 g, 0.219 mmol, 99\%). A sample of 4.3 for microanalysis was recrystallized from toluene, with a few drops of PMe}_3 added, layered with (Me}_3\text{Si})_2\text{O (HMDSO) at –35 °C. The supernatant liquid was decanted, and the microcrystalline solid was rinsed with pentane and dried under vacuum for 5 min.}
\(^1\)H NMR (C\(_6\)D\(_6\), 400 MHz): \(\delta = 7.82\) (m, 4H), 7.56 (d, 2H, 8 Hz), 7.37 (d, 2H, 8 Hz), 7.27 (t, 2H, 8 Hz), 7.18 (t, 1H, 7 Hz), 7.13 (t, 1H, 7 Hz), 7.01 (t, 2H, 7 Hz), 6.94 (t, 2H, 7 Hz), 6.78 (d, 4H, 7Hz), 6.77 (s, 2H), 6.74 (s, 2H), 6.66 (s, 2H), 6.13 (dd, 2H, \(J_{HH} = 8\) Hz, \(J_{HP} = 6\) Hz), and 5.78 (dd, 2H, \(J_{HH} = 8\) Hz, \(J_{HP} = 6\) Hz) (ArH), 2.31 (s, 6H), 2.23 (s, 6H), 2.17 (s, 6H), 2.11 (s, 6H), 2.00 (s, 6H), 1.92 (s, 6H), 1.68 (s, 6H), and 1.43 (s, 6H) (ArCH\(_3\)), 0.27 (d, 9H, \(J_h = 6\) Hz, PMe\(_3\)).

\(^{31}\)P\(^{1}\)H NMR (C\(_6\)D\(_6\), 162 MHz): \(\delta = 5.1\) (d, 1P, \(J_{pp} = 44\) Hz), 2.5 (s, 1P), \(-33.1\) (d, 1P, \(J_{pp} = 44\) Hz, PMe\(_3\)).

\(^{13}\)C\(^{1}\)H NMR (C\(_6\)D\(_6\), 101 MHz): \(\delta = 162.8\) (d, 29 Hz), 159.6 (d, 25 Hz), 143.0, 141.8, 137.7, 137.1, 135.8, 134.9, 134.3, 134.1, 133.9, 133.6, 133.2, 130.7, 130.0, 129.7, 129.6, 129.3, 129.0, 128.8, 128.7, 128.6, 128.5, 128.1, 127.9, 127.0, 125.7 (d, 5 Hz), 125.6, 118.0, 117.6, 114.7 (d, 9 Hz), and 113.5 (d, 11 Hz) (ArC), 21.0, 20.9, 20.5, 20.3, 19.8, 19.7, 17.7, and 16.0 (ArCH\(_3\)), 15.4 (d, 13 Hz, PMe\(_3\)).

Anal. Calcd. for 4.3(HMDSO)\(_{0.67}\): C\(_{83}\)H\(_{99}\)N\(_6\)P\(_3\)Zr\(_2\)Si\(_{1.35}\)O\(_{0.67}\): C, 66.27; H, 6.63; N, 5.59; Found: C, 66.38; H, 6.90; N, 5.22.

\{[NPN]\(^1\)Zr(PMe\(_3\))\}(\mu-\eta^2:\eta^2-^{15}\text{N}_2)\{\text{Zr}[\text{NPN}]\}^* \quad (4.3-^{15}\text{N}_2).\) Compound 4.3-^{15}\text{N}_2 was made by the same route used to prepare 4.3, from 4.1-^{15}\text{N}_2 (0.120 g, 82 \mu\text{mol}) and PMe\(_3\) (0.26 g, 0.30 mL, 3.5 mmol) in Et\(_2\)O (5 mL). The bright green solution was taken to dryness to obtain a bright green powder (0.114 g, 82 \mu\text{mol}, 99%). The \(^{31}\)P\(^{1}\)H and \(^1\)H NMR spectra were the same as those observed for 4.3.

\(^{15}\)N\(^{1}\)H NMR (C\(_6\)D\(_6\), 40 MHz): \(\delta = 119.3\) (bs, 1N), 117.9 (bs, 1N).
(4.4). To a stirred blue-green suspension of 4.1 (0.410 g, 0.280 mmol) in toluene (10 mL) was added PMe$_2$Ph (0.250 g, 1.81 mmol). The suspension turned bright green, and was stirred at rt for 30 min. to obtain a clear, emerald green solution. The reaction mixture was taken to dryness to obtain a green residue that was triturated and taken to dryness, first with toluene (5 mL), then with hexanes (3 × 5 mL). The deep green solids obtained were suspended in pentane (5 mL), and the mixture was chilled to −35 °C overnight. The solids were collected on a frit, rinsed with hexanes (5 mL), and dried for 1 h to obtain a bright green powder (0.335 g, 0.229 mmol, 82%). Small crystals of 4.4 suitable for microanalysis were grown by slow evaporation of a benzene/HMDSO solution of the complex. Crystals of 4.4 suitable for X-ray analysis were grown by slow evaporation of a concentrated hexanes solution of the compound.

$^1$H NMR (C$_6$D$_6$, 400 MHz): $\delta = 7.79$ (t, 2H, 9 Hz), 7.74 (t, 2H, 9 Hz), 7.51 (d, 2H, 7 Hz), 7.38 (d, 2H, 8 Hz), 7.25-7.15 (m, 3H), 6.98 (m, 2H), 6.91 (t, 2H, 7 Hz), 6.79-6.65 (m, 16H), 6.12 (dd, 2H, $J_{HH} = 8$ Hz, $J_{HP} = 6.5$ Hz), and 5.77 (dd, 2H, $J_{HH} = 8$ Hz, $J_{HP} = 6.5$ Hz) (ArH), 2.28 (s, 6H), 2.19 (s, 6H), 2.16 (s, 6H), 1.98 (s, 12H), 1.92 (s, 6H), 1.67 (s, 6H), and 1.48 (s, 6H) (ArCH$_3$), 0.80 (d, 6H, $J_{HP} = 6$ Hz).

$^{31}$P$^1$H NMR (C$_6$D$_6$, 162 MHz): $\delta = 7.3$ (d, 1P, $J_{pp} = 46$ Hz), 1.9 (s, 1P), −22.5 (d, 1P, $J_{pp} = 46$ Hz, PMe$_2$Ph).

$^{13}$C$^1$H NMR (C$_6$D$_6$, 101 MHz): $\delta = 162.9$ (d, 31 Hz), 159.4 (d, 26 Hz), 141.4, 137.8, 137.5 (d, 4 Hz), 136.1, 135.4, 135.0, 134.7, 134.3, 134.2, 133.9, 133.7, 133.6, 133.5, 133.4, 133.3, 131.7, 131.4, 131.3, 130.8 (d, 8 Hz), 129.7 (d, Hz), 129.2, 129.0, 128.7 (d, 3 Hz), 128.6 (d, 3 Hz), 127.9, 127.4 (d, 7.5 Hz), 127.1 (d, 5 Hz), 125.8 (d, 5 Hz), 118.1, 117.8, 117.6, 117.2, 114.5 (d, 9 Hz), and 113.6 (d, 11 Hz) (ArC), 21.1, 21.0, 20.5, 20.3, 19.5, 19.1, 17.9, and 16.1 (ArCH$_3$), 15.6 (d, 13 Hz, PPh(CH$_3$)$_2$).

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El-MS (m/z): 1320 (8, [M - PMe2Ph]+), 541 (100, [2.8 - Me]+).

Anal. Calcd. for 4.4·(C₆H₆)(HMDSO)₁₅·C₉₉H₁₅N₆O₅Si₃P₃Zr₂: C, 66.81; H, 6.91; N, 4.72; Found: C, 67.21; H, 6.86; N, 4.35.

UV-Vis (toluene) λₘₐₓ (ε) = 363 (1.1 x 10⁶), 699 (9.7 x 10⁵) nm (L mol⁻¹ cm⁻¹).

\{[NPN]^*Zr(PPPh₂)\}(μ-η²:\eta²-¹⁵N₂){Zr[NPN]^*} (4.4-¹⁵N₂). Complex 4.4-¹⁵N₂ (74 mg, 51 μmol, 97%) was prepared in an analogous fashion to 4.4 from 4.1-¹⁵N₂ (77 mg, 53 μmol) in toluene (1 mL) and PMe₂Ph (73 mg, 53 μmol). The ¹H NMR spectrum was identical to that observed for 4.4.

³¹P{¹H} NMR (toluene-d₆, 162 MHz, 253 K): δ = 7.3 (ddd, 1P, 2Jₚp = 46 Hz, 2JₚΝ = 4 Hz, 2JₚN = 7 Hz), -1.9 (s, 1P), -22.5 (dd, 1P, 2Jₚp = 46 Hz, 2JₚN = 7 Hz).

¹⁵N{¹H} NMR (toluene-d₆, 40 MHz, 253 K): δ = 119.0 (AA'XX' multiplet, 1N, 1Jₜ₦ = 8 Hz, 2JₜN = 7 Hz, 2JₜΡ = 4 Hz), 118.0 (AA'XX' multiplet, 1N, 1Jₜ₦ = 8 Hz, 2JₜN = 7 Hz, 2JₜΡ = 4 Hz).

EI-MS (m/z): 1322 (15, [M - PMe₂Ph]+), 541 (100, [2.8 - Me]+).

Reduction of [NPN]⁺Hf₁₂ under N₂. Complex 2.15 (1.33 g, 1.35 mmol) was transferred to a Teflon-sealed bomb, and THF (10 mL) was vacuum-transferred into the flask at 77 K. Upon warming to rt, the flask containing the bright orange solution was returned to the glovebox and Na/Hg amalgam (25 g, 0.7%, 7.39 mmol) was added. The flask was evacuated and filled with N₂ at 77 K. The reaction mixture was allowed to warm slowly to rt in a liquid-N₂/EtOH slurry behind a blast shield. When the solvent had thawed, the solution was stirred vigorously. A gradual colour change from bright orange to green was observed over 4
weeks of stirring at rt. The pressure was vented, and the THF solution was decanted from the mercury and filtered through Celite. The filtrate was concentrated under vacuum to ∼5 mL, hexanes (15 mL) were added, and the clear solution was heated to ca. 40 °C to obtain a white precipitate. The slurry was filtered through Celite to eliminate the white precipitate and the clear yellow-green solution was taken to dryness to obtain a dark yellow residue (0.83 g). Attempts to separate the products based on solubility differences in toluene/hexanes solutions at −35 °C, or by slow evaporation of a benzene/HMDSO solution of the mixture failed.

$^3$P{$^1$H} NMR (C$_5$D$_5$, 162 MHz): δ = −3.1 (s, 16%), −6.9 (s, 10%), −10.5 (s, 12%), −10.6 (s, 62%).

4.5 References.


43 Cardin, D. J.; Lappert, M. F.; Raston, C. L. Chemistry of Organo-zirconium and Hafnium Compounds; Ellis Horwood Ltd.: West Sussex, 1986, p. 21.


Chapter Five

Reactivity of Zirconium Dinitrogen Complexes

5.1 Introduction.

The economically and biologically important reaction to convert elemental nitrogen to ammonia is achieved in one of two ways: by nitrogen-fixing bacteria or by the Haber-Bosch process. Biological nitrogen fixation occurs in bacteria such as Azotobacter vinelandii at the active site of the nitrogenase enzyme, which contains an Fe, FeMo, or FeV cofactor. This reaction proceeds at ambient pressure and temperature, but it requires energy in the form of 16 equivalents of MgATP, the cell's energy carrier. The mechanism of this reaction is unknown, and investigations into the structure and function of nitrogenase are ongoing. It is estimated that nitrogen-fixing bacteria produce $10^8$ million tonnes of NH₃ worldwide per year. In industry, the Haber-Bosch process yields NH₃ from the reaction of nitrogen and hydrogen gases in the presence of an Fe or Ru catalyst at high temperature (400 °C) and pressure (200 atm). Today, the Haber-Bosch reaction also supplies the world with about $10^8$ tonnes of ammonia per year. There is no indication that this process, first implemented industrially in 1913, will be replaced by another method for ammonia synthesis in the near future.

After the first N₂ complexes were synthesized under mild conditions, chemists sought to develop a homogeneous transition-metal-catalyzed route to ammonia from N₂ at ambient temperature and pressure. Stoichiometric nitrogen gas, hydrazine, or ammonia may be produced if acid is added to an N₂ complex. Alternatively, a hydrazido complex (M=N-NH₂) may be obtained. While it can be difficult to predict what products will form during
protonation reactions, the extent of activation of N$_2$ in the complex, and the experimental conditions used (e.g., temperature, acid, solvent) can be important. Protonation of cis-[W(N$_2$)$_2$(PMe$_2$Ph)$_4$] yields nearly two equivalents of ammonia,$^6$ whereas protonation of trans-[M(N$_2$)$_2$(dppe)$_2$] (M = Mo, W; dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) with HCl gives trans-[M=NNH$_2$(Cl)(dppe)$_2$]Cl (Equation 5.1).$^7$ In 2003, Schrock and co-workers reported that about eight equivalents of ammonia are produced catalytically from N$_2$, a weak organic acid, a reducing agent, and a bulky triamidoamine Mo(III) catalyst under carefully designed experimental conditions.$^8$

\[
\text{HN/H} \quad \text{Ph$_2$ N Ph$_2$ Ph$_2$ N Ph$_2$} \quad 2 \text{HCl} \quad \text{Cl} (5.1)
\]

\[
M = \text{Mo, W}
\]

Transition-metal dinitrogen complexes are also known to react with electrophilic organic compounds. N–C bonds form when alkyl and acyl halides react with [M(N$_2$)$_2$(dppe)$_2$] (M = Mo, W) to produce [MX(NN(R)H)(dppe)$_2$]X or [MX(NN(R)C(=O)H)(dppe)$_2$]X (X = Cl, Br; R = Me, Et, "Pr, "Bu, Ph) upon work-up with HCl(aq).$^9$ Until recently, the majority of reactions for coordinated N$_2$ required two steps: protonation of a dinitrogen complex to generate a nucleophilic hydrazido complex, followed by reaction with an electrophile. Aldehydes and ketones react with coordinated [NNH$_2$]$^5$ by a condensation reaction to give hydrazonato complexes with new N–C bonds (Equation 5.2).$^{10}$ Metal-bound pyrroles, pyrazoles, pyridines, and indoles can also be synthesized stoichiometrically from hydrazido complexes and C=O containing electrophiles.$^{11}$ In some cases, the heterocycle is released.
from the complex upon addition of a reductant and a proton source to the reaction mixture.\textsuperscript{12}

\[
\begin{align*}
\text{HN/H} & \quad \text{Ph}_2 \quad \text{N} \quad \text{Ph}_2 \\
\text{R} & \quad \text{R} \\
\text{Cl} & \quad \text{Cl} \\
\text{M} = \text{Mo, W}\n\end{align*}
\]

As is discussed in chapter one, new transformations for coordinated dinitrogen have been discovered relatively recently, and many of these involve side-on bound N\textsubscript{2}. New N–H and N–Si bonds form when H\textsubscript{2} and \textsuperscript{9}BuSiH\textsubscript{3} add to N\textsubscript{2} in \(\{\text{P}_2\text{N}_2\text{Zr}\}_2(\mu-\eta^2:\eta^2-\text{N}_2)\) to yield \(\{\text{P}_2\text{N}_2\text{Zr}\}_2(\mu-\text{H})(\mu-\eta^2:\eta^2-\text{NNH})\) and \(\{\text{P}_2\text{N}_2\text{Zr}\}_2(\mu-\text{H})(\mu-\eta^2:\eta^2-\text{NNSi}^\text{Bu})\), respectively (Figure 5.1).\textsuperscript{13} H\textsubscript{2} also adds to \(\{(\text{C}_5\text{Me}_4\text{H})_2\text{Zr}\}_2(\mu-\eta^2:\eta^2-\text{N}_2)\) to provide \(\{(\text{C}_5\text{Me}_4\text{H})_2\text{Zr}(\text{H})\}_2(\mu-\eta^2:\eta^2-\text{N}_2\text{H}_2)\).\textsuperscript{14} Boranes, silanes, and alanes add to \(\{\text{NPN}\text{Ta}\}_2(\mu-\text{H}_2)(\mu-\eta^1:\eta^2-\text{N}_2)\) to produce N–B, N–Si, and N–Al bonds, in some cases with concomitant N–N bond cleavage.\textsuperscript{15} The formation of N–C bonds is observed upon addition of arylacetylenes (ArC\textsubscript{CH}) to \(\{\text{P}_2\text{N}_2\text{Zr}\}_2(\mu-\eta^2:\eta^2-\text{N}_2)\) to yield \(\{\text{P}_2\text{N}_2\text{Zr}\}_2(\mu-\text{CCAr})(\mu-\eta^2:\eta^2-\text{NNCH=CHAr})\) (Ar = Ph, \(\text{p-MeC}_6\text{H}_4\)), and \(\text{p}^\text{BuC}_6\text{H}_4\)) (Figure 5.1).\textsuperscript{16}
Figure 5.1. Formation of new N—E bonds from \((P_2N_2)_2(Zr)(\mu-\eta^2:\eta^2-N_2)\) \((E = H, Si, C)\) (silyl methyl groups of \(P_2N_2\) omitted for clarity).

In most cases, when coordinated dinitrogen or hydrazide is functionalized, the new N—E component is not readily released from the transition metal. This is one barrier to the development of catalytic N—E bond-forming processes based on transition-metal dinitrogen complexes. Catalytic N—Si bond formation provides a low yield of \((Me_3Si)_3N\) when TMSCl, Na, and \(N_2\) are mixed in the presence \(\text{cis-[Mo(N_2)_2(PMe}_2_2Ph)_4]\).\(^{17}\) Anilines can be prepared from aryl chlorides, \(Ti(O^\text{OPr})_4\), Li, TMSCl and \(N_2\) under Pd-catalyzed C—N cross-coupling conditions.\(^{18}\) Thus far, few catalytic processes are known for molecular nitrogen, and most are poorly understood.
In this chapter, the reactivity of the Zr-N₂ complexes described in chapter four with H–H, Si–H, C=O, C=N, and P=O containing compounds is presented. H₂ reacts with \{[NPN]⁺Zr(PMe₂R)₂(μ-η²:η²-N₂)\} (R = Me, Ph) to yield a new N–H bond. A new N–Si bond is obtained upon addition of PhSiH₃ to \{[NPN]⁺Zr(Py)₂(μ-η²:η²-N₂)\}. The reaction of 4,4'-dimethylbenzophenone with \{[NPN]⁺Zr(THF)₂(μ-η²:η²-N₂)\} provides a hydrazonato complex with a new N=C bond, and the reaction of \{[NPN]⁺Zr(Py)₂(μ-η²:η²-N₂)\} with benzophenone imine yields new N–H bonds.

5.2 Results and Discussion.

5.2.1 Reactions of N₂ complexes with H₂.

When a toluene solution of 4.3 is stirred under H₂, the bright green solution becomes yellow over two to three weeks, and an orange precipitate forms after five weeks. The yellow-orange toluene-soluble product, \{[NPN]⁺Zr(PMe₃)₂(μ-H)(μ-NNH)Zr[NPN]⁺\}, 5.1, can be prepared in high yield from 4.3 and PMe₃ in toluene solution under H₂ (1 atm) (Equation 5.3). Complex 5.1 can also be synthesized from 4.3 and H₂ without added PMe₃, but an unidentified brown by-product forms in about 10% yield by this method. Samples of 5.1 are stable in solution and in the solid state for months under N₂ at −35 °C.
NMR spectra of 5.1 were acquired in toluene-\textit{d}_6 solution. At 298 K, the $^{31}$P\{\textit{H}\} NMR spectrum of 5.1 shows three broad peaks at $\delta \sim 13$, $-2.5$, and $-36$, which decoalesce at 273 K to two doublets at $\delta$ 13.8 and $-34.5$ ($J_{PP} = 56.7$ Hz), and a singlet at $\delta$ $-2.2$ (Figure 5.2). Because the spectrum is reminiscent of that of starting material 4.3, a dinuclear structure in which one Zr atom is coordinated to [NPN]$^\ast$ ($\delta -2.2$), and the other Zr atom is coordinated to [NPN]$^\ast$ ($\delta$ 13.8), and PMe$_3$ ($\delta$ $-34.5$) is proposed for 5.1. The 56.7 Hz P-P coupling constant is typical for a two-bond coupling between trans-disposed phosphines in an early transition-metal complex.$^{19}$

In the $^1$H NMR spectrum at 298 K, some of the peaks in the ArH and ArCH$_3$ region are broad; however, a triplet and a broad singlet that each integrate to 1H are apparent at $\delta$ 4.83 ($J_{HP} = 11$ Hz) and 4.78, respectively. These are assigned to a hydride bridging the two Zr atoms (ZrHZr), and the hydrogen atom of bridging NNH (Figure 5.3). At 253 K, the peaks in the $^1$H NMR spectrum are sharper, and 13 singlets are observed at $\delta \sim 2.0$ that are assigned to ArCH$_3$ groups. Sixteen singlets are expected based on the C$_1$ symmetry of the product, but six of these singlets overlap and integrate to 6H each. A broad singlet at $\delta$ 0.09 due to coordinated PMe$_3$, and an overlapping triplet at $\delta$ 4.84 (ZrHZr), and broad singlet at $\delta$ 4.82 (NNH) are also apparent in the spectrum at this temperature.

In the $^1$H\{$^{31}$P\} NMR spectrum at 253 K, the resonances assigned to ZrHZr and NNH appear as two singlets at $\delta$ 4.84 and 4.82. Thus, the bridging hydride is a triplet in the $^1$H NMR spectrum because it couples to two inequivalent $^{31}$P nuclei. One possible explanation is that ZrHZr couples to $^{31}$P nuclei of two [NPN]$^\ast$ ligands, and that the weak Zr–P bond to PMe$_3$ and/or the H–Zr–PMe$_3$ torsion angle causes the coupling between ZrHZr and PMe$_3$ to be unobservable.
Figure 5.2. 202 MHz $^{31}$P{$^{1}$H} NMR spectrum of 5.1 in toluene-$d_{8}$ at 273 K.

Figure 5.3. ZrHZr and NNH resonances in the 500 MHz $^{1}$H NMR spectrum of 5.1 in toluene-$d_{8}$ at 298 K.

The solid-state molecular structure of 5.1 is illustrated in Figure 5.4. Unfortunately, the data are of poor quality, and only the connectivity of the non-hydrogen atoms has been established. The position of the bridging hydride and the hydrogen atom of bridging NNH
cannot be determined. Zr1 is coordinated to [NPN]\(^*\) and N\(_2\), and Zr2 is coordinated to [NPN]\(^*\), PMe\(_3\), and N\(_2\). It is apparent that P2 and P3 are nearly trans-disposed (\(\sim 161^\circ\)), and that P1 is bent away from the Zr---Zr axis compared to P2 (Zr---Zr---P angles of 120° and 89°, respectively). Also, there is a much greater butterfly distortion (\(\sim 109^\circ\)) between the two Zr-N\(_2\) planes than is observed for 4.1, 4.2, and 4.4 that is consistent with the presence of a bridging hydride between the two Zr atoms. The Zr---Zr distance (\(\sim 3.2 \text{ Å}\)) is similar to that observed in other hydride-bridged dinuclear Zr(IV) complexes,\(^{20}\) and it is slightly shorter than in others.\(^{21}\) A projection of the N, P, and Zr atoms is shown in Figure 5.5.

![Figure 5.4](image)

**Figure 5.4.** Ball-and-stick model of the solid-state molecular structure of \{[NPN]\(^*\)Zr(PMe\(_3\))\}(\mu-H)(\mu-NNH)(Zr[NPN]\(^*\)), \(\text{5.1.}\) Carbon atoms of the proximal Mes substituents (except C\(_{\text{prox}}\)) have been omitted for clarity.
Figure 5.5. Projection of 5.1 down the Zr2--Zr1 axis (only Zr, P, and N atoms included).

Over one to two weeks at 298 K under N2, yellow C6D6 solutions of 5.1 turn green. In the 31P{1H} NMR spectrum, peaks due to 5.1 are absent, and singlets at δ −5.0 (62%), −7.6 (13%), and −31.4 (19%) appear. There are no signals in the spectrum that can be attributed to free or coordinated PMe3. The major product at δ −5.0 has not been identified, but it may correspond to a PMe3-free complex such as \{[NPN]*Zr\}2(μ-H)(μ-NNH), or to \{[NPN]*Zr\}2(μ-N2), if H2 has been eliminated. The peak at δ −31.4 is due to [NPN]*H2 (2.8). Fortunately, in the presence of excess PMe3, solutions of 5.1 remain yellow for weeks at room temperature and no decomposition is detected by 31P{1H} NMR spectroscopy. Thus, as with 4.3, decomposition appears to involve loss of PMe3.

To confirm that the resonances at δ 4.84 and 4.82 originate from H2 gas, toluene-d8 solutions of 4.3 have been stored under H2 or D2 gas in sealed J. Young NMR tubes and monitored for several weeks. Whereas the reaction of 4.3 with H2 is complete in six weeks, the reaction with D2 takes about three months, and a mixture of \{[NPN]*Zr(PMe3)}(μ-D)(μ-NND){Zr[NPN]*}, 5.1-d8 and 5.1 is produced. In the 1H NMR spectrum at 253 K, the triplet and singlet resonances at δ 4.84 and 4.82 integrate to about 0.02H each relative to
one of the ArCH₃ resonances (set to 3H). Thus, the bridging hydride and NNH protons in 5.1 originate with H₂ gas. The resonances at δ 4.84 and 4.82 appear in spectra of 5.1-d₂ because there are trace HD impurities (0.4%) in the D₂. Since 4.3 reacts with H₂ faster than it reacts with D₂, the formation of 5.1 in this reaction cannot be prevented. Complex 5.1-d₂ can also be prepared as an orange solid on a larger scale (300 mg) from 4.3, PMe₃ and D₂ (4 atm). By integration of the resonances at δ 4.84 and 4.82 in the ¹H NMR spectrum in toluene-d₄ acquired at 253 K, 5.1-d₂ and 5.1 are present in a ~10:1 ratio. A signal attributable to the parent ion, [5.1-d₂]⁺, appears in the mass spectrum of the compound.

To determine if the hydrogenation of 4.3 can be extended to the PMe₂Ph congener, a toluene solution of 4.4 and PMe₂Ph has been stirred under 1 atm of H₂ gas. The green solution turns yellow after three weeks at room temperature, and a yellow precipitate forms after six weeks. Upon work-up, {[NPN]*Zr(PMe₂Ph)(µ-H)(µ-NNH)Zr[NPN]*}, 5.2, is isolated as a yellow solid in good yield (Equation 5.4).

\[
\text{(5.4)}
\]

Similar to 5.1, the ³¹P{¹H} NMR spectrum of 5.2 in toluene-d₄ at 298 K shows three broad singlets at δ 15, −2 and 25. At 253 K, the broad resonances decoalesce and a doublet at δ 14.6 (Jₓₓ = 57.4 Hz), a broad singlet at δ −24.6, and a singlet at δ −2.3 are observed. These signals correspond to [NPN]* and PMe₂Ph coordinated to one Zr, and [NPN]* coordinated to the other Zr, respectively. In the ¹H NMR spectrum at 233 K, the expected
signals due to ArH, ArCH₃, and PMe₂Ph groups in the C₂ symmetric dimer are apparent. In addition, a singlet at δ 4.94, and a broad singlet at δ 4.88 are attributable to NNH and ZrH₂Zr protons, respectively.

The formation of a new N–H bond upon hydrogenation of 4.4 has been confirmed by an isotopic labelling experiment. \([\text{[NPN]}^\ast \text{Zr(PMe}_2\text{Ph)}](\mu-\text{H})(\mu-^{15}\text{N}^{15}\text{NH})\{\text{Zr[NPN]}^\ast\}\), 5.2–

\(^{15}\text{N}_2\), can be prepared from 4.4–

\(^{15}\text{N}_2\), PMe₂Ph and H₂ (1 atm) in toluene solution. At 273 K, the \(^{31}\text{P}'\text{H}\) NMR spectrum of 5.2–

\(^{15}\text{N}_2\) shows the same peaks as that of 5.2, but the broad singlet at δ –24.6 is split into a broad doublet. In the \(^1\text{H}\) NMR spectrum acquired at 233 K, the ArH, ArCH₃, and PMe₂Ph resonances are analogous to those of 5.2, but the peak at δ 4.94 is a doublet (\(J_{\text{HN}} = 72\) Hz), and the peak at δ 4.88 is a broad triplet (\(J_{\text{HP}} = 9.7\) Hz). In the \(^{1}\text{H}'\text{P}\) NMR spectrum, the doublet at δ 4.94 is apparent, but the resonance at δ 4.88 is a singlet. The 72 Hz \(^{15}\text{N}–\text{H}\) coupling constant is typical for one-bond coupling, and is similar to that observed for \((\text{[P}_2\text{N}_2\text{]}\text{Zr}_2^\mu\mu\text{H})(\mu-^{15}\text{N}^{15}\text{NH})\).\(^{13}\) The \(^{15}\text{N}'\text{H}\) NMR spectrum at 273 K shows a singlet at δ 143.9 and a doublet at δ 29.8 (\(J_{\text{NP}} = 10\) Hz). In the mass spectrum, a peak due to [M – PMe₂Ph]⁻ is apparent.

\(\text{H}_2\) may add to 4.3 or 4.4 by a σ-bond metathesis mechanism across the Zr–N bond via a four-centred transition state: N of dinitrogen acts as a nucleophile and Zr acts as an electrophile in this reaction, which is an example of heterolytic H–H activation. A similar mechanism has been invoked for the addition of \(\text{H}_2\) to \((\text{[P}_2\text{N}_2\text{]}\text{Zr})_2^\mu(\mu-\eta^2:\eta^2\text{N}_2)\).\(^{13}\)

Whereas \(\text{H}_2\) adds to 4.3 and 4.4, \(\text{H}_2\) does not react with THF adduct 4.1. When a blue-green toluene solution of 4.1 is stirred under 4 atm of \(\text{H}_2\) gas for six weeks at room temperature, there is no colour change, and no new peaks appear in any NMR spectra. When a toluene solution of 4.2 is stirred under 4 atm of \(\text{H}_2\) for eight weeks, there is a
gradual colour change from green to yellow-brown. By $^{31}$P$^1$H NMR spectroscopy, there is a mixture of products, including 2.8 ([NPN]$^1$H$_2$). In the $^1$H NMR spectrum, no peaks diagnostic of bridging hydride or NNH protons are observed, and the major products could not be separated from each other.

As introduced in chapter one, in 1997, the Fryzuk group reported the first reaction of an N$_2$ complex with H$_2$ to yield a new N–H bond. Yellow ([P$_2$N$_2$]Zr)$_2$(μ-H)(μ-NNH) is prepared from blue ([P$_2$N$_2$]Zr)$_2$(μ-η$^2$:η$^2$-N$_2$) under 1 or 4 atm of H$_2$. A broad singlet at δ 5.53 and a multiplet at δ 2.07 observed in the $^1$H NMR spectrum are due to μ-NNH and μ-H groups, respectively. When the reaction is conducted under D$_2$ gas, these resonances disappear, and when H$_2$ reacts with ([P$_2$N$_2$]Zr)$_2$(μ-$^{15}$N$_2$), the NH resonance is split into a doublet ($J_{HN} = 71.3$ Hz). The ZrHZr resonances for 5.1 and 5.2 are about 3 ppm downfield compared to the hydride observed for ([P$_2$N$_2$]Zr)$_2$(μ-H)(μ-NNH), but are within the range of known chemical shifts for hydrides bridging two Zr atoms. The solid-state structure of ([P$_2$N$_2$]Zr)$_2$(μ-H)(μ-NNH) determined by neutron diffraction shows that the N–N and N–H bonds in the bridging hydrazide (NNH) are 1.39(2) and 0.93(6) Å, respectively.

In contrast to ([P$_2$N$_2$]Zr)$_2$(μ-η$^2$:η$^2$-N$_2$), ([PNP]ZrCl)$_2$(μ-η$^2$:η$^2$-N$_2$) and {[NPN]Zr(THF)}$_2$(μ-η$^2$:η$^2$-N$_2$) do not react with H$_2$ gas. Prior to 1997, attempts to generate N–H bonds by the reaction of a dinitrogen complex with hydrogen had been unsuccessful, but in some cases H$_2$ had been observed to react with a dinitrogen complex to produce a metal hydride complex and liberate N$_2$ gas. As discussed in chapter one, two new N–H bonds also form when H$_2$ adds to [(η$^5$-C$_5$Me$_4$H)$_2$Zr](μ-η$^2$:η$^2$-N$_2$) to provide [(η$^5$-C$_5$Me$_4$H)$_2$Zr(NH)]$_2$(μ-η$^2$:η$^2$-N$_2$H$_2$). Heating this complex under H$_2$ yields NH$_3$, whereas heating it under vacuum yields [(η$^5$-C$_5$Me$_4$H)$_2$Zr](μ-N)(μ-NH$_2$) in which the N–N bond is
cleaved. \([(\eta^5-C_5Me_5H)_2Hf](\mu-\eta^2:\eta^2-N_2)\) also reacts with H_2, and \([(\eta^5-C_5Me_5H)_2Hf(H)]_2(\mu-\eta^2:\eta^2-N_2H_2)\) is produced.\(^{26}\) Thus, 4.3 and 4.4 join a relatively small number of N_2 complexes that react with H_2 to provide new N–H bonds.

5.2.2 Reaction of N_2 complexes with phenylsilane.

Upon addition of 1.1 equivalents of PhSiH_3 to a toluene solution of 4.2, a colour change from deep blue-green to yellow-brown occurs. \({[\text{NPN}]^+Zr(\text{Py})}(\mu-H)(\mu-\eta^1:\eta^2-\text{NNSiH}_2\text{Ph})\{\text{Zr[\text{NPN}]^+}\}, \text{5.3}, \) is isolated as an orange-brown toluene-soluble powder in high yield upon work-up (Equation 5.5). In the mass spectrum of 5.3, the highest molecular weight peak can be assigned to \([M – Py]^+\). The results of microanalysis are consistent with the proposed formula plus co-crystallized solvent, as has been observed in 'H NMR spectra of crystals of 5.3 dissolved in toluene-d_6.

\[
\text{4.2} \xrightarrow{\text{PhSiH}_3 \text{toluene}} \text{5.3}
\]

The \(^{31}\text{P}'\text{H} \) NMR spectrum of 5.3 in C_6D_6 shows two singlets at \(\delta 14.9\) and \(-4.3\). The \(^1\text{H} \) NMR spectrum shows 13 singlets at \(\delta \sim 2.0\) assigned to ArCH_3 groups (six of the expected 16 peaks are accidentally coincident), and peaks in the aromatic region consistent with the proposed C_1 symmetric structure. Two doublets at \(\delta 5.17\) and 3.94 (\(^2J_{\text{HH}} = 9.5 \text{ Hz}\)) integrate to 1H each and are assigned to two diastereotopic SiH protons. Small satellites are
present that flank the SiH peaks ($J_{\text{HH}} = 208$ Hz, isotopic abundance $^{29}\text{Si} = 4.7\%$). There is also a doublet of doublets at δ 8.25 ($J_{\text{HP}} = 15$ Hz, $J_{\text{HH}} = 2$ Hz) assigned to a bridging hydride (ZrH2Zr) that couples strongly to one phosphine ($^{31}\text{P}$ at δ −4.3 according to $^1\text{H}-^{31}\text{P}$ HSQC) and weakly to the second phosphine. There are only a few examples of non-metallocene group 4 complexes with bridging hydrides. Most hydrides bridging dinuclear Zr complexes have chemical shifts between δ 2.0 and 6.0. The downfield chemical shift seen for the bridging hydride in 5.3, however, is not unprecedented among group 4 hydride complexes. Signals due to bridging hydrides are also often observed downfield of δ 5.0 in non-metallocene Ta complexes, such as ([NPN]Ta₂(μ-H)₄ (δ 10.62), and ([NPN]Ta₂(μ-H)(μ-η¹:η²-N₂) (δ 10.85).

In the $^{13}\text{C}({}^1\text{H})$ NMR spectrum of 5.3 in C₆D₆, 16 ArCH₃ singlets and 63 peaks in the aromatic region are observed, consistent with the C₁ symmetric structure proposed. By $^{29}\text{Si}({}^1\text{H})$ NMR spectroscopy, a doublet at δ −34.4 is apparent; the doublet is due to a three-bond coupling to phosphorus-31 ($J_{\text{SP}} = 10$ Hz). The chemical shift and coupling observed by $^{29}\text{Si}({}^1\text{H})$ NMR spectroscopy are similar to those of other complexes prepared in our group. For example, the addition of one equivalent of PhSiH₃ to ([NPN]Ta₂(μ-H)₂(μ-η¹:η²-N₂) induces a series of reactions. The final product, ([NPN]Ta(μ-NSiH₂Ph)(μ-N)Ta[NPN]), and an intermediate in the reaction, ([NPN]Ta(μ-H)₂(μ-η¹:η²-NNSiH₂Ph)Ta[NPN]), have peaks at δ −39 and −9, respectively, in their $^{29}\text{Si}$ NMR spectra.

To simplify the aromatic region of the $^1\text{H}$ NMR spectrum of 5.3, the Py-d₅ adduct has been prepared and characterized. {[NPN]⁺Zr(Py-d₅)}(μ-H)(μ-η¹:η²-NNSiH₂Ph){Zr[NPN]⁺}, 5.3-d₅, can be prepared from 4.2-d₁₀ and 1.1 equivalents of PhSiH₃. The $^1\text{H}$ NMR spectrum
of 5.3-\textit{d}_5 in C\textit{6}D\textit{6} is analogous to that of 5.3, except that the multiplets at \( \delta \) 6.73 and 5.84 integrate to only 1H and 2H each, respectively, rather than 3H and 5H (Figure 5.6).

**Figure 5.6.** 400 MHz \( ^1\text{H} \) NMR spectrum of 5.3-\textit{d}_5 in C\textit{6}D\textit{6}.

By the same route used to prepare 5.3, 5.3-\text{\textsuperscript{15}}N\textsubscript{2} is obtained from 4.2-\text{\textsuperscript{15}}N\textsubscript{2} and PhSiH\textsubscript{3}.

In the \( ^{31}\text{P}\{^1\text{H}\} \) NMR spectrum of the \text{\textsuperscript{15}}N-labelled compound in C\textit{6}D\textit{6} there is a singlet at \( \delta \) 14.9 and a doublet of doublets at \( \delta \) -4.2 (\( \gamma_{\text{PH}} = 10 \text{ Hz}, \gamma_{\text{PN}} = 3 \text{ Hz} \)). The \( ^1\text{H} \) NMR spectrum is similar to that of 5.3, but the doublet (\( \gamma_{\text{HH}} = 9.7 \text{ Hz} \)) observed for 5.3 appears to be a broad multiplet at \( \delta \) 3.94. In the \( ^1\text{H}\{^{31}\text{P}\} \) NMR spectrum additional coupling to the \text{\textsuperscript{15}}N nuclei is observed for the peak at \( \delta \) 3.94 (\( \gamma_{\text{HH}} = 10 \text{ Hz}, \gamma_{\text{HN}} = 5 \text{ Hz}, \gamma_{\text{HP}} = 3 \text{ Hz} \)). In the \( ^{15}\text{N}\{^1\text{H}\} \) NMR spectrum there are two doublets of doublets at \( \delta \) -9.7 and -105.6. The two inequivalent \text{\textsuperscript{15}}N nuclei of the \( \eta^1\eta^2\text{\textsuperscript{15}}\text{NSiH}_2\text{Ph} \) group are coupled to each other (\( \gamma_{\text{NN}} = 15 \text{ Hz} \)), and each is coupled to \( ^{31}\text{P} \) (\( \gamma_{\text{NP}} = 3 \text{ Hz}, \gamma_{\text{HP}} = 10 \text{ Hz} \)). In the \( ^{29}\text{Si}\{^1\text{H}\} \) NMR spectrum, an AMXX' multiplet (\( \gamma_{\text{SN}} = 7 \text{ Hz}, \gamma_{\text{SS}} = 6 \text{ Hz}, \gamma_{\text{SP}} = 3 \text{ Hz} \)) is observed for 5.3-
$^{15}\text{N}_2$, due to coupling to two different nitrogen-15 nuclei, and to one phosphorus-31 nucleus.\textsuperscript{30} As for 5.3, the highest molecular weight peak in the mass spectrum of 5.3-$^{15}\text{N}_2$ corresponds to [M – Py]$^+$. 

The ORTEP representation of the solid-state molecular structure of 5.3 is shown in Figure 5.7. Zr1 in the dinuclear C\textsubscript{1} symmetric complex is coordinated to [NPN]*, Py and N5 of the side-on–end-on bound NNSiH\textsubscript{2}Ph unit, whereas Zr2 is coordinated to [NPN]*, and N5 and N6 of $\mu$-η\textsuperscript{1}:η\textsuperscript{2}-NNSiH\textsubscript{2}Ph. The bridging hydride, H1, can be located from the electron density map and refines normally. The Zr–P and Zr–N bond lengths to [NPN]* are similar to others reported in this thesis, and are typical for Zr(IV) amide and phosphine complexes.\textsuperscript{31} The Zr1–N7 bond (2.408(3) Å) is not unusual for Py coordinated to Zr,\textsuperscript{32} and is slightly shorter than the Zr–N bonds to Py in starting material 4.2, which average to 2.44 Å. The Zr1–N5 bond is short (1.958(3) Å) relative to the Zr2–N5 (2.142(3) Å) and Zr2–N6 (2.064(3) Å) bonds, reflecting the end-on vs. side-on bonding modes to Zr1 and Zr2, respectively. At 1.407(4) Å, the N5–N6 bond is shorter than in the starting material, but can still be considered as a single bond. Also, the N5–N6 bond length is similar to other N–N bonds observed in the Fryzuk group for η\textsuperscript{1}:η\textsuperscript{2}-coordinated dinitrogen and functionalized dinitrogen units.\textsuperscript{15,28} The N6–Si1 bond is 1.737(3) Å, typical of a N–Si single bond. The angles around N6 add to ~357°, indicating that N6 is nearly planar. Two views of the N, P, Si, and Zr atoms are shown in Figure 5.8.
Figure 5.7. ORTEP drawing of the solid-state molecular structure of \{[NPN]*Zr(Py)}{(µ-H)(µ-NNSiH2Ph)}{Zr[NPN]}^*, 5.3, (ellipsoids drawn at the 50% probability level). Carbon atoms of the Mes substituents (except C₉) and all hydrogen atoms (except bridging hydride H1 and H1Si, H2Si) have been omitted for clarity. Selected bond lengths (Å) and angles (°):

Zr1–P1 2.6853(11), Zr2–P2 2.7311(11), Zr1–N1 2.288(3), Zr1–N2 2.172(3), Zr1–N7 2.408(3), Zr2–N3 2.175(3), Zr2–N4 2.146(3), Zr1–N5 1.958(3), Zr2–N5 2.142(3), Zr2–N6 2.064(3), N5–N6 1.407(4), N6–Si1 1.737(3), Si1–C82 1.867(4), Zr1—Zr2 3.2256(6), N1–Zr1–P1 69.12(8), N2–Zr1–P1 74.71(9), N3–Zr2–P2 70.60(8), N4–Zr2–P2 74.01(9), Zr1–N5–Zr2 103.68(13), Zr1–N5–N6 170.7(2), Zr2–N6–Si1 160.9(2), N6–Si1–C82 113.60(17), N1–Zr1–N7 100.73(12), N5–N6–Si1 122.3(2).
As mentioned in chapter one, ([P₂N₂]Zr₂)(μ-H)(μ-NNSiH₂''Bu) is synthesized from ([P₂N₂]Zr₂)(μ-η²:η²-N₂) and ''BuSiH₃, and is an example of the formation of an N—Si bond by functionalization of coordinated dinitrogen (see Figure 5.1). The ¹H NMR spectrum of ([P₂N₂]Zr₂)(μ-H)(μ-η²:η²-NNSiH₂''Bu) shows broad singlets at δ 5.07 and 4.80 due to inequivalent SiH groups, and a broad quintet at δ 1.53 assigned to the bridging hydride. Whereas product 5.3 has a shorter N—N bond than is observed for starting material 4.2, the N—N bond in ([P₂N₂]Zr₂)(μ-H)(μ-NNSiH₂''Bu) is 1.530(4) Å, significantly longer than the N—N bond in starting material ([P₂N₂]Zr₂)(μ-η²:η²-N₂) (1.43(1) Å). That the N—N bond in 5.3 is shorter than the N—N bond in starting material 4.2, and in ([P₂N₂]Zr₂)(μ-H)(μ-NNSiH₂''Bu) is not surprising; shorter N—N bonds are typically observed when the N₂ or NNR groups are coordinated in the side-on–end-on mode rather than in the side-on mode. Thus far, it is unclear why NNSiH₂R coordinates side-on–end-on to the two Zr atoms in 5.3.

Figure 5.8. Two views of the N, P, Si, and Zr atoms in 5.3.
The presence of one molecule of Py, however, means that both of the Zr atoms are six-coordinate.

Another reaction between Si–H and coordinated N₂ introduced in chapter one is the addition of silanes to \([\text{NPN}][\text{Ta}]_2(\mu-\text{H})_2(\mu-\eta^1:\eta^2-\text{N}_2)\). The N–N bond is cleaved, and a new N–Si bond is formed in this reaction. Two equivalents of \(^n\text{BuSiH}_3\) react with \([\text{NPN}][\text{Ta}]_2(\mu-\eta^1:\eta^2-\text{N}_2)\) to yield the bis(silylimide) complex, \([\text{NPN}][\text{Ta}]_2(\mu-\text{NSiH}_2\text{Bu})_2\).\(^{15c}\) PhSiH₃ adds to the Ta-N₂ complex to produce \([\text{NPN}][\text{Ta}(\text{H})](\mu-\text{H})_2(\mu-\eta^1:\eta^2-\text{NNSiH}_2\text{Ph})(\text{Ta}[\text{NPN}])\), with a new N–Si bond.\(^{29}\) This complex spontaneously decomposes to give \([\text{NPN}][\text{Ta}(\text{H})](\mu-\text{N})_2(\mu-\text{NSiH}_2\text{Ph})(\text{Ta}[\text{NPN}])\), in which the N–N bond is cleaved.

It has been proposed that the reaction of \(\text{RSiH}_3\) with the Ta-N₂ complex proceeds via Si–H addition across one of the Ta–N bonds to yield a new N–Si bond and a terminal tantalum hydride. Complex 5.3 may form by a similar mechanism: Si–H addition across a Zr–N bond in 4.2. Dinitrogen complexes 4.1 and 4.4 also react with PhSiH₃ to produce N–Si containing complexes, \([\text{NPN}][\text{Zr}(\text{THF})](\mu-\text{H})_2(\mu-\eta^1:\eta^2-\text{NNSiH}_2\text{Ph})(\text{Zr}[\text{NPN}])\) and \([\text{NPN}][\text{Zr}(\text{PMe}_2\text{Ph})](\mu-\text{H})_2(\mu-\eta^1:\eta^2-\text{NNSiH}_2\text{Ph})(\text{Zr}[\text{NPN}])\), respectively.

5.2.3 Reaction of 4.1 with 4,4’-dimethylbenzophenone.

The addition of one equivalent of 4,4’-dimethylbenzophenone to a toluene solution of 4.1 initiates a blue-green to red-brown to orange colour change over 15 min. at room temperature. Upon work-up, \([\text{NPN}][\text{Zr}]_2(\mu-\text{O})(\mu-\eta^1:\eta^2-\text{NN}C(4-\text{MeC}_6\text{H}_4)\text{H})_2\), 5.4, is isolated as a yellow-orange toluene-soluble powder in high yield (Equation 5.6). Although there are no peaks with \(m/z > 556\) \([\text{NPN}][\text{H}_2]\) in the mass spectrum, the results of
elemental analysis are consistent with the proposed formula plus co-crystallized benzene as is observed in $^1$H NMR spectra of crystals of 5.4 dissolved in THF-$d_8$.

In the $^3$P{$^1$H} NMR spectrum of 5.4 in C$_6$D$_6$ there are two singlets at $\delta$ –7.7 and –10.4. In the $^1$H NMR spectrum there are eight singlets at $\delta$ ~ 2.0, each integrating to 6H, due to ArCH$_3$ groups of [NPN]$^+$, two singlets at $\delta$ ~ 2.2 integrating to 3H each due to ($p$-CH$_3$C$_6$H$_4$)$_2$C=N groups, and ArH resonances consistent with the proposed C$_s$ symmetric structure. Similarly, the predicted 10 ArCH$_3$ singlets at $\delta$ ~ 20, and 41 peaks attributable to ArC and C=N groups appear in the $^{13}$C{$^1$H} NMR spectrum. There are no resonances characteristic of free or coordinated THF in the $^1$H or $^{13}$C{$^1$H} NMR spectra. Although strong peaks are apparent in the IR spectrum of 5.4 at about 1500 cm$^{-1}$ that can be attributed to a C=N stretch, several peaks are typically observed in this region for [NPN]$^+$ complexes such as 4.1, and no single peak could be attributed to this functional group definitively.

The ORTEP representation of the solid-state molecular structure of 5.4 is shown in Figure 5.9. Each Zr atom in the dinuclear structure is coordinated to one [NPN]$^+$ ligand, and an oxo group, and the NNC($p$-MeC$_6$H$_4$)$_2$ fragment bridge the two Zr atoms. The N5–N6 bond length is 1.357(10) Å, which is intermediate between a single and double N–N bond,
and shorter than in the starting material 4.1 (1.503(6) Å). The N–N bond is slightly shorter than that observed for side-on–end-on bound NNSiH2Ph in 5.3 at 1.407(4) Å, and is within the range of N–N bond lengths observed for side-on–end-on dinitrogen complexes. As was mentioned in chapter one, the N–N bond length in ([NPN]Ta)2(µ-H)2(µ-η¹:η²-N2) is 1.319(6) Å. The N6–C77 bond length is 1.347(12) Å, consistent with a C–N double bond, and the N5–N6–C77 angle is 120.6(8)°. The hydrazonato group coordinates to the two Zr atoms in an η¹:η² bonding mode. The Zr1–N5 bond length is 2.016(7) Å, whereas the Zr2–N5 and Zr2–N6 bonds are much longer at 2.241(9) and 2.351(9) Å, respectively. The Zr1–N5–Zr2 angle is 93.0(3)°, and the Zr1–N5–N6 angle is 155.0(6)°. The other bond lengths and angles within the bridging hydrazonato group are unremarkable. The Zr1–O1 and Zr2–O1 bonds are the same, within error, and average to ~ 1.97 Å. The Zr1–P1 bond (2.711(2) Å) is slightly longer than the Zr2–P2 bond (2.687(3) Å), whereas the Zr1–N1, Zr1–N2, Zr2–N3, and Zr2–N4 bonds are essentially the same length (~2.16 Å, on average). The other bond lengths and angles are similar to those of the other [NPN]*Zr(IV) complexes reported here.

Overall, this structure is reminiscent of [(η⁵-MeC₅H₅)₂Zr]₂(µ-η¹:η²-NNCHPh)(µ-η¹-NNCHPh), which contains one equivalent of µ-η¹:η²- hydrazonate and is prepared from (η⁵-MeC₅H₅)₂ZrCl₂, H₂NNCHPh, and BuLi (Figure 5.10). An example of a mononuclear complex with a side-on bound hydrazonate is Cp²₂U(η²-(N₄N₇)-MeN–N=CPh₂)(OTf), which is synthesized from Ph₂C=N=N and Cp²₂U(OTf)(Me). This actinide complex has a C=N double bond (1.32(3) Å) and an N–N single bond (1.41(3) Å) (Figure 5.10). While these complexes are not examples of N₂ activation or functionalization, they provide a useful structural comparison to 5.4.
Figure 5.9. ORTEP drawing of the solid-state molecular structure of \([\text{[NPNN]}^+\text{Zr}]_2(\mu-\text{O})(\mu-\eta^1:\eta^1-\text{NCC}(4-\text{MeC}_6\text{H}_4)_2]\), 5.4, (ellipsoids drawn at the 50% probability level). Carbon atoms of the proximal Mes substituents (except C_\text{Mes}) and all hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Zr1–P1 2.711(2), Zr2–P2 2.687(3), Zr1–N1 2.166(8), Zr1–N2 2.145(7), Zr2–N3 2.189(9), Zr2–N4 2.160(7), Zr1–O1 1.962(6), Zr2–O1 1.982(6), Zr1–N5 2.016(7), Zr2–N5 2.241(9), Zr2–N6 2.351(9), N5–N6 1.357(10), N6–C77 1.347(12), C77–C78 1.460(14), C77–C85 1.475(13), Zr1–Zr2 3.0932(12), Zr1–O1–Zr2 103.3(3), Zr1–N5–Zr2 93.0(3), N5–Zr2–N6 34.3(3), N5–Zr2–N6 34.3(3), N5–N6–C77 120.6(8), C77–N5–Zr2 161.7(8), Zr1–N5–N6 155.0(6), N5–Zr1–P1 161.8(2), N5–Zr2–P2 149.4(2), N6–Zr2–P2 166.0(2), O1–Zr2–N6 111.2(3).
The reaction of 4.1 with 4,4'-dimethylbenzophenone in toluene-$d_6$ can be followed at low temperature by $^{31}P\{^1H\}$ NMR spectroscopy. After mixing the two reagents at 253 K, the singlet at δ 5.0 due to starting material 4.1 decreases in intensity and two singlets integrating to 1P each at δ -5.9 and -8.4 increase in intensity over 25 min. at this temperature. About 10 min. after warming the sample to 273 K, two singlets appear at δ -7.7 and -10.4 that integrate to 1P each and are assigned to 5.4. The peaks due to 5.4 continue to increase in intensity over 20 min. at 273 K, and over 15 min. at 300 K, but the peaks at δ 5.0, -5.9 and -8.4 do not disappear. After 24 h at 300 K, the peaks at δ -5.9 and -8.4 have disappeared, and peaks attributable to 5.4, 4.1, and minor impurities are observed in the $^{31}P\{^1H\}$ NMR spectrum.

From this evidence it appears that the peaks at δ -5.9 and -8.4 are due to an intermediate in the formation of 5.4, which may be a dinuclear complex with two inequivalent phosphines. One proposed formulation is $\{[NPN]^*\text{Zr}\}$$^1-\text{NNCHPh}$ and $\text{Cp}^*_2\text{U}$$^1-\text{MeN}^\text{N}^\text{CPh}2$ (OTf).
\( \text{N}_2 \}{[\text{NPN}]^\ast \text{Zr}[\text{O} = \text{C}(\rho-\text{MeC}_6\text{H}_4)_2]} \), the ketone adduct of the dinitrogen complex, with one equivalent of 4,4'-dimethylbenzophenone coordinated. By analogy with the synthesis of PMe_2Ph adduct 4.4, one equivalent of the bulky donor ligand replaces two equivalents of coordinated THF in the starting complex. A mechanism for the formation of 5.4 is proposed in Figure 5.11.

Figure 5.11. Proposed mechanism for the formation of 5.4 from 4.1.
Thus far, the only evidence for the mechanism outlined in Figure 5.11 is the observation of an intermediate with two inequivalent P atoms by $^{31}\text{P} \{^1\text{H}\}$ NMR spectroscopy at low temperature. It may be possible to obtain further mechanistic insight by following the reaction by IR spectroscopy, or by UV-visible absorption spectroscopy. It should also be noted that impurities that also appear to be dinuclear Zr complexes with inequivalent phosphines (two equal intensity singlets in the $^{31}\text{P} \{^1\text{H}\}$ NMR spectrum) form during this reaction if two or three equivalents of the ketone are added to 4.1, or if THF is used as the solvent.

A new N=C bond forms when 4,4'-dimethylbenzophenone reacts with the hydrazido (N$_2^+$) fragment in 4.1 to produce the hydrazonato complex 5.4. In organic chemistry, hydrazones are prepared by the condensation reaction of hydrazine with an aldehyde or ketone. The direct formation of N=C bonds from dinitrogen complexes and aldehydes or ketones is unusual. One example includes the addition of two equivalents of benzaldehyde to a Nb-N$_2$ complex, [Na(diglyme)$_2$]$_2$[{(calix-[4]-O)Nb}$_2$(μ-η¹:η¹-N$_2$)], to generate PhHC=N=N=CHPh with two new N=C bonds, and two equivalents of the Nb oxo complex, [Na(THF)$_4$][(calix-[4]-O)Nb=O]. Another example involves the addition of acetone to [TaCl$_3$(PET$_3$)$_2$(μ-N$_2$)] to give Me$_2$C=N=N=CMMe$_2$. The authors also report the reverse of this reaction: PhHC=NN=CHPh reacts with M(CHCMe$_3$)(THF)$_2$Cl$_3$ (M = Nb, Ta) to generate $\{\text{MCl}_3(\text{THF})_2\}_2$(μ-η¹:η¹-N$_2$).

As mentioned in the introduction, another way to prepare N=C bonds from dinitrogen complexes is by a two-step process. First, a hydrazido complex is prepared by protonation of an N$_2$ complex; next, the condensation reaction between the hydrazido complex and an aldehyde or ketone furnishes the hydrazonato complex. For example, trans-[MF(NN=CRR')(dppe)$_2$][BF$_4$] (M = Mo, W; R = Et, Ph, Me; R' = H, Me) forms upon
addition of \( RR'C=O \) to trans-[MF(NNH\textsubscript{2})(dppe)\textsubscript{2}][BF\textsubscript{4}]\textsuperscript{−}.\textsuperscript{39} Similarly, trans-[MBr(NNH\textsubscript{2})(depe)\textsubscript{2}]Br (M = Mo, W; depe = Et\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}PEt\textsubscript{2}) reacts with acetaldehyde to give trans-[MBr(NN=CHMe)(depe)\textsubscript{2}]Br, which can be reduced by LiAlH\textsubscript{4} to yield trans-[MBr(NNEt)(depe)\textsubscript{2}]Br.\textsuperscript{40} The addition of FcC(=O)H or FcC(=O)Me (Fc = (\( \eta^{5}\)-C\textsubscript{5}H\textsubscript{4})Fe(\( \eta^{5}\)-C\textsubscript{5}H\textsubscript{5})) to cis,mer-[WC\textsubscript{2}(NNH\textsubscript{2})(PMe\textsubscript{2}Ph)\textsubscript{3}] in the presence of catalytic HCl(aq) yields cis,mer-[WC\textsubscript{2}(NN=C(Fc)(R))(PMe\textsubscript{2}Ph)\textsubscript{3}] (R = H, Me).\textsuperscript{41} In the presence of the acidic hydride HFeCo\textsubscript{3}(CO)\textsubscript{12}, acetone adds to trans-[W(OH)(NNH\textsubscript{2})(dppe)\textsubscript{2}]PF\textsubscript{6} to produce trans-[W(OH)(NNCMe\textsubscript{2})(dppe)\textsubscript{2}]PF\textsubscript{6}.\textsuperscript{42} Mo and W hydrazido complexes are transformed into a wide range of complexes with coordinated hydrazones. Efforts directed at releasing these organic moieties from the metal complex have mostly been unfruitful. A high yield of Me\textsubscript{2}C=N-N=CMe\textsubscript{2} can be obtained, however, from cis-[W(N\textsubscript{2})\textsubscript{2}(PMe\textsubscript{2}Ph)\textsubscript{4}] and acetone in the presence of an unusual proton source, [[[(Ph\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2})\textsubscript{2}P]Fe\textsubscript{2}(\mu-SH)\textsubscript{2}]BF\textsubscript{4}]\textsuperscript{−}.\textsuperscript{43}

The synthesis of new N=C bonds from group 6 hydrazido complexes and aldehydes or ketones proceeds via elimination of one equivalent of water. In contrast, group 4 or 5 transition-metal dinitrogen complexes react with aldehydes or ketones to produce stable metal-oxo complexes. The formation of 5.4 from N\textsubscript{2} complex 4.1 is likely driven by the nucleophilicity of coordinated dinitrogen and the oxophilicity of Zr. Although it may be possible to release an organic compound such as H\textsubscript{2}N-N=C(4-MeC\textsubscript{6}H\textsubscript{4})\textsubscript{2} from 5.4 by adding acid or water to the complex, strong Zr–O bonds are expected to form, and it is difficult to envision a catalytic N=C bond forming reaction based on this process.
5.2.4 Reaction of 4.1 or 4.2 with \((\text{CH}_3)_3\text{CC}(=\text{O})\text{H}\).

The addition of one or two equivalents of \((\text{CH}_3)_3\text{CC}(=\text{O})\text{H}\) to benzene or toluene solutions of 4.1 or 4.2 produces an instant blue-green to yellow colour change (Scheme 5.1). Upon work-up, a hexanes-soluble yellow powder is obtained that contains multiple products by NMR spectroscopy. For the product formed from 4.2 and \((\text{CH}_3)_3\text{CC}(=\text{O})\text{H}\), the \(^{31}\text{P}\{'\text{H}\}\) NMR spectrum of the mixture dissolved in \(\text{C}_6\text{D}_6\) shows several peaks upfield of \(\delta\) 0 that can be assigned to a mixture of at least four complexes with two inequivalent phosphines each (Figure 5.12). When the yellow powder is recrystallized from hexanes, a small amount of a yellow crystalline solid is obtained. Although the crystals still contain a mixture of compounds, there is one major product with peaks at \(\delta\) -10.7 and -14.9 in the \(^{31}\text{P}\{'\text{H}\}\) NMR spectrum of the crystals dissolved in \(\text{C}_6\text{D}_6\). The \(^1\text{H}\) NMR spectrum shows singlets at \(\delta\) 4.71 and 0.80 that integrate in a 1:9 ratio, consistent with the presence of an \(\text{N}=\text{CHC}((\text{CH}_3)_3\) unit. There are 13 large peaks at \(\delta\) ~2.0, a feature consistent with the major product being a \(C_1\) symmetric dimer. If a complex such as \([\text{NPN}]^{*}\text{Zr}\)\(_2\)(\(\mu\)-\(\text{O}\))\((\mu\text{-NNC}(\text{H})\text{C}(\text{CH}_3)_3\)) is the major product, two diastereomers with different orientations of the \(H\) and \('\text{Bu}\) groups relative to the \(\text{C}=\text{N}\) bond may be present in the mixture (Scheme 5.1).

It may be possible to obtain one product selectively from the reaction of an aldehyde with coordinated dinitrogen by modifying the reaction conditions used, or by choosing a different aldehyde. As with ketones, the condensation of an aldehyde with a hydrazido complex is well known. For example, \([\text{WF}(\text{NNH})_2(\text{dppe})_2]\text{[BF}_4\text{]}\) reacts with salicylaldehyde to give \([\text{WF}(\text{NNCHC}_6\text{H}_4-2\text{-OH})(\text{dppe})_2]\text{[BF}_4\text{]}\).
Figure 5.12. 162 MHz $^{31}\text{P}^{1\text{H}}$ NMR spectrum of the yellow product (in C$_6$D$_6$) obtained from the reaction of (CH$_3$)$_3$CC(=O)H and 4.2.

Scheme 5.1.
5.2.5 Reaction of 4.1 or 4.2 with benzophenone imine.

Coordinated dinitrogen in 4.1 reacts with 4,4'-dimethylbenzophenone to yield a hydrazonato complex with a bridging oxo group. In an attempt to find new reactions for [NPN]*Zr-N₂ with electrophilic organic compounds, the addition of benzophenone imine to 4.1 and 4.2 was studied. The addition of 2.1 equivalents of benzophenone imine to a toluene solution of 4.1 or 4.2 induces a blue-green to brown colour change. After about 15 min., the reaction mixture becomes clear red, and a bright red, toluene-soluble powder, ([NPN]*Zr(NCPh₂)₂(μ-η²-η²-N₂)₂, 5.5, is isolated in high yield upon work-up (Equation 5.7). The same product forms regardless of whether 4.1 or 4.2 is used as the starting material.

\[
\text{2Ph}_2\text{C}=\text{NH} \quad \text{toluene}
\]

In the \(^{31}\text{P}\{\text{H}\}\) NMR spectrum of 5.5 in C₆D₆, two singlets of equal intensity appear at δ 1.2 and −9.2. By analogy with 5.3 and 5.4, the red product is a dimeric complex with two different \(^{31}\text{P}\) environments. In the \(^{1}\text{H}\) NMR spectrum acquired at 298 K, the peaks are broad and overlapping. At 273 K the \(^{1}\text{H}\) NMR spectrum of 5.5 in toluene-\(d₆\) shows 14 peaks at δ ~ 2.0, attributable to 16 inequivalent ArCH₃ groups (there are two sets of overlapping peaks), and two doublets (\(\delta J_{HH} = 13.7 \text{ Hz}\)) at δ 4.45 and 3.51 that each integrate to 1H and correspond to two inequivalent NH groups. There are also ArH resonances consistent with
the proposed C\textsubscript{1} symmetric structure, although this region is complicated by the presence of many inequivalent protons on the two [NPN]\textsuperscript{\textbullet} and two Ph\textsubscript{2}C=N ligands. In the $^{13}$C\textsuperscript{$\text{H}$} NMR spectrum acquired at 248 K there are 16 peaks that can be assigned to ArCH\textsubscript{3} groups, and 72 peaks in the aromatic region, as expected for the C\textsubscript{1} symmetric complex. In addition, two doublets at $\delta$ 175.4 ($J_{CP} = 7$ Hz) and 170.5 ($J_{CP} = 8$ Hz) can be assigned to inequivalent N=CPh\textsubscript{2} nuclei in the complex.

In the mass spectrum of 5.5, the highest molecular weight peak corresponds to $m/z = \left[([NPN]^{\textbullet}Zr)_2(NH)(N=CPh_2)\right]^+$ ([M – (N + HN=CPh\textsubscript{2})]$^+$), and the results of microanalysis are consistent with the proposed formula, plus co-crystallized solvent. By IR spectroscopy, two peaks at 3390 and 3250 cm\textsuperscript{-1} are observed that can be assigned to $\nu$(N-H), and two peaks at 1623 and 1615 cm\textsuperscript{-1} are observed that can be assigned to $\nu$(C=N).\textsuperscript{45} It should be noted that the structure of 5.5 could not be determined with confidence until the results of X-ray analysis were obtained.

The ORTEP representation of the solid-state molecular structure of the red product, $\left([NPN]^{\textbullet}Zr(N=CPh_2)\right)_2(\mu-\eta^2: \eta^2-N_2H_2)$, 5.5 is shown in Figure 5.13. Each Zr atom is coordinated to [NPN]\textsuperscript{\textbullet}, a ketimido group (Ph\textsubscript{2}C=N), and a side-on N\textsubscript{2}H\textsubscript{2} unit bridges the two Zr atoms in the dimer. Two peaks consistent with hydrogen atoms bound to N5 and N6 are apparent in the electron density map of the compound, but are not amenable to refinement. The ketimido fragments contain N=C double bonds (N7–C77 1.273(5) Å, N8–C90 1.279(5) Å), and coordinate to Zr with bond lengths that are shorter than Zr–N bonds to [NPN]\textsuperscript{\textbullet} (Zr1–N7 2.015(3) Å, Zr2–N8 2.007(4) Å). The orientation of [NPN]\textsuperscript{\textbullet} on Zr1 makes one of the ketimido fragments nearly trans to P (P1–Zr1–N7 167º), whereas the ketimido on Zr2 is ~cis to P of [NPN]\textsuperscript{\textbullet} (P2–Zr2–N8 78º). The angles around C77 and C90
add to \(360^\circ\) and \(362^\circ\), respectively, suggesting that both C atoms are planar and sp\(^2\) hybridized. At 1.507(4) Å, the N5–N6 bond is slightly longer than is observed for starting material 4.2 (1.481(5) Å), consistent with the presence of an N–N single bond. The N\(_2\)H\(_2\) unit is not coplanar with the Zr atoms: the two ZrN\(_2\) planes meet at a 138° angle. This represents a larger butterfly distortion than is observed for the N\(_2\) complexes 4.1, 4.2, and 4.4, but a smaller butterfly distortion relative to the hydride-bridged dimer, 5.1. The Zr–N bond lengths to the N\(_2\) unit are essentially the same, at about 2.22 Å, and are longer than the Zr–N bonds to N\(_2\) in 4.1, 4.2, and 4.4 (average to 2.05 Å). This is not unexpected since a bridging [N\(_2\)H\(_2\)]\(^2\) unit is present in 5.5, rather than an N\(_2^+\) unit. The other bond lengths and angles in the complex are unremarkable. Two views of the N, P, and Zr atoms in 5.5 are shown in Figure 5.14. The two phosphines are staggered (P1—Zr1---Zr2—P2 167°) across the Zr—Zr axis, whereas the amides of [NPN]\(^\ast\) on each Zr atom are nearly eclipsed (N1—Zr1---Zr2—N3 22°, N2—Zr1---Zr2—N4 3°). The two ketimido N atoms are also nearly eclipsed (N7—Zr1---Zr2—N8 23°).
Figure 5.13. ORTEP drawing of the solid-state molecular structure of
\{[NPN]^\*Zr(N=CPh_2)\}_2(\mu-\eta^2: \eta^4-N_2H_2), 5.5, (ellipsoids drawn at the 50% probability level).
Carbon atoms of the Mes substituents (except C_{ph}) and all hydrogen atoms have been
omitted for clarity. Selected bond lengths (Å) and angles (°): Zr1–P1 2.7718(11), Zr2–P2
2.7222(12), Zr1–N1 2.172(3), Zr1–N2 2.179(3), Zr1–N5 2.229(3), Zr1–N6 2.224(3), Zr1–N7
2.015(3), Zr2–N3 2.179(3), Zr2–N4 2.203(3), Zr2–N5 2.205(3), Zr2–N6 2.239(3), Zr2–N8
2.007(4), N5–N6 1.507(4), N7–C77 1.273(5), N8–C90 1.279(5), N1–Zr1–N7 112.99(13),
N7–Zr1–N2 94.97(12), N7–Zr1–N6 98.82(12), N7–Zr1–N5 113.78(12), N7–Zr1–P1
166.52(9), N5–Zr1–P1 78.43(9), N6–Zr1–P1 87.15(9), N8–Zr2–N5 101.49(13), N5–Zr2–P2
160.63(8), N8–Zr2–N4 121.64(13), Zr2–N5–Zr1 123.53(14), Zr1–N6–Zr2 122.16(13), C77–
N7–Zr1 165.1(3), C90–N8–Zr2 173.1(3).
Overall, the reaction of benzophenone imine with 4.2 protonates coordinated N\textsubscript{2} to yield a dinuclear hydrazido complex with two Zr-coordinated ketimido (Ph\textsubscript{2}C=N) ligands. The mechanism of formation of 5.5 from 4.2 has not been explored, however, it may proceed by initial coordination of Ph\textsubscript{2}C=NH to Zr, followed by proton transfer to the nucleophilic coordinated dinitrogen. Another example of a ketimido complex is Cp\textsubscript{2}Ti(N=CPh\textsubscript{2})(NHCHPh\textsubscript{2}), which also contains cyclopentadienyl and alkylamido ligands.\textsuperscript{45A} This complex is prepared from Cp\textsubscript{2}Ti(Me\textsubscript{3}SiC≡CSiMe\textsubscript{3}) and two equivalents of benzophenone imine, but the protons are transferred to one of the ketimido ligands to give Ti-NHCHPh\textsubscript{2}. Although this complex is not an example of N\textsubscript{2} activation, it provides a useful structural comparison.

Coordinated N\textsubscript{2} in 4.2 acts as a base in the reaction with benzophenone imine. As described in chapter one, side-on bound N\textsubscript{2} acts as a base in the reaction of HNR\textsubscript{2} (NR\textsubscript{2} = NMe\textsubscript{2}, N(H)NMe\textsubscript{2}) with [(η\textsuperscript{5}-C\textsubscript{5}Me\textsubscript{4}H\textsubscript{2}Zr]_2(μ-η\textsuperscript{3}:η\textsuperscript{2}-N\textsubscript{2}) to yield [(η\textsuperscript{5}-C\textsubscript{5}Me\textsubscript{4}H\textsubscript{2}Zr(NR\textsubscript{2})]_2(μ-η\textsuperscript{3}:η\textsuperscript{1}-N\textsubscript{2}H\textsubscript{2}).\textsuperscript{46} New N–H bonds also form upon addition of alkynes, R≡CH (R = Ph, 'Bu, "Bu), to this Zr-N\textsubscript{2} complex to yield [(η\textsuperscript{5}-C\textsubscript{5}Me\textsubscript{4}H\textsubscript{2}Zr(C≡CR)]_2(μ-η\textsuperscript{3}:η\textsuperscript{2}-N\textsubscript{2}H\textsubscript{2}).\textsuperscript{46}

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**Figure 5.14.** Two views of N, P, and Zr atoms in 5.5.
5.2.6 Reaction of N₂ complexes with CO.

When toluene solutions of 4.1 or 4.4 are stirred under 1 atm of CO a colour change from deep green to dark yellow is observed. A yellow powder, [[NPN]⁺Zr₂(μ-O)₂], 5.6, is isolated upon work-up in good yield (Equation 5.8). The 3¹P(¹H) NMR spectrum of 5.6 in C₆D₆ shows one singlet at δ -19.2. With four ArCH₃ singlets, and eight resonances in the aromatic region, the ¹H NMR spectrum of 5.6 (Figure 5.15) is consistent with the proposed C₂h symmetric complex. The ¹³C(¹H) NMR spectrum also shows the expected four ArCH₃ singlets, and 16 aromatic resonances. The molecular ion for 5.6 was detected by EI-MS, and the microanalytical data are consistent with the formula proposed.
The formation of 5.6 under the conditions described above is reproducible. To determine if any carbon-containing products form, the reaction described above was repeated in C₆D₆ solution. Complex 5.6 can be separated from the yellow-brown supernatant liquid by filtration. The ³¹P{¹H} NMR spectrum of the supernatant liquid shows peaks due to two major products: a singlet due to free PMe₂Ph, and two doublets present in a 1:1 ratio at δ —4.6 (7.5 Hz) and —9.4 (7.5 Hz). The chemical shifts of these resonances are typical for phosphines of [NPN]⁺ coordinated to Zr, and are tentatively assigned to a dinuclear complex with inequivalent phosphorus-31 nuclei that couple to each other. Such a complex with the [NPN]⁺ ligand is not known to us: all of the dimeric species with inequivalent phosphines, e.g., 5.4, do not show coupling P-P coupling between [NPN]⁺ ligands. For steric reasons, it is unlikely that {[NPN]⁺}₂Zr can form. Instead, a complex with a Zr–Zr bond may be present.

Figure 5.15. 500 MHz ¹H NMR spectrum of 5.6 in C₆D₆.
It has proved difficult to isolate such a complex, or to obtain meaningful information on this product and others that may be present in the supernatant liquid by GC-MS, EI-MS, ESI-MS or NMR spectroscopy.

When a $\text{C}_6\text{D}_6$ solution of 4.4 is stirred under 1 atm of $^{13}\text{CO}$ gas, a blue-green to yellow-brown colour change is observed over three hours. After two days, an aliquot of the clear yellow-brown solution shows a singlet due to free PMe$_2$Ph (50% by integration), and the two doublets at $\delta$ $-4.6$ and $-9.4$ ($\delta_{pp} = 7.4$ Hz, $\sim 30\%$ by integration) as is observed when the reaction is conducted under unlabelled CO. Two singlets at $\delta$ $-7.1$ (14%) and $-7.7$ (20%) due to two unidentified products, and two singlets that can be assigned to 5.6 (2%) and $[\text{NPN}]^*\text{H}_2$ (2.8) (1%) also appear in the $^{31}\text{P}^*{\text{H}}$ NMR spectrum. It is unclear why such a high yield of 5.6 is obtained when regular CO gas, rather than $^{13}$CO gas is used in this reaction. The formation of 5.6 from $\text{O}_2$ or $\text{H}_2\text{O}$ impurities in the CO cannot be ruled out at this point, but decomposition reactions have not been observed when other air- and moisture-sensitive Zr complexes are treated with CO from the same cylinders used for this reaction. In addition, only a small volume of CO gas is used in these reactions; it would have to contain a large percentage of $\text{O}_2$ to produce the amount of 5.6 observed.

In the $^{13}\text{C}^*{\text{H}}$ NMR spectrum of the reaction mixture two large doublets are observed at $\delta$ 177.5 (5.3 Hz) and 124.5 (8.4 Hz). These peaks do not resonate at chemical shifts expected for zirconium carbonyl compounds. The reaction of 4.4 with higher purity CO gas, and attempts to characterize the products by mass spectrometry, IR spectroscopy, and other techniques is currently ongoing. The formation of N–C bonds by the reaction of CO with dinitrogen complexes is as yet unknown.

The ball-and-stick representation of the solid-state molecular structure of 5.6 is shown in Figure 5.16. It is apparent that 5.6 is a dinuclear $\text{C}_2$ symmetric compound with two
bridging oxo groups. Two views of the stereochemistry of N, P, and O donors around Zr1
and Zr2 are shown in Figure 5.17. The Zr–P (2.7390(9) Å) and Zr–N (2.13 Å on average)
bond lengths are typical for Zr(IV) amidophosphine complexes,32 and for the other
[NPN]°Zr(IV) complexes reported herein. The Zr–O bond lengths average to about 1.98 Å,
which is similar to Zr–O bond lengths reported for other dinuclear Zr(IV) compounds with
bridging oxygen ligands. Examples of such complexes include [ZrCl2(μ-OH)(bdmpza)]2
(bdmpza = bis(3,5-dimethylpyrazol-1-yl)acetate) (Zr–O: 2.09 Å),48 {Zr[OB(Mes)2](μ-OH)}2,
(Zr–O: 1.96 Å),49 and (Cp2ZrCl)2(μ-O) (Zr–O: 1.945 Å).50

The Zr–Zr separation in 5.6 is 3.0116(8) Å, which is consistent with the presence of
two Zr(IV) centres bridged by O²⁻ ions. If the bridging groups were OH⁻ rather than O²⁻, Zr
in 5.6 would be in the 3+ oxidation state. Since 5.6 is neutral and diamagnetic, a Zr–Zr bond
would be present, and a smaller Zr–Zr separation would be expected. Examples of Zr–Zr
bonded species with bridging O²⁻ ligands appear to be absent from the literature, however,
Zr–Zr bonded species with bridging Cl⁻, Br⁻, and I⁻ ligands are well known. The Zr–Zr bond
is typically between 3.1 and 3.2 Å for chloride-bridged dimers, although the presence of Zr–Zr
bonds has also been inferred for complexes with longer Zr–Zr distances in the solid
state. Thus far, the 3.0 Å Zr–Zr separation observed for 5.6 is typical for an oxo-bridged
Zr(IV) dimer. In contrast to the N₂ complexes described in chapter four, there is only a
slight butterfly distortion between the ZrO₂ planes: the two ZrO₂ planes are ~178 ° disposed
to one another.
Figure 5.16. Ball-and-stick representation of the solid-state molecular structure of \{[NPN]^{\text{Zr}}_2(\mu-O)_2, 5.6, \} (ellipsoids drawn at the 50% probability level). Carbon atoms of the Mes substituents (except C_{\text{Mes}}) and all hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Zr1–P1 2.7390(9), Zr1–O1 1.9800(19), Zr1–O1' 1.9819(19), Zr1–N1 2.144(2), Zr1–N2 2.111(2), Zr---Zr 3.0116(8), Zr1–O1–Zr1' 98.95(9), O1–Zr1–O1' 80.58(9), P1–Zr1–O1 164.13(6), P1–Zr1–O1' 90.64(6), N1–Zr1–P1 70.01(6), N2–Zr1–P1 74.64(7), N2–Zr1–N1 111.67(10), O1–Zr1–N1 103.81(8), O1'–Zr1–N1 123.29(8), O1–Zr1–N2 120.96(9), O1'–Zr1–N2 113.32(9).
5.2.7 Reactivity of 4.1 with ethylene.

When a blue-green toluene solution of 4.1 is stirred under 1 atm of ethylene gas at room temperature for four weeks, the reaction mixture does not appear to change. The absence of any new peaks in the $^{31}\text{P}\{^1\text{H}\}$ and $^1\text{H}$ NMR spectra indicates that no reaction has occurred. In contrast to the lack of reactivity observed for 4.1, $\text{C}_6\text{D}_6$ solutions of $\{[\text{NPN}]\text{Zr(THF)}\}_2(\mu-\eta^2:\eta^2-\text{N}_2)$ react with ethylene to give a white precipitate. By $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, the purple supernatant liquid only contains the dinitrogen complex, and the white precipitate, although it has not been characterized, may be polyethylene. The reaction of ethylene with a dinitrogen complex to generate an N–C bond is intriguing, albeit unknown. Olefin polymerization catalyzed by dinitrogen complexes, however, is not unprecedented. For example, a heterobimetallic Ti-N$_2$ complex, $(\text{Cp}^*\text{Cl}_2\text{Ti})(\mu-\eta^1:\eta^1-\text{N}_2)(\text{W(depe)}_2\text{Cl})$ is a highly active catalyst for ethylene/1-hexene copolymerization in the presence of modified methylaluminoxane.$^{51}$

Figure 5.17. Two views of the stereochemistry around Zr in 5.6.
5.2.8 Reaction of 4.1 with triphenylphosphine oxide.

The addition of one equivalent of triphenylphosphine oxide to a toluene solution of 4.1 produces an instant blue-green to bright blue colour change. Small teal blue crystals, \([\text{[NPN]}^\bullet \text{Zr}(\text{OPPh}_3)\{\mu-\eta^2: \eta^2-\text{N}_2\}\{\text{Zr[PN]}^\bullet\}]\), 5.7, are obtained upon work-up (Equation 5.9). The \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum of 5.7 in C\(_6\)D\(_6\) shows three singlets at \(\delta\) 40.4, 4.7, and 0.1, integrating to 1P each (Figure 5.18). The two singlets at \(\delta\) 4.7 and 0.1 are characteristic of a dinuclear complex with two different \([\text{NPN}]^\bullet\) coordination environments, whereas the peak at \(\delta\) 40.4 is at a chemical shift expected for coordinated triphenylphosphine oxide.\(^{52}\) Eight singlets due to ArCH\(_3\) groups in the C\(_5\) symmetric complex are apparent in the \(^1\text{H}\) NMR spectrum, and resonances in the aryl region are consistent with \([\text{NPN}]^\bullet\) and Ph\(_3\)PO protons. There are no signals that can be assigned to free or coordinated THF. Similarly, the \(^{13}\text{C}\{^1\text{H}\}\) NMR spectrum indicates that the complex is C\(_5\) symmetric, since there are eight ArCH\(_3\) singlets and 40 peaks in the aromatic region.
Figure 5.18. 162 MHz $^{31}$P{$^1$H} NMR spectrum taken one hour after addition of triphenylphosphine oxide to 4.1 in C$_6$D$_6$.

Unfortunately, crystals of 5.7 suitable for X-ray analysis could not be obtained from hexanes solutions of the blue compound. Upon dissolution of 5.7 in benzene or toluene, the blue solution turns green over 24 h, concomitant with the formation of a mixture of products indicated by $^{31}$P{$^1$H} NMR spectroscopy. By analogy with the formation of $\{[\text{NPN}]^*\text{Zr}_2(\mu-O)(\mu-\eta^1:\eta^2-\text{NN}=\text{C}(4-\text{CH}_3\text{C}_6\text{H}_4)_2)\}$, $\{[\text{NPN}]^*\text{Zr}_2(\mu-O)(\mu-\eta^1:\eta^2-\text{NN}=\text{PPh}_3)\}$ may be present in the green mixture, along with 5.7 and other compounds. After several days at room temperature, there are still many peaks in the $^{31}$P{$^1$H} NMR spectrum of the green solution. The oxophilicity of Zr and the nucleophilicity of coordinated N$_2$ may drive the formation of a dimer with bridging oxo and phosphinimide groups, and it may be necessary to change the reaction conditions, or the phosphine oxide to obtain a phosphinimide complex selectively. Coordinated N$_2$ in a Ti-N$_2$ complex acts as a nucleophile by attacking the phosphine donor of [NPN] to yield $\{[\text{NP}(=\text{N})\text{N}]\text{Ti}\}_2$ ($[\text{NP}(=\text{N})\text{N}] = \ldots$
Another interesting facet of the reaction of Ph$_3$PO with 4.1 is the fact that Ph$_3$PO does not react with Py adduct 4.2 at room temperature in C$_6$D$_6$ over two weeks. The strength of Py donation and steric factors may block this reaction.

5.3. Conclusions.

In this chapter, the formation of N–H, N–Si, and N=C bonds from dinitrogen complexes is described. The reaction of H$_2$ and \{[NPN]$^\ast$Zr(PMe$_3$)$_2$(μ-η$^2$:η$^2$-N$_2$)\} provides \{[NPN]$^\ast$Zr(PMe$_3$)$_2$(μ-H)(μ-η$^2$:η$^2$-NNH)\} in high yield, with new N–H and Zr–H bonds. The product was characterized by solution NMR spectroscopy, isotopic labelling experiments, and by a low-resolution solid-state molecular structure. Similarly, \{[NPN]$^\ast$Zr(PMe$_2$Ph)$_2$(μ-H)(μ-η$^2$:η$^2$-NNH)\} can be prepared from \{[NPN]$^\ast$Zr(PMe$_2$Ph)$_2$(μ-η$^2$:η$^2$-N$_2$)\} and H$_2$ in toluene.

A new N–Si bond forms when PhSiH$_3$ reacts with \{[NPN]$^\ast$Zr(Py)$_2$(μ-η$^2$:η$^2$-N$_2$)\} in toluene to give \{[NPN]$^\ast$Zr(Py)$_2$(μ-H)(μ-η$^2$:η$^2$-NNSiH$_2$Ph)\} in high yield. The C$_1$ symmetric complex has been characterized in solution by multinuclear NMR spectroscopy, and in the solid state by X-ray analysis. The NNSiH$_2$Ph fragment is coordinated side-on–end-on to two Zr atoms, and the N–N bond length is 1.372(14) Å. Synthesis and characterization of labelled \{[NPN]$^\ast$Zr(Py-d$_2$)$_2$(μ-H)(μ-η$^2$:η$^2$-NNSiH$_2$Ph)\} and \{[NPN]$^\ast$Zr(Py)$_2$(μ-H)(μ-η$^2$-15N$^1$$^5$NNSiH$_2$Ph)\} also support the proposed structure.

The addition of 4,4′-dimethylbenzophenone to \{[NPN]$^\ast$Zr(THF)$_2$(μ-η$^2$:η$^2$-N$_2$)\} provides \{[NPN]$^\ast$Zr$_2$(μ-O)(μ-η$^2$-NN=C(4-CH$_3$C$_6$H$_4$)$_2$\} in high yield. The solid-state
molecular structure indicates that the dimeric compound is C₂-symmetric with bridging oxo and side-on-end-on hydrazonato ([{(p-MeC₆H₄)₂C=N—N}_2]²⁻) groups coordinated. The N—N bond is 1.357(10) Å, intermediate between a single and double bond, and the C=N bond is 1.347(12) Å, typical for a C=N double bond. Benzophenone imine reacts with {[NPN]*Zr(Py)}₂(μ-η²:η²-N₂) to yield {[NPN]*Zr(N=CPh₂)}₂(μ-η²:η²-N₂H₂), in which coordinated dinitrogen is protonated. The addition of Ph₃P=O to {[NPN]*Zr(THF)}₂(μ-η²:η²-N₂) initially provides a blue complex, {[NPN]*Zr(O=PPPh₃)}(μ-η²:η²-N₂){Zr[NPN]*}, that continues to react in benzene solution to yield a green mixture of products.

The dinitrogen complexes described in chapter four react with a variety of compounds including H₂, PhSiH₃, and 4,4'-dimethylbenzophenone to generate new N—H, N—Si, and N=C bonds. Preliminary results indicate that the reactions of 4.1 with (CH₃)₂CC(=O)H or Ph₃P=O may be worth pursuing. In addition, when other aldehydes, ketones, phosphine oxides, or silanes react with the N₂ complexes, new and interesting transformations may be observed. Clearly, it is worth exploring the reactivity of the N₂ complexes with other substrates. In particular, the reactivity of the N₂ complexes with arylacetylenes, boranes, alanes, CS₂, CO₂, or organometallic compounds such as Cp₂ZrH₂ may be profitable, since these compounds have been observed to react with other N₂ complexes.²⁹,⁵⁴

5.4. Experimental.

5.4.1. General experimental.

General experimental procedures follow those of chapter two. ¹⁵N{¹H} NMR spectra were recorded on a Bruker AV-400 direct detect spectrometer operating at 400.1 MHz for ¹H NMR spectra and were referenced externally to MeNO₂ at δ 0. ²⁹Si{¹H} NMR spectra
were collected on a Bruker AV-400 instrument operating at 400.0 MHz for $^1$H NMR spectra and were referenced externally to TMS ($\delta$ 0).

5.4.2. Starting materials and reagents.

Hydrogen, carbon monoxide and ethylene gases were obtained from Praxair. Deuterium gas (HD 0.4%) and $^{13}$CO gas (<2% $^{12}$CO) were purchased from Cambridge Isotopes Ltd. Toluene, benzene, and Et$_2$O used as reaction solvents were purified according to the procedure outlined in chapter two, then stirred over sodium sand, and filtered through Celite prior to use. PhSiH$_3$ was degassed by three freeze-pump-thaw cycles. (CH$_3$)$_3$CC(=O)H and benzophenone imine were stored over activated Linde 4Å molecular sieves and degassed by three freeze-pump-thaw cycles. All other reagents were obtained from commercial sources and used without further purification.

$\{[\text{NPN}]^+\text{Zr}(\text{PMe}_3))\}(\mu-\text{H})(\mu-\text{NNH})(\text{Zr}[\text{NPN}]^+)\ (5.1)$. Complex 4.3 (0.400 g, 0.287 mmol) was dissolved in toluene (10 mL), and PMe$_3$ (0.010 g, 0.132 mmol) was added. The solution was transferred to a Teflon-sealed bomb and degassed by three freeze-pump-thaw cycles. At rt, the flask was filled with 1 atm of H$_2$ gas and sealed, and the contents of the flask were stirred vigorously for 6 weeks. Over 2 – 3 weeks, the bright green solution became light yellow-green, and after 5 – 6 weeks an orange precipitate formed. In the glovebox, the precipitate was collected on a frit, rinsed with pentane (10 mL), and dried under vacuum for 10 min. to obtain a yellow-orange powder (0.224 g, 0.160 mmol, 56%). The filtrate was stored under H$_2$ (1 atm) in a Teflon-sealed bomb for one week to obtain yellow crystals that were collected on a frit and dried under vacuum (0.105 g, 0.075 mmol, 26%). Samples of 5.1 can be stored in solution or in the solid state at −35 °C for months.
without decomposition. At rt, toluene solutions of 5.1 with added PMe₃ (∼10 mg per 1 mL toluene) can be stored for weeks without decomposition. Small yellow-orange crystals were grown from toluene/HMDSO at −35 °C. The amount of co-crystallized HMDSO was consistent with the results of ¹H NMR spectroscopy performed on crystalline samples dissolved in C₆D₆. Orange single crystals suitable for X-ray analysis were grown in an NMR tube under H₂ by vapour diffusion of pentane into a C₆H₆ solution of the compound with ∼10 mg PMe₃ added per 1 mL of benzene.

¹H NMR (C₆D₆, 400 MHz, 298 K): δ = 7.98 (bt, 4H, 5 Hz), 7.45-7.25 (m, 4H), 7.14-7.00 (m, 4H), 6.91-6.68 (m, 12H), 6.07 (dd, 1H, J_HH = 8 Hz, J_HP = 6 Hz), 6.01 (dd, 1H, J_HH = 8 Hz, J_HP = 6 Hz), 5.86 (bs, 1H), 5.83 (s, 1H), 5.71 (bs, 1H), and 5.47 (bs, 1H) (ArH), 4.83 (t, 1H, J_HP = 11 Hz, ZrHZr), 4.78 (bs, 1H, NNH), 2.41 (s, 3H), 2.39 (s, 3H), 2.26 (s, 3H), 2.25 (s, 3H), 2.16 (s, 3H), 2.13 (s, 6H), 1.99 (s, 6H), 1.97 (s, 6H), 1.94 (s, 3H), 1.93 (s, 3H), 1.90 (s, 3H), 1.88 (s, 3H), and 1.59 (s, 3H) (ArCH₃), 0.19 (d, 9H, J_HP = 5 Hz, P(CH₃)₃).

¹H NMR (toluene-d₈, 500 MHz, 253 K): δ = 8.14 (dd, 2H, J_HH = 8 Hz, J_HP = 8 Hz), 7.62 (d, 1H, 7 Hz), 7.48 (d, 1H, 8 Hz), 7.45 (d, 1H, 8 Hz), 7.34 (d, 1H, 9 Hz), 7.18 (m, 4H), 7.06 (m, 2H), 6.99 (m, 4H), 6.86 (d, 1H, 8.5 Hz), 6.80 (d, 1H, 8.5 Hz), 6.76 (bs, 3H), 6.72 (s, 1H), 6.67 (s, 2H), 6.57 (d, 2H, 8 Hz), 6.16 (dd, 1H, J_HH = 8 Hz, J_HP = 6 Hz), 5.94 (dd, 1H, J_HH = 8 Hz, J_HP = 6 Hz), 5.79 (dd, 1H, J_HH = 8 Hz, J_HP = 6 Hz), and 5.70 (dd, 1H, J_HH = 8 Hz, J_HP = 6 Hz) (ArH), 4.84 (t, 1H, J_HP = 11 Hz, ZrHZr), 4.82 (bs, 1H, NNH), 2.65 (s, 3H), 2.27 (s, 3H), 2.25 (s, 3H), 2.19 (s, 3H), 2.14 (s, 6H), 2.08 (s, 6H), 2.01 (s, 3H), 1.99 (s, 6H), 1.95 (s, 3H), 1.94 (s, 3H), 1.80 (s, 3H), 1.69 (s, 3H), and 1.64 (s, 3H) (ArCH₃), 0.09 (bs, 9H, P(CH₃)₃).

³¹P{¹H} NMR (toluene-d₈, 202 MHz, 273 K): δ = 13.8 (d, 1P, J_pp = 56.7 Hz), −2.2 (s, 1P), −34.5 (d, 1P, J_pp = 56.7 Hz).

Anal. Calcd. for 5.1\textsuperscript{(HMDSO)}\textsubscript{0.67}: C\textsubscript{83}H\textsubscript{101}N\textsubscript{6}P\textsubscript{3}O\textsubscript{6.67}Si\textsubscript{1.33}Zr\textsubscript{2}: C, 66.19; H, 6.76; N, 5.58; Anal. Found C, 65.98; H, 6.60; N, 5.50.

**Decomposition of 5.1.** A yellow solution of 5.1 (30 mg) in toluene-\textit{d}_\textsubscript{8} (0.7 mL) was stored at rt for two weeks under N\textsubscript{2} and gradually became light green. The major peaks in the $^{31}$P\{\textit{H}\} NMR spectrum and the approximate percentages based on integration are listed below.

$^{31}$P\{\textit{H}\} NMR (toluene-\textit{d}_\textsubscript{8}, 202 MHz): $\delta =$ —5.0 (62%), —7.6 (13%), and —31.4 (19%).

$\{[\text{NPN}^+\text{Zr}(\text{PMe}_3)](\mu-\text{D})(\mu-\text{NND})\text{Zr[PNP]}^+\}$ (5.1-\textit{d}_2). Complex 4.3 (0.300 g, 0.215 mmol) was dissolved in toluene (5 mL) and PMe\textsubscript{3} (0.010 g, 0.132 mmol) was added. The solution was transferred to a Teflon-sealed bomb, and was degassed by three freeze-pump-thaw cycles. D\textsubscript{2} gas was added to the flask at rt. The solution was stirred vigorously for four weeks to obtain a deep green solution with a small amount of a yellow-green precipitate. The flask was then refilled with D\textsubscript{2} at 77 K and allowed to warm to rt (4 atm D\textsubscript{2} pressure) behind a blast shield. After the solution had been stirred vigorously for four weeks, the reaction mixture was a dark-orange suspension. The pressure was vented, and the reaction mixture was taken to dryness to obtain a dark orange solid. The solid was triturated with hexanes to obtain an orange powder that was collected on a frit, washed with pentane (3 $\times$ 5 mL), and dried under vacuum (0.185 g, 0.132 mmol, 61%). A 10:1 mixture of 5.1-\textit{d}_2 and 5.1 was obtained. The $^{31}$P\{\textit{H}\} NMR spectrum was identical to that of 5.1.

\textit{H} NMR (toluene-\textit{d}_\textsubscript{8}, 400 MHz, 253 K): $\delta =$ same as for 5.1 except the resonances at $\delta$ 4.84 and 4.82 integrate to 0.1H each rather than 1H relative to one of the ArCH\textsubscript{3} resonances.

EI-MS ($m/\text{z}$): 1396 (1, [M]^\textsuperscript{+}), 541 (100, [2.8 – Me]^\textsuperscript{+}).
\([\{\text{NPN}\}^+\text{Zr(\text{PMe}_2\text{Ph})}\}(\mu-\text{H})(\mu-\text{NNH})\{\text{Zr[}\text{NPN}\}^+}\) (5.2). Complex 4.4 (0.380 g, 0.261 mmol) and \text{PMe}_2\text{Ph} (0.010 g, 0.073 mmol) were dissolved in toluene (7 mL). The bright green solution was transferred to a Teflon-sealed bomb and degassed by three freeze-pump-thaw cycles. At rt the flask was filled with 1 atm of \text{H}_2 gas, the bomb was sealed, and the reaction mixture was stirred vigorously for 6 weeks. Over several weeks, the bright green solution gradually became light yellow-green and an orange precipitate formed. In the glovebox, the reaction mixture was taken to dryness, and pentane (10 mL) was added to obtain a yellow suspension that was chilled to \(-35 \, ^\circ\text{C}\). The yellow solid was collected on a frit and dried (0.275 g, 0.188 mmol, 72\%). Small yellow crystals were grown from toluene/\text{HMDSO} at \(-35 \, ^\circ\text{C}\), and the amount of co-crystallized \text{HMDSO} was confirmed by \textsuperscript{1}H NMR spectroscopy of samples of the crystals dissolved in \text{C}_6\text{D}_6.

\textsuperscript{1}H NMR (toluene-\textit{d}_8, 400 MHz, 233 K): \(\delta = 7.99 \) (t, 2H, 8 Hz), 7.80 (t, 1H, 8 Hz), 7.49 (d, 1H, 7.5 Hz), 7.41 (d, 1H, 7.5 Hz), 7.32 (d, 1H, 7.5 Hz), 7.27 (d, 1H, 7.5 Hz), 7.09 (m, 2H), 7.05 (s, 1H), 6.97 (s, 2H), 6.89 (s, 2H), 6.81 (s, 1H), 6.64 (m, 10H), 6.54 (s, 1H), 6.49 (s, 1H), 6.36 (bm, 2H), 6.07 (dd, 2H, \(J_{\text{HH}} = 8 \, \text{Hz}, J_{\text{HP}} = 6 \, \text{Hz}\)), 5.89 (m, 2H), 5.70 (t, 1H, 7 Hz), 5.48 (t, 1H, 7 Hz) (ArH), 4.94 (s, 1H, NNH), 4.88 (bs, 1H, ZrHZr), 2.64 (s, 3H), 2.25 (s, 3H), 2.02 (s, 6H), 2.00 (s, 9H), 1.95 (s, 3H), 1.92 (s, 3H), 1.89 (s, 3H), 1.87 (s, 3H), 1.84 (s, 6H), 1.79 (s, 3H), 1.59 (s, 3H), 1.55 (s, 3H) (ArCH	extsubscript{3}), 0.53 (bs, 3H), and 0.33 (bs, 3H) (P(CH	extsubscript{3})	extsubscript{2}Ph).

\textsuperscript{31}P\textsuperscript{1}H) NMR (toluene-\textit{d}_8, 162 MHz, 253 K): \(\delta = 14.6 \) (d, \(J_{\text{pp}} = 57.4 \, \text{Hz}, 1\text{P}\)), \(-2.3 \) (s, 1P), \(-24.6 \) (bs, 1P).

EI-MS (m/z): 1318 (\([\text{M} - \text{PMe}_2\text{Ph}]^+\), (100, \([2.8 - \text{Me}]^+\)).

Anal. Calcd. for 5.2-(\text{HMDSO})_{0.33}: C\textsubscript{46}H\textsubscript{97}N\textsubscript{8}P\textsubscript{3}O\textsubscript{0.33}Si\textsubscript{0.67}Zr\textsubscript{2}: C, 68.22; H, 6.46; N, 5.55; Anal. Found C, 68.48; H, 6.62; N, 5.90.
\{[\text{NPN}]^{*}\text{Zr(PE}_{2}\text{Ph})}\}(\mu-\text{H})(\mu-^{15}\text{NH})\{\text{Zr[NPN]}^{*}\} \quad (5.2-^{15}\text{N}_2). \text{ Complex 5.2-^{15}\text{N}_2 (0.163 \text{ g, 0.112 mmol, 82\%}) was prepared in an analogous manner to 5.2 from 4.4-^{15}\text{N}_2 (0.200 \text{ g, 0.137 mmol), PE}_{2}\text{Ph (0.010 g, 0.073 mmol) and H}_2 in toluene (5 mL).}

\text{^1H NMR spectrum (toluene-\text{d}_8, 400 MHz, 233 K) is the same as that of 5.2, but the resonance at } \delta 4.94 \text{ is a doublet (1H, } J_{\text{HN}} = 72 \text{ Hz), and the resonance at } \delta 4.88 \text{ is a broad triplet (1H, } J_{\text{HP}} = 9.8 \text{ Hz).}

\text{^1H\{^{31}\text{P}\} NMR (toluene-\text{d}_8, 400 MHz, 233 K): } \delta = 7.99 \text{ (d, 2H, 7 Hz), 7.80 (d, 1H, 7.5 Hz),}
7.49 \text{ (s, 1H), 7.41 (s, 1H), 7.32 (s, 1H), 7.27 (s, 1H), 7.09 (m, 2H), 7.05 (s, 1H), 6.97 (s, 2H),}
6.89 \text{ (s, 2H), 6.81 (s, 1H), 6.64 (m, 10H), 6.54 (s, 1H), 6.49 (s, 1H), 6.36 (bm, 2H), 6.06 (d, 2H, 8 Hz),}
5.89 \text{ (d, 2H, 8 Hz), 5.70 (d, 1H, 7 Hz), and 5.48 (d, 1H, 7 Hz) (ArH), 4.94 (d, 1H,}
J_{\text{HN}} = 72 \text{ Hz, NNH), 4.88 (bs, 1H, ZrHZr), 2.64 (s, 3H), 2.25 (s, 3H), 2.02 (s, 6H), 2.00 (s,}
9H), 1.95 (s, 3H), 1.92 (s, 3H), 1.89 (s, 3H), 1.87 (s, 3H), 1.84 (s, 6H), 1.79 (s, 3H), 1.59 (s,}
3H), and 1.55 (s, 3H) (ArCH$_3$), 0.53 (bs, 3H, P(CH$_3$)$_2$Ph), 0.33 (bs, 3H, P(CH$_3$)$_2$Ph).

\text{^{31}\text{P}\{^{1}\text{H}\} NMR (toluene-\text{d}_8, 162 MHz, 253 K): } \delta = 14.6 \text{ (d, 1P, } J_{\text{PP}} = 57.4 \text{ Hz), –2.3 (s, 1P), –}
24.6 (bd, 1P, } J_{\text{PP}} = 51.5 \text{ Hz).

\text{^{15}\text{N}\{^{1}\text{H}\} NMR (toluene-\text{d}_8, 40 MHz, 298 K): } \delta = 143.9 \text{ (s), 29.8 (d, } J_{\text{NP}} = 10 \text{ Hz).}

\text{EI-MS (m/\text{z}): 1320 (12, [M – PE}_{2}\text{Ph])}, 541 (100, [2.8 – Me$^+$]).

\textbf{Reaction of 4.1 with H$_2$. A solution of 4.1 (0.365 g, 0.249 mmol) in toluene (10 mL) in a}
\text{thick-walled Teflon-sealed bomb was degassed by three freeze-pump-thaw cycles. At 77 K}
\text{the flask was filled with H$_2$. The solution was warmed slowly to rt behind a blast shield. The}
\text{deep green solution was stirred for 6 weeks. No change was observed visually or detected by}
\text{^{31}\text{P}\{^{1}\text{H}\} NMR spectroscopy.}
Reaction of 4.2 with $\text{H}_2$. A solution of 4.2 (0.430 g, 0.291 mmol) in toluene (15 mL) was transferred to a thick-walled Teflon-sealed bomb and degassed by three freeze-pump-thaw cycles. At 77 K, the flask was filled with $\text{H}_2$ gas, and allowed to warm slowly to rt behind a blast shield. The solution was stirred vigorously for 8 weeks, and a gradual green to yellow colour change was observed. The pressure was vented, and the yellow reaction mixture was taken to dryness to obtain a yellow hexanes-soluble solid.

$^{31}\text{P}{'\text{H}}$ NMR (C$_6$D$_6$, 121 MHz): $\delta = -7.6$ (s), $-8.0$ (s), $-21.3$ (s), $-31.4$ (s).

$\{\text{[NPN]}^{\text{'Zr(Py)}}(\mu-\text{H})(\mu-\eta^1:\eta^2-\text{NNSiH}_2\text{Ph})\text{[Zr[NPN]}^\text{'}\} \ (5.3)$. To a stirred solution of 4.2 (0.430 g, 0.291 mmol) in toluene (5 mL) at $-35 \ ^\circ\text{C}$ was added dropwise a solution of phenylsilane (35 mg, 0.32 mmol) in toluene (2 mL). The reaction mixture was warmed slowly to rt, and it turned orange-brown after 5 min. After 1 h, the clear orange-brown solution was taken to dryness to obtain a brown residue. Hexanes (5 mL) were added to precipitate a brown solid that was collected on a frit, washed with pentane (2 x 5 mL), and dried under vacuum to obtain a light brown powder (0.378 g, 0.248 mmol, 85%). Small crystals of 5.3 suitable for elemental analysis were grown by slow evaporation of a benzene/HMDSO solution of the compound. Samples obtained in this manner contain approximately 1 equivalent of HMDSO and 1 – 2 equivalents of benzene of solvation, as determined by $^1\text{H}$ NMR spectroscopy of the crystals dissolved in toluene-$d_8$. Larger single crystals of 5.3 were grown by slow evaporation of a benzene solution of the compound.

$^1\text{H}$ NMR (C$_6$D$_6$, 400 MHz): $\delta = 8.25$ (dd, 1H, $^2J_{\text{HH}} = 15$ Hz, $^2J_{\text{HP}} = 2$ Hz, ZrHZr), 7.92 (bs, 1H), 7.86 (t, 2H, 8 Hz), 7.60 (bd, 1H, 7 Hz), 7.44 (bd, 1H, 8 Hz), 7.29 (bd, 2H, 7 Hz), 7.15-7.02 (m, 7H), 7.00 (s, 1H), 6.92 (m, 5H), 6.86-6.77 (m, 6H), 6.73 (d, 3H, 7 Hz), 6.64 (s, 2H), 221
6.58 (s, 1H), 6.09 (dd, 1H, J\textsubscript{HH} = 8 Hz, J\textsubscript{HP} = 6 Hz), 5.84 (m, 5H), 5.82 (s, 1H), and 5.72 (dd, 1H, J\textsubscript{HH} = 8 Hz, J\textsubscript{HP} = 6 Hz) (ArH), 5.17 (d, 1H, 9.5 Hz), and 3.94 (d, 1H, 9.5 Hz) (SiH\textsubscript{2}), 2.57 (s, 3H), 2.47 (s, 3H), 2.22 (s, 3H), 2.16 (s, 9H), 2.07 (s, 3H), 1.98 (s, 3H), 1.97 (s, 6H), 1.92 (s, 3H), 1.89 (s, 3H), 1.69 (s, 3H), 1.68 (s, 3H), 1.53 (s, 3H), and 1.24 (s, 3H) (ArCH\textsubscript{3}).

\textsuperscript{31}P{\textsuperscript{1}H} NMR (C\textsubscript{6}D\textsubscript{6}, 162 MHz): δ = 14.9 (s, 1P), -4.3 (s, 1P).

\textsuperscript{29}Si{\textsuperscript{1}H} NMR (C\textsubscript{6}D\textsubscript{6}, 80 MHz): δ = -34.4 (d, J\textsubscript{sp} = 10 Hz).

\textsuperscript{13}C{\textsuperscript{1}H} NMR (C\textsubscript{6}D\textsubscript{6}, 101 MHz): δ = 162.7 (d, 27 Hz), 161.8 (d, 29 Hz), 160.6 (d, 31 Hz), 159.6 (d, 23 Hz), 152.6, 147.7, 147.5, 146.9, 146.7, 143.4, 139.6, 138.5, 137.8, 137.6, 137.5, 136.9, 136.6, 136.4, 136.1, 135.8, 135.1, 134.9, 134.7, 134.6, 134.5, 134.4, 134.0, 133.9, 133.8, 133.5, 133.4 (d, 3 Hz), 133.2, 133.0, 132.8, 132.5, 132.0, 131.9, 131.8, 131.6, 131.5, 130.3, 130.1, 129.9, 129.6, 129.5, 129.3, 129.2, 128.8 (d, 3 Hz), 127.3, 126.9 (d, 4 Hz), 125.6, 123.9 (d, 6 Hz), 123.2, 122.8 (d, 31 Hz), 121.9 (d, 32 Hz), 119.9 (d, 40 Hz), 118.9 (d, 26 Hz), 118.1 (d, 7 Hz), 116.5 (d, 8 Hz), 115.2 (d, 11 Hz), 113.7 (d, 20 Hz), 113.6, and 112.7 (d, 19 Hz) (ArC), 21.1, 21.0, 20.94, 20.91, 20.8, 20.6, 20.47, 20.45, 20.37, 20.30, 20.08, 19.81, 18.83, 18.61, 18.54, and 17.98 (ArCH\textsubscript{3}).

EI-MS (m/\varepsilon): 1424 (10, [M – Py]+), 541 (80, [2.8 – Me]+).

Anal. Calcd. for 5.3-\textsuperscript{14}C\textsubscript{6}H\textsubscript{14}O\textsubscript{15}N\textsubscript{7}P\textsubscript{2}Zr\textsubscript{2}Si\textsubscript{3}: C, 68.57; H, 6.66; N, 5.49;

Anal. Found C, 68.59; H, 6.40; N, 5.60.

\{[\textsuperscript{NPN}]\textsuperscript{*}Zr(Py-d\textsubscript{4})(\mu-H)(\mu-\eta^1:\eta^2-NNSiH\textsubscript{2}Ph)\{Zr[\textsuperscript{NPN}]\textsuperscript{*}\} (5.3-d\textsubscript{4}). Complex 5.3-d\textsubscript{4} was prepared by the method used to prepare 5.3 from 4.2-d\textsubscript{10} (0.120 g, 0.081 mmol), and PhSiH\textsubscript{3} (10 mg, 0.089 mmol) in toluene (5 mL).
$^1$H NMR (CD$_6$, 400 MHz): $\delta =$ 8.25 (dd, 1H, $^2J_{HP} =$15 Hz, $^2J_{HP} =$ 2 Hz, ZrHZr), 7.92 (bs, 1H), 7.86 (t, 2H, 8 Hz), 7.60 (bd, 1H, 7 Hz), 7.44 (bd, 1H, 8 Hz), 7.29 (bd, 2H, 7 Hz), 7.15-7.06 (m, 7H), 7.00 (s, 1H), 6.92 (m, 5H), 6.86-6.77 (m, 6H), 6.73 (d, 1H, 7 Hz), 6.64 (s, 2H), 6.58 (s, 1H), 6.09 (dd, 1H, $^1J_{HH} =$ 8 Hz, $^1J_{HP} =$ 6 Hz), 5.88 (dd, 1H, $^1J_{HH} =$ 8 Hz, $^1J_{HP} =$ 6 Hz), 5.84 (dd, 1H, $^1J_{HH} =$ 8 Hz, $^1J_{HP} =$ 6 Hz), 5.82 (s, 1H), and 5.72 (dd, 1H, $^1J_{HH} =$ 8 Hz, $^1J_{HP} =$ 6 Hz) (ArH), 5.17 (d, 1H, 9.5 Hz), and 3.94 (d, 1H, 9.5 Hz) (SiH$_2$), 2.57 (s, 3H), 2.47 (s, 3H), 2.22 (s, 3H), 2.16 (s, 9H), 2.07 (s, 3H), 1.98 (s, 3H), 1.97 (s, 6H), 1.92 (s, 3H), 1.89 (s, 3H), 1.69 (s, 3H), 1.68 (s, 3H), 1.53 (s, 3H), and 1.24 (s, 3H) (ArCH$_3$).

$\{[NPN]^+Zr(Py)}(\mu-H)(\mu-\eta^1:\eta^2^{15}N^{15}NSiH$_2$Ph)\{Zr[NPN]$^+\}$ (5.3-$^{15}$N$_2$). Complex 5.3-$^{15}$N$_2$ was prepared by the same route used to prepare 5.3, from 4.2-$^{15}$N$_2$ (40 mg, 27 µmol) and phenylsilane (4 mg, 37 µmol) in toluene solution.

$^1$H NMR (CD$_6$, 400 MHz): same as for 5.3, but resonance at $\delta$ 3.94 is a broad multiplet.

$^1$H{${}^{31}$P} (CD$_6$, 400 MHz): $\delta =$ 8.25 (s, 1H, ZrHZr), 7.92 (bs, 1H), 7.86 (d, 2H, 8 Hz), 7.60 (s, 1H), 7.44 (s, 1H), 7.29 (s, 2H), 7.13-6.77 (m, 19H), 6.73 (d, 3H, 7 Hz), 6.64 (s, 2H), 6.58 (s, 1H), 6.09 (d, 1H, 8 Hz), 5.86 (m, 6H), and 5.72 (d, 1H, 8 Hz) (ArH), 5.17 (d, 1H, 9.5 Hz), and 3.94 (bm, 1H, $^2^J_{HH} =$ 10 Hz, $^2^J_{HN} =$ 5 Hz, $^2^J_{HN} =$ 3 Hz) (SiH$_2$), 2.57 (s, 3H), 2.47 (s, 3H), 2.22 (s, 3H), 2.15 (s, 3H), 2.14 (s, 3H), 2.12 (s, 3H), 2.05 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H), 1.97 (s, 6H), 1.92 (s, 3H), 1.89 (s, 3H), 1.69 (s, 3H), 1.68 (s, 3H), and 1.53 (s, 3H) (ArCH$_3$).

$^{31}$P{${}^1$H} NMR (CD$_6$, 162 MHz): $\delta =$14.9 (s, 1P), $-4.2$ (dd, 1P, $^2^J_{PN} =$ 10 Hz, $^2^J_{PN} =$ 3 Hz).

$^{29}$Si{${}^1$H} NMR (CD$_6$, 80 MHz): $\delta =$ $-34.4$ (dd, $^2^J_{SN} =$ 5.5 Hz, $^2^J_{SN} =$ 9.5 Hz, $^3^J_{SP} =$ 10 Hz).

$^{15}$N{${}^1$H} NMR (CD$_6$, 40 MHz): $\delta =$ $-9.7$ (dd, $^1^J_{NN} =$ 15 Hz, $^2^J_{NP} =$ 3 Hz) $-105.6$ (dd, $^1^J_{NN} =$ 15 Hz, $^2^J_{NP} =$ 10 Hz).
EI-MS (m/z): 1426 (30, [M – Py]⁺), 541 (40, [2.8 – Me]⁺), 78 (100, [C₆H₆]⁺).

\{[NPN]²Zr\}_₂(μ-O)(μ-η¹,η²-N=N=C(4-MeC₆H₄)) \ (5.4). A solution of 4.1 (0.380 g, 0.260 mmol) in toluene (5 mL) was chilled to −35 °C. To this stirred solution was added 4,4'-dimethylbenzophenone (57 mg, 0.27 mmol) in toluene (2 mL) dropwise. The reaction mixture was allowed to warm to rt, whereupon it became brown after 10 min. After 30 min., the reaction mixture was a clear orange solution. After 4 h, the solution was taken to dryness to obtain a dark orange solid. Upon addition of pentane (15 mL), a yellow-orange solid remained, which was isolated on a frit, washed with pentane (2 × 5 mL), and dried to give a bright yellow-orange powder (0.330 g, 0.216 mmol, 83%). Compound 5.4 was recrystallized from benzene, and orange single crystals of 5.4 suitable for X-ray analysis were grown by slow evaporation of a benzene solution of the compound. The ratio of 5.4 to benzene in the crystals was consistent with that observed by \(^1\)H NMR spectroscopy of crystals of 5.4 dissolved in THF-\(d_₈\), and by X-ray analysis before solvent suppression.

\(^1\)H NMR (C₆D₆, 400 MHz): δ = 7.79 (t, 2H, 8 Hz), 7.71 (t, 2H, 8 Hz), 7.40 (d, 2H, 8 Hz), 7.36 (d, 2H, 7 Hz), 7.08 (m, 5H), 6.93 (d, 2H, 8 Hz), 6.88 (d, 2H, 8 Hz), 6.83-6.74 (m, 11H), 6.70 (s, 2H), 6.62 (d, 2H, 8 Hz), 6.55 (s, 2H), 5.84 (dd, 2H, \(J_{HH} = 8\) Hz, \(J_{HP} = 6\) Hz), and 5.81 (dd, 2H, \(J_{HH} = 8\) Hz, \(J_{HP} = 6\) Hz) (ArH), 2.22 (s, 3H), and 2.20 (s, 3H) (N=CC₆H₄CH₃), 2.13 (s, 6H), 2.09 (s, 6H), 2.04 (s, 6H), 1.99 (s, 6H), 1.94 (s, 6H), 1.92 (s, 6H), 1.83 (bs, 6H), and 1.68 (s, 6H) (ArCH₃).

\(^{31}\)P\(^1\)H NMR (C₆D₆, 162 MHz): δ = −7.7 (s, 1P), −10.4 (s, 1P).

\(^{13}\)C\(^1\)H NMR (C₆D₆, 101 MHz): δ = 162.1 (d, 30 Hz), 161.0 (d, 25 Hz), 151.7, 143.2, 142.9 (d, 3 Hz), 138.6, 137.9, 137.3, 137.2, 136.84, 136.81, 136.5, 135.9 (d, 14 Hz), 134.6, 134.34, 134.28, 134.04, 133.95, 133.8, 133.6, 133.5, 133.4, 133.3, 132.6 (d, 8 Hz), 132.3, 130.75,
130.71, 130.5, 130.4, 130.1, 129.7, 129.3, 129.0, 128.9, 128.5, 128.3, 128.1, 127.9, 127.6, 119.5 (d, 33 Hz), and 115.0 (d, 10 Hz) (ArC and CN), 21.5, 21.4, 21.2, 21.0, 20.3, 20.2, 19.4, 19.19, 19.16, and 19.08 (ArCH3).

Anal. Calcd. for 5.4·2.5C6H6·C106H107N6P2Zr2O: C, 73.79; H, 6.25; N, 4.87; Anal. Found C, 73.52; H, 6.61; N, 4.49.

IR (KBr): 3005 (w), 2952 (w), 2918 (m), 2855 (w), 2723 (w), 2030 (w), 1601 (s), 1509 (s), 1494 (s), 1468 (s), 1436 (m), 1390 (m), 1271 (s), 1242 (s), 1191 (m), 1155 (m), 1087 (m), and 1057 (m) cm⁻¹.

**Low temperature reaction of 4.1 with 4,4'-dimethylbenzophenone.** In a 3-mL vial, 4.1 (10 mg, 6.8 μmol) was dissolved in toluene-δ6 (0.8 mL), and the blue-green solution was transferred to an NMR tube. In a separate 3-mL vial, 4,4'-dimethylbenzophenone (3 mg, 14 μmol) was dissolved in toluene-δ6 (0.1 mL) and transferred very carefully to a melting point capillary tube via syringe. One edge of the open end of the capillary tube was chipped away, and the tube was transferred open-end-up to the NMR tube. The NMR sample was cooled to 253 K in the spectrometer probe, and a 31P{1H} NMR spectrum was acquired. The NMR tube was then removed from the spectrometer, shaken vigorously to mix for 30 s, and returned to the cooled probe. 31P{1H} NMR spectra were acquired every 5 min. at 253 K for 30 min., then every 5 min. at 273 K for 30 min., then every 5 min. at 300 K for 15 min. A final 31P{1H} NMR spectrum was acquired after the sample was stored in an N2-filled glovebox at rt for 24 h.

**Reaction of 4.2 with (CH₃)₃CC(=O)H.** To a stirred solution of 4.2 (0.489 g, 0.331 mmol) in toluene (7 mL) at −35 °C was added dropwise a solution of (CH₃)₃CC(=O)H (61 mg, 0.71
mmol) in toluene (2 mL). The reaction mixture turned brown, then red, then yellow throughout the addition. After 24 h, the yellow solution was taken to dryness to obtain a yellow residue. The residue was triturated with hexanes (15 mL), and the yellow extracts were filtered through Celite, and taken to dryness to obtain a yellow powder (0.230 g).

$^3P\{^1H\}$ NMR ($C_6D_6$, 162 MHz): $\delta = -6.5\ (s), -6.6\ (s), -9.3\ (s), -10.7\ (s), -13.7\ (s), -14.9\ (s)$. Yellow crystals (60 mg) grew from a hexanes solution of the yellow powder at rt.

$^3P\{^1H\}$ NMR ($C_6D_6$, 162 MHz): $\delta = -6.6\ (s, 1P), -10.7\ (s, 7P), -13.7\ (s, 1P), -14.9\ (s, 7P)$. Peaks that appear consistent with the major product are noted below:

$^1H$ NMR ($C_6D_6$, 400 MHz): $\delta = 7.67\ (t, 2H, 7\ Hz), 7.49\ (d, 1H, 7\ Hz), 7.29\ (d, 1H, 7\ Hz), 7.18-6.97\ (m, 8H), 6.89-6.73\ (m, 12H), 6.66\ (s, 2H), 6.24\ (dd, 1H, J_{HH} = 8\ Hz, J_{HP} = 6\ Hz), 6.13\ (t, 2H, 7\ Hz), \text{ and } 5.43\ (dd, 1H, J_{HH} = 8\ Hz, J_{HP} = 6\ Hz)\ (ArH), 4.71\ (s, 1H)\ (N=CHR), 2.53\ (s, 3H), 2.46\ (s, 3H), 2.30\ (s, 3H), 2.25\ (s, 3H), 2.20\ (s, 3H), 2.15\ (s, 6H), 2.13\ (s, 3H), 2.10\ (s, 3H), 2.09\ (s, 6H), 2.06\ (s, 6H), 1.95\ (s, 3H), 1.88\ (s, 3H), \text{ and } 1.68\ (s, 3H)\ (ArCH_3), 0.80\ (s, 9H)\ (C(CH_3)_3).

$\{[NPN]^7Zr(N=CPH_3}\}_2(\mu-\eta^2:\eta^2-N_2H_2)\ (5.5)$. To a stirred solution of 4.2 (0.360 g, 0.244 mmol) in toluene (5 mL) was added dropwise a solution of benzophenone imine (93 mg, 0.51 mmol) in toluene (2 mL). The reaction mixture turned brown through the addition, and it was bright red after 5 min. The reaction mixture was stirred for 24 h, and the clear red solution was taken to dryness to obtain a red solid that was suspended in pentane (2 × 5 mL), collected on a frit, rinsed with hexanes (5 mL), and dried (0.390 g, 0.232 mmol, 95%). Small crystals of 5.5 were grown by layer diffusion of HMDSO into a solution of the compound in benzene. The amount of co-crystallized solvent observed by microanalysis is consistent with that observed by $^1H$ NMR spectroscopy of samples dissolved in toluene-$d_8$. 226
Single crystals of 5.5 suitable for X-ray analysis were grown by slow evaporation of a benzene solution of the compound.

$^1$H NMR (toluene-$d_6$, 400 MHz, 273 K): $\delta = 7.25$ (m, 14H), 7.11 (m, 6H), 6.93 (m, 10H), 6.84 (s, 2H), 6.77 (d, 2H, 7.5 Hz), 6.67 (m, 2H), 6.53 (m, 3H), 6.42 (t, 2H, $J_{HP} = 6$ Hz), 6.26 (bt, 2H), 6.13 (s, 1H), 6.04 (bs, 1H), 5.97 (bs, 4H), and 5.65 (bt, 1H) (ArH), 4.45 (d, 1H, 13.7 Hz), and 3.51 (d, 1H, 13.7 Hz) (NH), 2.53 (s, 3H), 2.45 (s, 6H), 2.42 (s, 3H), 2.32 (s, 3H), 2.17 (s, 3H), 2.12 (s, 3H), 2.01 (s, 3H), 1.95 (s, 3H), 1.92 (s, 3H), 1.86 (s, 3H), 1.82 (s, 3H), 1.75 (s, 6H), 1.42 (s, 3H), and 1.14 (s, 3H) (ArCH$_3$).

$^{31}$P{$^1$H} NMR (C$_6$D$_6$, 162 MHz, 300 K): $\delta = 1.2$ (s, 1P), $-9.2$ (s, 1P).

$^{13}$C{$^1$H} NMR (THF-$d_6$, 101 MHz, 248 K): $\delta = 175.4$ (d, 7 Hz), and 170.5 (d, 8 Hz) (C=N), 165.2 (d, 30 Hz), 165.1 (d, 29 Hz), 162.1 (d, 26 Hz), 161.6 (d, 29 Hz), 149.8, 147.8, 146.8, 146.7, 141.7, 140.3, 140.2, 139.7, 139.3, 138.9, 137.5, 137.2, 136.9, 136.3, 136.0, 135.9, 135.6, 135.4, 135.3, 135.2, 134.8, 134.6, 134.4, 133.8, 133.7, 133.3, 133.0, 132.9, 132.7, 132.1, 132.0, 131.9, 131.5, 131.4, 131.2, 130.7, 130.6, 130.5, 130.3, 130.2, 130.1, 130.0, 129.9, 129.6, 129.4, 129.1, 128.9, 128.7, 128.6, 128.2, 128.1 (d, 2 Hz), 127.8, 127.4, 126.9, 126.7 (d, 4 Hz), 126.5 (d, 4 Hz), 121.1, 120.8, 120.7, 120.4, 118.4 (d, 8 Hz), 118.2 (d, 8 Hz), 117.8 (d, 2 Hz), 116.4 (d, 7 Hz), 115.4 (d, 8 Hz), 114.6 (d, 9 Hz), 114.4 (d, 9 Hz), and 112.7 (ArC), 21.9, 21.7, 21.6, 21.4, 21.3, 21.2, 20.8, 20.7, 20.5, 20.3, 19.3, 19.2, 19.1, 18.7, 18.5, and 18.4 (ArCH$_3$).

EI-MS ($m/z$): 1484 (20, [{[NPN]$^*$Zr$_2$(NH)(N=CPh$_2$)]$^+$}, 1318 (80, [{[NPN]$^*$Zr$_2$(N$_2$)]$^+$}, 541 (100, [2.8 – Me]$^+$).

Anal. Calcd. for 5.5( HMDSO)$_{0.5}$: C$_{105}$H$_{109}$N$_8$P$_2$SiO$_{0.5}$Zr$_2$; C, 71.51; H, 6.23; N, 6.35; Anal. Found C, 71.54; H, 6.33; N, 6.48.
IR (KBr): 3390 (w), 3250 (w), 3051 (m), 3003 (m), 2854 (m), 1623 (s), 1615 (s), 1574 (s), 1519 (m), 1514 (w), 1494 (m), 1469 (s), 1393 (m), 1302 (w), 1269 (m), 1241 (s), 1190 (m), 1154 (m), 864 (s), 813 (m), and 696 (s) cm⁻¹.

{[NPN]⁺Zr}₄(µ-O)₅ (5.6). A solution of 4.4 (0.150 g, 0.103 mmol) in C₆D₆ (2 mL) in a 40-mL Teflon-sealed bomb was degassed with three freeze-pump-thaw cycles. At rt, the flask was filled with CO gas. The reaction mixture turned yellow after 30 s of shaking. The solution was stirred overnight to obtain a yellow-brown suspension. The solution was then stirred under a flow of N₂ for 1 h. In the glovebox, the yellow precipitate was collected on a frit, washed with hexanes (2 × 5 mL), and dried (0.106 g, 0.080 mmol, 78%). Single crystals of 5.6 were grown by slow evaporation of a benzene solution of the compound in an NMR tube.

¹H NMR (C₆D₆, 500 MHz): δ = 7.93 (t, 4H, 8.5 Hz), 7.41 (d, 4H, 6 Hz), 7.15 (m, 4H), 7.03 (t, 2H, 8 Hz), 6.78 (s, 4H), 6.77 (d, 4H, 8.5 Hz), 6.67 (s, 4H), and 5.98 (dd, 4H, 8 Hz, 6 Hz) (ArH), 2.30 (s, 12H), 2.23 (s, 12H), 1.97 (s, 12H), and 1.92 (s, 12H) (ArCH₃).

³¹P{¹H} NMR (C₆D₆, 202 MHz): δ = -19.2 (s).

¹³C{¹H} NMR (C₂D₆, 126 MHz): δ = 159.7 (d, Hz), 140.4, 137.6, 136.7, 134.6, 134.4, 134.0, 133.6 (d, Hz), 130.7, 129.8, 129.5, 129.2 (d, Hz), 128.5, 125.6, 119.6 (d, Hz), and 115.0 (ArC), 21.2, 20.8, 19.6, and 18.5 (ArCH₃).

EI-MS (m/z): 1322 (60, [M⁺]), 541 (100, [2.8–Me⁺]).

Anal. Calcd. for 5.6: C₇₆H₇₈N₄O₂P₂Zr₂; C, 68.95; H, 5.94; N, 4.23; Anal. Found C, 68.60; H, 5.90; N, 4.63.
Reaction of 4.4 with $^{13}$CO. A solution of 4.4 (0.150 g, 0.103 mmol) in C$_6$D$_6$ (2 mL) in a 40-mL Teflon-sealed bomb was degassed by three freeze-pump-thaw cycles, and refilled with $^{13}$CO gas at rt (1 atm). The reaction mixture was stirred vigorously and turned yellow-brown after 3 h. After 2 d, the flask was stirred under a flow of N$_2$ for 1 h. In the glovebox, a portion of the yellow brown solution was transferred to an NMR tube.

$^{31}$P{¹H} NMR (C$_6$D$_6$, 162 MHz): $\delta = -4.6$ (d, 17%, 7.4 Hz), $-7.1$ (s, 14%), $-7.7$ (bs, 20%), $-9.5$ (d, 17%, 7.4 Hz), $-19.2$ (s, 2.5%, 5.6), $-31.4$ (s, 0.8%, 2.8), $-46.5$ (s, 50%, PMe$_2$Ph).

$^{13}$C{¹H} NMR (C$_6$D$_6$, 162 MHz): $\delta = 177.5$ (d, 5.3 Hz), 124.5 (d, 8.4 Hz).

Reaction of 4.1 with ethylene. A solution of 4.1 (0.350 g, 0.239 mmol) in toluene (7 mL) in a 100-mL Teflon-sealed bomb was degassed by three freeze-pump-thaw cycles and filled with C$_2$H$_4$ at rt (1 atm). The deep green solution was stirred for 1 month. No change was observed visually or detected by $^{31}$P{¹H} NMR spectroscopy.

Reaction of 4.1 with triphenylphosphine oxide. To a stirred solution of 4.1 (85 mg, 0.058 mmol) in toluene (3 mL) at $-35$ °C was added a solution of triphenylphosphine oxide (18 mg, 0.065 mmol) in toluene (1 mL) dropwise over 5 min. The reaction mixture turned bright blue throughout the addition, and was stirred for 30 min. at rt. The bright blue solution was taken to dryness, and the blue-green solid was triturated with hexanes (10 mL). The blue extracts were filtered through Celite, and the filtrate was allowed to concentrate overnight at rt to obtain small teal blue crystals. The pale blue-green supernatant liquid was decanted, and the crystals were dried under vacuum for 30 min. (39 mg, 0.024 mmol, 42%).

$^1$H NMR (C$_6$D$_6$, 400 MHz): $\delta = 7.86$ (t, 2H, 8 Hz), 7.53 (d, 2H, 8 Hz), 7.46 (d, 2H, 7.5 Hz), 7.43 (d, 2H, 7.5 Hz), 7.28 (m, 3H), 7.22 (t, 1H, 7.5 Hz), 7.11 (m, 4H), 6.87 (s, 2H), 6.80 (m,
16H), 6.53 (s, 2H), 6.58 (t, 1H, 7 Hz), 6.37 (t, 2H, 7 Hz), 6.33 (s, 2H), 6.14 (dd, 2H, J_{HH} = 8 Hz, J_{HP} = 6 Hz), and 5.82 (dd, 2H, J_{HH} = 8 Hz, J_{HP} = 6 Hz) (ArH), 2.40 (s, 6H), 2.23 (s, 6H), 1.99 (s, 6H), 1.96 (s, 6H), 1.93 (s, 12H), 1.70 (s, 6H), and 1.62 (s, 6H) (ArCH₃).

$^{31}$P$\{^1$H$\}$ NMR (C$_6$D$_6$, 162 MHz): $\delta = 40.4$ (s, 1P), 4.7 (s, 1P), 0.1 (s, 1P).

$^{13}$C$\{^1$H$\}$ NMR (C$_6$D$_6$, 101 MHz): $\delta = 163.2$ (d, 32 Hz), 159.4 (d, 25 Hz), 145.5 (d, 4 Hz), 143.3, 139.3 (d, 28 Hz), 137.2, 136.6, 135.6, 135.1, 134.8, 134.4, 134.3, 134.2, 134.1, 133.8, 133.7, 133.6, 133.5, 133.4, 133.3, 133.1, 132.9, 132.8, 132.7, 132.4, 132.2, 131.5 (d, 3 Hz), 130.2, 129.7, 129.3, 128.9, 128.7, 128.4, 127.8, 125.6, 125.5, 118.3 (d, 34 Hz), 117.5 (d, 29 Hz), 114.3 (d, 8 Hz), and 113.4 (d, 11 Hz) (ArC), 21.1, 20.9, 20.5, 20.3, 19.8, 19.1, 18.5, and 15.7 (ArCH₃).

The blue crystals were dissolved in C$_6$D$_6$ and the blue solution became green over 24 h at rt. After 24 h at rt, the green solution was analyzed by $^{31}$P$\{^1$H$\}$ NMR spectroscopy.

$^{31}$P$\{^1$H$\}$ NMR (C$_6$D$_6$, 162 MHz): $\delta = 43.2$ (s), 42.4 (s), 40.4 (s), 6.2 (s), 4.7 (s), 0.1 (s), $-3.8$ (s), $-8.9$ (s), $-12.8$ (s), $-17.4$ (s), $-18.1$ (s).

5.5 References.


30 Some coupling constants have been determined by simulation of NMR spectra using the program MestRe-C available at: www.mestrec.com.


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6.1 Thesis overview.

This thesis describes a new arene-bridged diamidophosphine ligand, \([\text{NPN}]^*\text{Li}_2(S)\) (\(S = p-C_6H_4O_2, \text{THF}\)), its coordination to Zr(IV) and Hf(IV), and the application of \([\text{NPN}]^*\text{Zr}\) complexes to the activation and functionalization of \(\text{N}_2\). At the outset, \([\text{NPN}]^*\) was designed to mimic the steric and electronic properties of the \(-\text{SiMe}_2\text{CH}_2-\) bridged \([\text{NPN}]\) ligand, but with the reactive and moisture-sensitive N–Si bond replaced by an N–C bond. Remarkably, the solution and solid-state structures of \([\text{NPN}]^*\text{Li}_2\) and \([\text{NPN}]\text{Li}_2\) are nearly identical.\(^1\) Both compounds feature a P–Li bond and a diamond-shaped Li\(_2\text{N}_2\) core. One major difference between the two ligands is that \([\text{NPN}]^*\text{Li}_2\) is prepared from air-stable organic compounds, and PhPCl\(_2\), whereas \([\text{NPN}]\text{Li}_2\) is prepared from air- and moisture-sensitive PhN(H)SiMe\(_2\text{CH}_2\text{Cl}\), and pyrophoric PhPH\(_2\). In terms of structure and reactivity, there are also many similarities between analogous \([\text{NPN}]^*\text{Zr}\) and \([\text{NPN}]\text{Zr}\) complexes.

Another compelling similarity between \([\text{NPN}]\) and \([\text{NPN}]^*\) is that both ligands support Zr-N\(_2\) complexes. \({\{[\text{NPN}]\text{Zr(THF)}\}_2(\mu-\eta^2:\eta^2-\text{N}_2)\}\) and \({\{[\text{NPN}]^*\text{Zr(THF)}\}_2(\mu-\eta^2:\eta^2-\text{N}_2)\}\) are prepared by KC\(_8\) reduction of dichlorozirconium complexes in THF under N\(_2\).\(^2\) The solution and solid-state structures of these two complexes, as well as those of the corresponding Py adducts, \({\{[\text{NPN}]\text{Zr(Py)}\}_2(\mu-\eta^2:\eta^2-\text{N}_2)\}\) and \({\{[\text{NPN}]^*\text{Zr(Py)}\}_2(\mu-\eta^2:\eta^2-\text{N}_2)\}\), are essentially the same in terms of connectivity and stereochemistry.\(^3\) Phosphine adducts could not be prepared from \({\{[\text{NPN}]\text{Zr(THF)}\}_2(\mu-\eta^2:\eta^2-\text{N}_2)\}\); however, the addition of
PMe₂R (R = Me, Ph) to \([\text{NPN}]^\bullet\text{Zr(THF)}\)₂(μ-η²:η²-N₂) gives \([\text{NPN}]^\bullet\text{Zr(PMe₂R)}\)₂(μ-η²:η²-N₂)\{\text{Zr[NPN]}^\bullet\} in high yield. This type of dinitrogen complex is unique because the two Zr atoms have different coordination environments. From the solid-state molecular structure of the PMe₂Ph complex, it appears that [NPN]⁺ blocks the coordination of a second equivalent of PMe₂R to these derivatives. The [NPN]Zr and [NPN]⁺Zr dinitrogen complexes are the first early transition-metal dinitrogen complexes for which the coordination environment at the metal can be altered simply by adding a donor molecule to a dinitrogen complex. In contrast, ([PNP]ZrCl)₂(μ-η²:η²-N₂) and its congeners, ([PNP]Zr(O-2,6-Me₂C₆H₃)₂(μ-η²:η²-N₂) and ([PNP]ZrCp)₂(μ-η¹:η¹-N₂), are prepared by reducing separately prepared metal precursors under N₂.⁴

The reactivity of the Zr-N₂ complexes of [NPN] and [NPN]⁺ can also be compared. When solutions of \([\text{NPN}]^\bullet\text{Zr(THF)}\)₂(μ-η²:η²-N₂) or \([\text{NPN}]\text{Zr(THF)}\)₂(μ-η²:η²-N₂) are exposed to H₂ gas, no reaction takes place.³ For both \([\text{NPN}]^\bullet\text{Zr(Py)}\)₂(μ-η²:η²-N₂) and \([\text{NPN}]\text{Zr(Py)}\)₂(μ-η²:η²-N₂), the reactions with H₂ provide a mixture of products that could not be separated. Finally, the addition of H₂ to \([\text{NPN}]^\bullet\text{Zr(PMe₂R)}\)₂(μ-η²:η²-N₂)\{Zr[NPN]⁺\} generates \([\text{NPN}]^\bullet\text{Zr(PMe₂R)}\)(μ-H)(μ-η²:η²-NNH)\{Zr[NPN]⁺\} with a new N–H bond. This reaction offers no direct comparison with the [NPN]Zr-N₂ complexes because no PR₃ adduct could be synthesized from \([\text{NPN}]\text{Zr(THF)}\)₂(μ-η²:η²-N₂). However, it may only be possible to synthesize \([\text{NPN}]^\bullet\text{Zr(PMe₂R)}\)(μ-η²:η²-N₂)\{Zr[NPN]⁺\} because of the unique properties of the [NPN]⁺ ligand. What is clear is that the hydrogenation of side-on bound N₂ is not observed when [NPN] is the ancillary ligand, but it is observed in one case when [NPN]⁺ is the ancillary ligand. As is described in chapter one, the formation of new N–H bonds from H₂ and a dinitrogen complex has been

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observed three other times: ([P₂N₂]Zr)₂(μ-η²:η²-N₂H₃) forms from ([P₂N₂]Zr)₂(μ-η²:η²-N₂),⁵ and ([η⁵-C₅Me₅H]₂M(Η)]₂(μ-η²:η²-N₂H₂) forms from [(η⁵-C₅Me₅H]₂M)₂(μ-η²:η²-N₂), for M = Zr and Hf.⁶ Thus, the hydrogenation of the PMe₂R adducts is the fourth example of an N–H bond forming from side-on bound dinitrogen.

The addition of PhSiH₃ to the [NPN]*Zr-N₂ and [NPN]Zr-N₂ complexes provides another opportunity to compare the reactivities of these two systems. ([NPN]*Zr(Py)]₂(μ-η²:η²-N₂) reacts with PhSiH₃ to yield {[NPN]*Zr(Py)}(μ-H)(μ-η¹:η²-NNSiH₂Ph){Zr[NPN]*} with a new N–Si bond. In contrast, the reaction of {[NPN]Zr(THF)}₂(μ-η²:η²-N₂) with PhSiH₃ provides an intractable mixture of products.³ In chapters one and five, some other examples of the functionalization of coordinated dinitrogen with silanes are described.

The reaction of the [NPN]*Zr-N₂ and [NPN]Zr-N₂ complexes with ethylene gas offers the final comparison for the two systems. ([NPN]*Zr(THF)}₂(μ-η²:η²-N₂) does not react with ethylene gas. In contrast, stirring a benzene solution of {[NPN]Zr(THF)}₂(μ-η²:η²-N₂) under 1 atm of ethylene results in the formation of a white precipitate that may be polyethylene.³ The other reactions that have been carried out using the [NPN]*Zr-N₂ or [NPN]-ZrN₂ complexes cannot be compared since different reagents have been used. When {[NPN]Zr(THF)}₂(μ-η²:η²-N₂) is reacted with p-tolylethylene, allene, BH₃·THF, CH₃CN, or "BuSiH₃, mixtures of products are obtained.³ It is unclear whether any of these products form as a result of [NPN] decomposition.

Several reactions of the [NPN]*Zr-N₂ complexes proceed selectively. For example, {[NPN]*Zr(THF)}₂(μ-η²:η²-N₂) reacts with 4,4'-dimethylbenzophenone to give {[NPN]*Zr}₂(μ-O)(μ-η¹:η²-NN=C(4-MeC₆H₄)₂) in high yield. Also, only one product forms
from the reaction of the THF or Py adducts of \{[NPN]^*Zr\}_2(\mu-\eta^2:\eta^2-N_2) with benzophenone imine. A red complex, \{[NPN]^*Zr(N=CPh_2)_2(\mu-\eta^2:\eta^2-N_2H_2)\}, is obtained in high yield. The addition of Ph_3P=O to \{[NPN]^*Zr(THF)_2(\mu-\eta^2:\eta^2-N_2)\} initially generates one product selectively, bright blue \{[NPN]^*Zr(O=PPh_3)_2(\mu-\eta^2:\eta^2-N_2)\}{Zr[NPN]^*}.

At this point the following question remains unanswered: is the [NPN]^* ligand superior to [NPN] in terms of supporting new chemistry for coordinated dinitrogen and minimizing non-productive side reactions? So far, no ligand decomposition reactions or unusual donor atom migrations have been observed for complexes of [NPN]^*. Further investigations may reveal whether side reactions have been minimized by eliminating the reactive N–Si bond from the backbone of [NPN], or by decreasing the flexibility of this diamidophosphine. The results reported in chapter five represent all of the reactions that have been attempted for the [NPN]^*Zr-N_2 complexes. Based on the numerous transformations observed so far, it seems likely that other new and interesting reactions can be achieved starting from \{[NPN]^*Zr(THF)_2(\mu-\eta^2:\eta^2-N_2)\}.

In this chapter, the synthesis of a phenyl-bridged diamidophosphine ligand with MesN and ArN (Ar = 4-'PrC_6H_4) substituents (denoted Ph,Mes[NPN]' and Ph,Ar[NPN]') is presented. This ligand only differs from [NPN]' reported in chapter two (section 2.2.1) in the substituents at N, but it is prepared in two steps from commercially available reagents. First, the bromodiarylamine ligand precursor is prepared in one pot from a substituted aniline and 1,2-dibromobenzene by a Pd-catalyzed cross-coupling reaction. Second, as with [NPN]^*, the lithiated ligands, Ph,Mes[NPN]'Li_2(p-C_6H_5O_2), and Ph,Ar[NPN]'Li_2(S) (S = THF, p-C_6H_5O_2), are obtained from the bromodiarylamine, two equivalents of "BuLi and ~0.5 equivalents of
PhPCl₂. \( \text{Ph}^{\text{Ar}}[\text{NPN}]^*\text{Zr(NMe}_2)_2 \) is prepared in two steps from \( \text{Ph}^{\text{Ar}}[\text{NPN}]^*\text{Li}_2(\text{THF})_2 \) by the protonolysis method used to prepare \( \text{[NPN]}^*\text{Zr(NMe}_2)_2 \).

6.2 Ongoing and Future Projects.

From commercially available compounds, the synthesis of \( \text{[NPN]}^*\text{Li}_2(\beta\text{-C}_4\text{H}_9\text{O}_2) \) can be accomplished in three or four steps, depending on whether \( \beta \)-tolylboronic acid used to prepare \( \text{(Mes)}(\text{Tol})\text{NH} \) is purchased, or prepared by a Grignard reaction.⁷ An alternative approach to an arene-bridged diamidophosphine ligand is via \( \text{(Ar)(2-BrC}_6\text{H}_4)\text{NH} \), which can be prepared in one pot from commercially available anilines and 1,2-dibromobenzene by Pd-catalyzed cross-coupling. Although very few reports of C–N coupling reactions from 1,2-dibromobenzene are available,⁸ it seemed unlikely that disubstituted \( 1,2-(\text{ArNH})_2\text{C}_6\text{H}_4 \) would form in high yield due to steric congestion, at least for \( \text{Ar} = \text{Mes} \). \( \text{Ph}^{\text{Ar}}[\text{NPN}]^*\text{Li}_2 \) is synthesized from \( \text{(Ar)(2-BrC}_6\text{H}_4)\text{NH}, \ \text{BuLi}, \) and \( \text{PhPCl}_2 \). As was outlined in chapter two, phenyl-bridged diamidophosphine ligands are denoted \( \text{[NPN]}^* \), and changes to P or N substituents are indicated by superscripts before the square brackets (e.g., with \( \text{PhP} \) and \( \text{ArN} \) substituents, a phenyl-bridged ligand is denoted \( \text{Ph}^{\text{Ar}}[\text{NPN}]^*\text{Li}_2 \)).

6.2.1 Synthesis and characterization of \( \text{Ph}^{\text{Mes}}[\text{NPN}]^* \).

\( 2,4,6-\text{Me}_3\text{C}_6\text{H}_2)(2-\text{BrC}_6\text{H}_4)\text{NH, 6.1,} \) can be prepared in one pot from 2,4,6-trimethylaniline and 1,2-dibromobenzene, in the presence of 2 mol % \( \text{(DPPF)}\text{PdCl}_2 \) (DPPF = \( 1,1'\text{-bis(diphenylphosphino)ferrocene} \), 4 mol % DPPF, and KO\'Bu in 1,4-dioxane upon heating at 80 °C for three days (Equation 6.1). It is isolated as a white crystalline solid in fair yield (53%) upon work-up. Thus far, attempts to improve the yield of this reaction by increasing the amount of catalyst or trimethylaniline, heating the reaction for seven days, or
by using a different catalyst and ligand (Pd₂(dba)₃ and rac-BINAP) have failed. Excess dibromobenzene and trimethylaniline can be removed from 6.1 by flash column chromatography, but filtering the reaction mixture through silica, followed by recrystallization, is also an effective method of purification. Compound 6.1 has been characterized by ¹H and ¹³C{¹H} NMR spectroscopy, GC-MS, and combustion analysis.

![Reaction Scheme](image)

PhMes[NPN][Li₂(p-C₄H₈O₂)] ([N-(2,4,6-Me₃C₆H₂)(2-N(Li)C₆H₄)]₂PhP(p-C₄H₈O₂)), 6.2(p-C₄H₈O₂), can be prepared from 6.1, two equivalents of "BuLi and 0.48 equivalents of PhPCl₂ in Et₂O by the same method used to prepare 2.7(p-C₄H₈O₂) (Equation 6.2). Toluene-soluble 6.2(p-C₄H₈O₂) is isolated as a yellow solid in high yield. It has been characterized in C₆D₆ solution by ¹H, ³¹P{¹H}, ¹³C{¹H}, and ⁷Li{¹H} NMR spectroscopy, and in the solid-state by single crystal X-ray diffraction.

![Reaction Scheme](image)

There is a quartet in the ³¹P{¹H} NMR spectrum of 6.2(p-C₄H₈O₂) at δ —35.2 (JPLi = 41 Hz), and a doublet (δ 0.05) and singlet (δ —1.89) appear in the ⁷Li{¹H} NMR spectrum. In the ¹H NMR spectrum there are three singlets at ~ δ 2.3 assigned to ArCH₃ groups. As for
2.7\( \cdot \)(\( p \)-C\(_4\)H\(_8\)O\(_2\))\), the ortho-methyl groups on MesN are inequivalent due to restricted rotation about N—C\(_{ph}\). Resonances attributable to ArH protons in the C\(_4\) symmetric compound and one equivalent of coordinated dioxane are also evident. The peaks in the \(^{13}\)C\{\(^1\)H\} NMR spectrum are also consistent with the proposed structure.

The solid-state molecular structure of 6.2\( \cdot \)(\( p \)-C\(_4\)H\(_8\)O\(_2\)) is shown in Figure 6.1. The compound forms chains of 6.2 linked by dioxane molecules, and one half of each dioxane coordinated to 6.2 is shown in Figure 6.1. As with 2.7\( \cdot \)2THF, there are two Li environments. Li2 is coordinated to N1, N2 and P1 of \([\text{NPN}]^+\), and O1 of dioxane, whereas Li1 is coordinated to N1 and N2, and O2 of another molecule of dioxane. The stereochemistry around Li1 is distorted tetrahedral, and the stereochemistry around Li2 is distorted trigonal. The bond lengths are essentially the same as those in 2.7\( \cdot \)2THF, within error. The P—Li1 bond length is 2.484(8) Å, the Li1—N bond lengths average to about 2.06 Å, and the Li2—N bond lengths average to about 2.02 Å. The Li1—Li2 separation is 2.474(12) Å. The bond lengths and angles are similar to those of \(-\text{SiMe}_2\text{CH}_2-\) bridged 6.2\( \cdot \)THF, \(\text{Cy}_{\text{Mes}}[\text{NPN}]\text{Li}_2(\text{THF}),\)
\(\text{Cy}_{\text{Ph}}[\text{NPN}]\text{Li}_2(\text{THF})_2,\) and \(\text{Ph}_{\text{Ph}}[\text{NPN}]\text{Li}_2(\text{THF})_2\).\(^{1,10}\)
Figure 6.1. ORTEP drawing of the solid-state molecular structure of $^{\text{PhMe}}[\text{NPN}]^+\text{Li}_2^-(\rho$-dioxane), 6.2$(\rho\text{-C}_8\text{H}_8\text{O}_2)$ (ellipsoids drawn at the 50% probability level). Half of each molecule of dioxane coordinated to 6.2 in the 1-D network is shown. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P01–Li01 2.484(8), N01–Li01 2.065(9), N01–Li02 2.014(10), Li01–Li02 2.474(12), O01–Li02 1.910(9), O2–Li01 1.892(9), N02–Li02 1.892(9), N02–Li01 2.056(9), P01–Li01–Li02 77.4(3), N01–Li01–N02 103.7(4), Li01–N01–Li02 74.7(4), O01–Li02–N01 126.3(5), O01–Li02–N02 122.7(5), O02–Li01–N01 123.8(5), O02–Li01–N02 118.8(4).

The proligand, $[\text{NPN}]^+\text{H}_2$, 6.3, can be prepared from 6.2$(\rho\text{-C}_8\text{H}_8\text{O}_2)$ and Me$_3$N·HCl in THF (Equation 6.3), and is isolated as a white solid in quantitative yield. In C$_6$D$_6$ solution, 6.3 is similar to $[\text{NPN}]^+\text{H}_2$ (2.8). There is a singlet in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at $\delta$ −34.3. In the $^1\text{H}$ NMR spectrum, there is a sharp singlet at $\delta$ 2.14, due to para-methyl on MesN, and two broad singlets at $\delta$ 2.06 and 1.92, due to two ortho-methyl groups on MesN. There are
also two broad singlets at δ 6.77 and 6.72 assigned to meta C–H groups. As with 2.8, hindered rotation about N–C<sub>meta</sub> broadens resonances on MesN. In the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 6.3, peaks due to ortho-methyl (δ 18.2 and 18.0) and meta carbons (δ 135.9 and 135.8) are also broad. The other resonances observed in the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra can all be assigned to groups in the proposed C<sub>s</sub> symmetric diaminophosphine.

The solid-state molecular structure of 6.3 is shown in Figure 6.2. The P–C bond lengths are the same within error, at ~1.83 Å, and the C–P–C angles are ~103°, with C16–P1–C22 slightly shorter at 102.24(10)°, possibly due to crystal packing effects. The bond lengths and angles are similar to those of N-(2,6-tBu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(2-NC<sub>6</sub>H<sub>4</sub>)PPh<sub>2</sub>.<sup>11</sup> There is a distance of 3.66 Å between C19 on the (C<sub>6</sub>H<sub>5</sub>)P group of 6.3 in the asymmetric unit and C20 of the other molecule of 6.3 in the unit cell (Figure 6.3), which is consistent with the presence of weak intermolecular π–π interactions in the solid state.<sup>12</sup>
Figure 6.2. ORTEP drawing of the solid-state molecular structure of \( \text{PhMeS}[\text{NPN}]\text{H}_2 \). (ellipsoids drawn at the 50% probability level). All hydrogen atoms except H1N and H2N (located from the electron density map) have been omitted for clarity. Selected bond lengths (Å) and angles (°): N1–C1 1.436(3), N1–C10 1.390(3), P1–C15 1.835(2), P1–C16 1.833(2), P1–C22 1.830(2), N2–C27 1.400(3), C15–P–C16 103.11(10), C15–P1–C22 102.83(9), C16–P1–C22 102.24(10), C10–N1–C1 121.10(18), N1–C1–C2 119.30(19), C27–N2–C28 123.99(18).
Figure 6.3. ORTEP representation of crystal packing in 6.3. π-stacking interactions may be responsible for close contact of \((C_6H_5)P\) substituents (3.66 Å) at the centre of the unit cell.

Phenyl-bridged 6.2 and 6.3 are similar to \([NPN]^\cdot Li_2(p-C_6H_5O_2)\) (2.7) and \([NPN]^\cdot H_2\) (2.8) by all the methods used to characterize the compounds thus far. The electronic and steric effects of replacing one Me group on the arene backbone with hydrogen are probably minimal, and the synthesis of group 4 complexes of \(PhMe[NPN]^\cdot\) by a protonolysis route is ongoing. Although 6.2 and 2.7 are similar, other modifications to the arene-bridged amidophosphines may have a greater impact on the structure and reactivity of the ligand and its complexes. It is likely that amidophosphine ligands could be synthesized with different P or N substituents, and the nature of the backbone could also be altered.
6.2.2 Synthesis and characterization of $^{\text{PhAr}}\text{[NPN]}'$ ($\text{Ar} = 4^\text{-PrC}_6\text{H}_4$).

The synthesis of bromo(diarylamine) ligand precursors from 1,2-dibromobenzene is a convenient new route to diamidophosphine ligands with different amide substituents. For example, (4-$^\text{-PrC}_6\text{H}_4$)(2-BrC$_6$H$_4$)NH, 6.4, can be prepared in moderate yield as a colourless oil by refluxing 4-$^\text{-PrC}_6\text{H}_4$NH$_2$, 1,2-dibromobenzene, and NaO'Bu in the presence of Pd$_2$(dba)$_3$ (1 mol %) and rac-BINAP (2 mol %) in toluene (Equation 6.4). Since 6.4 is a liquid at room temperature, it cannot be purified easily by recrystallization. Instead, 6.4 must be separated from unreacted 1,2-dibromobenzene by column chromatography. As with 6.1, the optimization of the synthesis of 6.4 is ongoing. The compound has been characterized by $^1$H and $^{13}$C($^1$H) NMR spectroscopies, EI-MS, and combustion analysis.

$$\begin{align*}
\text{Ph}_2\text{P} \quad \text{Pd}_2(\text{dba})_3 \\
\text{NaO}^\text{Bu} \quad \text{rac-BINAP} \quad (6.4)
\end{align*}$$

$^{\text{PhAr}}\text{[NPN]}'$Li$_2$($p$-C$_6$H$_5$O$_2$), 6.5($p$-C$_6$H$_5$O$_2$), can be prepared from 6.4, two equivalents of $^\text{BuLi}$, and 0.48 equivalents of PhPCl$_2$ in Et$_2$O (Equation 6.5). The product is isolated in high yield as a yellow solid that is freely soluble in toluene, and somewhat soluble in hexanes. The major peaks in the $^1$H NMR spectrum can be assigned to protons in the C$_i$ symmetric complex, and minor peaks are consistent with the presence of about 5% of (4-$^\text{-PrC}_6\text{H}_4$)(2-$^\text{-LiC}_6\text{H}_4$)NLi. When 6.5($p$-C$_6$H$_5$O$_2$) is recrystallized from hexanes/THF at $-35 \degree$C, 6.5·2THF is obtained. In the $^1$H NMR spectrum, signals due to coordinated THF appear and there is no peak due to dioxane. In addition, only peaks attributable to the major product are present. The isolated yield of 6.5, however, is decreased upon recrystallization. There is a
quartet \( (J_{PL} = 42 \text{ Hz}) \) at \( \delta -34.8 \) in the \(^{31}\text{P}\{^1\text{H}\} \) NMR spectrum, and a doublet (\( \delta -0.36 \)) and
singlet (\( \delta -1.70 \)) appear in the \(^7\text{Li}\{^1\text{H}\} \) NMR spectrum of 6.5·2THF in \( \text{C}_6\text{D}_6 \) (Figure 6.4). In
the \(^1\text{H}\) NMR spectrum, a heptet at \( \delta 2.83 \) and two doublets at \( \delta 1.26 \) and 1.25 are assigned to
\( \text{CH(CH}_3)_2 \) and two inequivalent \( \text{CH(CH}_3)_2 \) groups, respectively. Resonances in the aromatic
region can be assigned to protons in \( \text{C}_5 \) symmetric 6.5, and there are two resonances
consistent with the presence of two equivalents of coordinated THF. In the \(^{13}\text{C}\{^1\text{H}\} \) NMR
spectrum, the expected resonances for \( \text{ArC, CH(CH}_3)_2, \text{CH(CH}_3)_2, \) and coordinated THF
appear. Ongoing efforts to optimize this reaction indicate that 6.5·(\( p\)-\( \text{C}_4\text{H}_8\text{O}_2 \)) forms in
higher yield and purity by adding exactly 0.50 equivalents of \text{PhPCl}_2 slowly to the \( \text{Et}_2\text{O} \)
solution of the proposed intermediate, (4-\( \text{PrC}_6\text{H}_4 \))(2-\( \text{LiC}_6\text{H}_4 \))\( \text{NLi} \), slowly warming the
reaction mixture to room temperature, and finally, heating the reaction mixture to reflux
overnight.\(^{13}\)

Figure 6.4. \(^{31}\text{P}\{^1\text{H}\} \) and \(^7\text{Li}\{^1\text{H}\} \) NMR spectra of 6.5·2THF in \( \text{C}_6\text{D}_6 \).

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The ORTEP representation of the solid-state molecular structure of 6.5·(p-C₆H₄O₂) is shown in Figure 6.5. The compound forms a one-dimensional chain of Ph₆[NPN]Li₂ units bridged by 1,4-dioxane. The P1–Li2 bond length is 2.477(7) Å. The N–Li1 bond lengths are similar and average to 1.98 Å, and the N–Li2 bond lengths are similar, but average to ~2.06 Å. The O–Li bond lengths are identical, within error, at about 1.87 Å, and the Li1—Li2 separation is 2.418(10) Å. The bond lengths are very similar to those of 6.2·(p-C₆H₄O₂) and are slightly shorter than those of 2.7·2THF.
Figure 6.5. ORTEP drawing of the solid-state molecular structure of $^{\text{Ph}}_{\text{Ar}}$[NPN]$:\text{Li}_2$$(p$-$C_6H_4O_2)$, 6.5$(p$-$C_6H_4O_2)$ (ellipsoids drawn at the 50% probability level). All hydrogen atoms and the carbon atoms of dioxane have been omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): P1–Li2 2.477(7), N1–Li1 1.974(9), N1–Li2 2.050(9), N2–Li2 2.079(8), N2–Li1 1.978(9), O1–Li1 1.867(8), O2–Li2 1.868(8), Li1–Li2 2.418(10), P1–Li1–Li2 80.9(3), N1–Li2–N2 102.8(3), Li1–N1–Li2 73.8(3), Li1–N2–Li2 73.1(3), O1–Li1–N1 123.4(5), O1–Li1–N2 126.7(5), O2–Li2–N1 131.3(4), O2–Li2–N2 120.0(4).

$^{\text{Ph}}_{\text{Ar}}$[NPN]$^*_{\text{Zr}}$(NMe$_2$)$_2$, 6.6, can be prepared in two steps from 6.5·2THF by the same route used to prepare [NPN]$^*$Zr(NMe$_2$)$_2$ (2.9) (Scheme 6.1). First, excess Me$_3$NH·HCl is added to a THF solution of the lithiated ligand. The yellow suspension turns white instantly, and $^{\text{Ph}}_{\text{Ar}}$[NPN]$^*_{\text{H}}$ is isolated in quantitative yield as a white translucent residue upon work-up. There is a singlet at $\delta$ –32.4 in the $^{31}$P{$^1$H} NMR spectrum of $^{\text{Ph}}_{\text{Ar}}$[NPN]$^*_{\text{H}}$ in C$_6$D$_6$. The $^1$H NMR spectrum (Figure 6.6) features a doublet ($^{J\text{PH}}$ = 6 Hz) at $\delta$ 6.39 assigned to NH, a heptet at $\delta$ 2.66 assigned to CH(CH$_3$)$_2$, and a doublet at $\delta$ 1.12 assigned to CH(CH$_3$)$_2$, as well
as the expected aromatic protons. The peaks in the $^{13}$C{\textsuperscript{1}H} NMR spectrum are also consistent with the proposed structure for the proligand.

\[ \text{CH(CH}_3\text{)}_2 \]

Figure 6.6. 500 MHz $^1$H NMR spectrum of $^{\text{Ph}}\text{Ar[NPN]}\text{H}_2$ in $\text{C}_6\text{D}_6$.

In the second step, $^{\text{Ph}}\text{Ar[NPN]}\text{H}_2$ is mixed with equimolar $\text{Zr(NMe}_2\text{)}_4$ in toluene. $^{\text{Ph}}\text{Ar[NPN]}\text{Zr(NMe}_2\text{)}_2$ (6.6) is obtained in high yield as a toluene-soluble yellow powder (see Scheme 6.1). A singlet is observed at $\delta -10.0$ in the $^{31}$P{\textsuperscript{1}H} NMR spectrum of 6.6 in $\text{C}_6\text{D}_6$. In the $^1$H NMR spectrum (Figure 6.7), there are singlets due to two inequivalent $\text{N(CH}_3\text{)}_2$ groups at $\delta 2.84$ and 2.51, and a heptet ($\delta 2.76$) and doublet ($\delta 1.19$) due to $\text{CH(CH}_3\text{)}_2$ and $\text{CH(CH}_3\text{)}_2$ groups of the para-isopropyl substituents, as well as the expected ArH peaks for the C\textsubscript{4} symmetric complex. Although two doublets are expected for the two inequivalent $\text{CH(CH}_3\text{)}_2$ groups ($\delta \sim 1.2$), these resonances overlap. Two singlets are observed for the inequivalent $\text{CH(CH}_3\text{)}_2$ groups at $\delta 24.3$ and 24.2 in the $^{13}$C{\textsuperscript{1}H} NMR spectrum. The expected $\text{CH(CH}_3\text{)}_2$ ($\delta 34.0$), $\text{N(CH}_3\text{)}_2$ ($\delta 41.5$, and 40.7), and ArC peaks also appear.
Scheme 6.1.

Figure 6.7. 500 MHz $^1$H NMR spectrum of 6.6 in C$_6$D$_6$.

The ORTEP representation of the solid-state molecular structure of 6.6 is shown in Figure 6.8. Tridentate [NPN]$^+$ coordinates to Zr facially, and the P1–Zr1–N1 (72.06(5)$^\circ$), and P1–Zr1–N2 (70.70(5)$^\circ$) angles are less than 90$^\circ$, as was observed for [NPN]$^+$ complexes of Zr and Hf. The geometry at Zr can best be described as intermediate between trigonal
The bond lengths and angles are as expected: the P1–Zr bond length is 2.7353(6) Å. The N–Zr bonds to [NPN]' are the same within error, at about 2.16 Å. The N3–Zr bond to N(CH3)2 approximately trans to P (2.053(2) Å) is slightly longer than the N4–Zr bond (2.0253(19) Å). The solid-state molecular structure of complex 6.6 can be compared to that of [NPN]*Hf(NMe2)2 (2.14). The two structures have similar M–P and M–N bond lengths, and these fall within the range of expected values. In 2.14, the P1–Hf–N1 and P1–Hf–N2 angles (72.89(4), and 70.71(4)°) are similar to those in 6.6. The P1–Zr–N3 angle (155.11(6)°) is slightly more acute than the P1–Hf–N3 angle (163.60(6)°). The N1–Zr–N2 (125.14(7)°) and N3–Zr–N4 angles (104.44(8)°) are slightly more obtuse than N1–Hf–N2 (120.91(6)°) and N3–Hf–N4 (100.92(8)°). It will be necessary to prepare other group 4 [NPN]' complexes to determine if 6.6 differs from 2.14 because the diamidophosphine ligand is less bulky, or because of other factors (e.g., identity of the metal, crystal packing).
6.8 (ellipsoids drawn at the 50% probability level). All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P1–Zr01 2.7353(6), N1–Zr01 2.1563(19), N2–Zr01 2.159(2), N3–Zr01 2.053(2), N4–Zr01 2.0253(19), P1–Zr01–N1 72.06(5), P1–Zr01–N2 70.70(5), N3–Zr01–N4 104.44(8), N1–Zr01–N2 125.14(7), P1–Zr01–N3 155.11(6), P1–Zr01–N4 100.37(6), N1–Zr01–N4 115.42(8), N2–Zr01–N3 98.62(8).

The preparation of Ph\textsubscript{Ar}[NPN]\textsuperscript{+}ZrCl\textsubscript{2} and its application to nitrogen activation are ongoing projects in the Fryzuk group. The Ph\textsubscript{Ar}[NPN]\textsuperscript{+} ligand may support very different chemistry than [NPN]\textsuperscript{+}. For example, the intramolecular cyclometalation reaction that occurs spontaneously for [NPN]\textsuperscript{+}Zr(CH\textsubscript{2}Ph)\textsubscript{2} and [NPN]\textsuperscript{+}Zr(CH\textsubscript{2}SiMe\textsubscript{3})\textsubscript{2} cannot occur for the proposed complex Ph\textsubscript{Ar}[NPN]\textsuperscript{+}Zr(CH\textsubscript{2}Ph)\textsubscript{2} because it lacks ortho-methyl substituents. If
alkylzirconium complexes of [NPN]' can be prepared, their reactivity with H₂ should be explored; zirconium hydrides are attractive starting materials for Zr-N₂ complexes. Since [NPN] and [NPN]' ligands support dinuclear side-on Zr-N₂ complexes, it is likely that a similar N₂ complex can be prepared with [NPN]''. It will be interesting to determine the effect the [NPN]' ligand has on the structure and reactivity of a Zr-N₂ complex.

PhAr[NPN]' is expected to mimic [NPN] more closely than [NPN]' does because both contain ArN substituents without bulky ortho- or meta-substituents. [NPN]TaMe₃ reacts with H₂ to yield ([NPN]Ta)₂(μ-H)₄, which reacts with N₂ to give ([NPN]Ta)₂(μ-H)₂(μ-η¹:η²-N₂).¹⁶ This unusual reaction has proven difficult to replicate when other N substituents on [NPN] are present. For example, when PhAr[NPN]TaMe₃ (Ar = 2,6-Me₂C₆H₃) is stirred under H₂, (PhAr[NPN]Ta)₂(μ-H)₄ does not form.¹⁷ Only one other [NPN] ligand, Cy₂Ph[NPN], supports a Ta(V) trimethyl complex that yields a Ta(IV) tetrahydride upon reaction with H₂.¹⁸ The sensitivity of this reaction to the amide substituent of [NPN] is a compelling reason to prepare a complex such as PhAr[NPN]'TaMe₃ and characterize its reactivity with H₂.

[NPN]' has bulky MesN substituents compared to PhAr[NPN]''. There are, however, other amide substituents that would provide even greater steric bulk. For example, it may be possible to synthesize bulky PhAr[NPN]'Li₂(S)₂ (Ar = 2,6-Pr₂C₆H₃, S = p-C₄H₈O₂, THF) (Figure 6.9) by a similar route used to prepare 6.5(p-C₄H₈O₂) from 2,6-Pr₂C₆H₃ and 1,2-dibromobenzene. If a super-bulky diamidophosphine ligand, such as PhAr[NPN]'Li₂(S)₂ (Ar = 3,5-(2,6-Pr₂C₆H₃)₂C₆H₃) (Figure 6.9) can be prepared, it may support new reactivity for coordinated N₂. Extremely bulky triamidoamine ligands were recently used to carry out the first catalytic formation of NH₃ from N₂.¹⁹ A simpler diamidophosphine ligand, PhAr[NPN]'Li₂(S)₂ (Figure 6.9) is less bulky than [NPN]', but the alkyl substituents will
increase the basicity of the amides. Thus, the 'PrN-substituted ligand may not be ideal for the synthesis of dinitrogen complexes, but the ligand may be suited to other applications.

Figure 6.9. [NPN]' ligands with 2,6-'Pr₂C₆H₃, [3,5-(2,6-'Pr₂C₆H₃)₂C₆H₃], and 'Pr substituents on N (S = THF or dioxane).

Some other variations of [NPN]' are illustrated in Figure 6.10. The synthesis of ligands such as Cy-Mer[NPN]'Li₂(S)₂ and 'Pr-Mer[NPN]'Li₂(S)₂ should be possible if commercially available CyPCl₂ and 'PrPCl₂ are used instead of PhPCl₂ in the metathesis reaction with 6.1. The use of substituted anilines should allow the electronic properties of the ligand to be tuned. For example, (4-CF₃C₆H₄)N donors will make Ph-Ar[NPN]'Li₂(S)₂ less basic, whereas (4-MeOC₆H₄)N donors will make the amide donor more basic.

Figure 6.10. Variations on [NPN]' with CyP, 'PrP, and (4-CF₃C₆H₄)N substituents.
In addition to varying the N and P substituents of a diamidophosphine ligand, the backbone itself may be altered. Although the use of Si–N bonds in the backbone should be avoided, other C–N bridged ligands could be explored. A 2,3-substituted naphthalene-linked diamidophosphine ligand may be a starting point in the design of hemilabile ligands for late transition metals with applications to photochemistry (Figure 6.11). It should be possible to tune the ligand electronics by adding electron-donating or -withdrawing groups to the linker. For example, it may be possible to prepare ([N-(MesN)-2-N(Li)-5-CF₃C₆H₃)₂PPh₂(S)] (Figure 6.11) by the same route used to prepare [NPN]⁺, from 4-CF₃C₆H₄NH₂ and ρ-MeC₆H₄B(OH)₂. It may be possible to synthesize chiral diamidophosphine ligands with alkyl linkers (Figure 6.11) for applications to chiral synthesis.

Figure 6.11. Diamidophosphine ligands with alternative bridging groups.

### 6.2.3 Other reactions of zirconium dinitrogen complexes.

The reactions of H₂, PhSiH₃, CO, ethylene, 4,4'-dimethylbenzophenone, benzophenone imine, Ph₃PO, and Me₃CC(=O)H with Zr-N₂ complexes are explored to some extent in this thesis. The addition of other silanes, ketones, phosphine oxides, and aldehydes to the Zr-N₂ complexes may help to shed light on the factors governing these reactions. In addition, the reactions of 4.4 with H₂, 4.1 with 4,4'-dimethylbenzophenone or Ph₃PO, or 4.2 with benzophenone imine may be good candidates for mechanistic study.
because of the time required for the reaction, the colour changes observed, and the potential to use UV-vis, IR or NMR spectroscopy to follow the formation of products or intermediates. Other reactions that may yield new N-element bonds include the addition of boranes, alanes, or transition metal hydrides (e.g., Cp₂ZrH₂) to the Zr-N₂ complexes. The reaction of alkynes with Zr-N₂ complexes should be attempted because new N–C bonds form from the addition of ArC≡CH to ([P₂N₂]Zr)₂(μ-η²:η²-N₂). The addition of aldehydes or ketones that contain additional functional groups, such as olefins, may yield interesting new products. For example, the addition of dibenzylideneacetone (dba) to 4.1 may generate a new C=N bond, followed by reaction of Zr with an olefin group. There are many potentially interesting reactions between the Zr-N₂ complexes described in chapter four and organic or inorganic reagents that have not yet been explored.

6.3 Conclusions.

In this chapter, an ortho-phenylene-bridged diamidophosphine ligand, \( \text{PhMe}\{\text{NPN}\}^\text{Li}_2(\text{p-C}_6\text{H}_5\text{O}_2) \), is described. The bromodiarylamine precursor to this ligand is synthesized from 1,2-dibromobenzene and 2,4,6-Me₃C₆H₂NH₂ in one pot by a Pd-catalyzed C–N coupling reaction. By a similar procedure, the bromodiarylamine ligand precursor, (4-PrC₆H₄)NH(2-BrC₆H₄), is prepared in one pot from 4-PrC₆H₄NH₂ and 1,2-dibromobenzene. From this compound, the less bulky diamidophosphine ligand, \( \text{PhAr}\{\text{NPN}\}^\text{Li}_2(\text{p-C}_6\text{H}_5\text{O}_2) \) (Ar = 4-PrC₆H₄), is synthesized. A Zr(IV) complex, \( \text{PhAr}\{\text{NPN}\}^\text{Zr(NMe}_2)_2 \), is prepared from the lithiated ligand by a two-step protonolysis route.

The Pd-catalyzed C–N coupling route to bromodiarylamine ligand precursors described in this chapter allows arene-bridged diamidophosphine ligands with different substituents at N to be prepared. Thus far, this synthetic strategy has provided two ligands:
one with a bulky MesN substituent, and one with a $4^1$PrC$_6$H$_4$N substituent. The synthesis of group 4 complexes of these ligands, and the application of these complexes to the activation and functionalization of molecular nitrogen are ongoing projects in the Fryzuk group.

6.4 Experimental.

6.4.1 General experimental.

General experimental conditions are as given in chapter two. GC-MS spectra were recorded on an Agilent series 6890 GC system with a 5973 Mass selective detector.

6.4.2 Starting materials and reagents.

Zr(NMe$_2$)$_4$,$^{24}$ Pd$_2$(dba)$_3$,$^{25}$ DPPF,$^{26}$ and (DPPF)PdCl$_2$,$^{27}$ were prepared according to literature methods. Dichlorophenylphosphine, and 2,4,6-trimethylaniline were distilled prior to use. Trimethylamine hydrochloride was suspended in benzene and heated to reflux overnight in a Dean-Stark apparatus to remove water. 1,2-Dibromobenzene was stored over activated Linde 4 Å molecular sieves and sparged with N$_2$ prior to use. $^t$BuLi (~1.6 M in hexanes) was titrated against benzoic acid in THF with $o$-phenanthroline as an indicator. All other compounds were purchased from commercial suppliers and used as received.

$(2,4,6$-Me$_3$C$_6$H$_2)(2$-BrC$_6$H$_4)NH$ (6.1). (DPPF)PdCl$_2$ (0.620 g, 0.848 mmol) and DPPF (0.939 g, 1.69 mmol) were added to 1,4-dioxane (100 mL). To this mixture was added KO'Bu (6.2 g, 55.4 mmol), 1,2-dibromobenzene (10 g, 42.4 mmol), and 2,4,6-trimethylaniline (7.4 g, 54.8 mmol). The orange-brown mixture was heated to reflux for 3 d, cooled, and taken to dryness to obtain a brown residue. The residue was suspended in EtOAc (100 mL) and the suspension was filtered through a plug (~5 cm deep) of silica in a
120-mL glass frit. The dark yellow filtrate was taken to dryness to obtain a light brown residue. The residue was dissolved in petroleum ether (50 mL), and the solution was transferred by 5-mL aliquots onto a plug (~5 cm deep) of silica in a 120-mL glass frit. The silica was then rinsed with 5-mL aliquots of petroleum ether until the yellow product was eluted from the silica. A brown by-product remained on the top layer of silica. The filtrate was taken to dryness to obtain a yellow residue that was dissolved in EtOH. Dilute hydrochloric acid (0.01 M) was added dropwise to the yellow EtOH solution until the mixture became cloudy. The mixture was heated until it became clear yellow, and was cooled slowly to obtain white flaky crystals. The crystals were collected on a frit, rinsed with petroleum ether (2 x 5 mL), and dried (6.5 g, 22.5 mmol, 53%). To ensure that 6.1 was dry and acid-free before use, the white crystals were dissolved in EtO and extracted with a saturated aqueous solution of K₂CO₃. The organic layer was separated, dried over Na₂SO₄, filtered, and taken to dryness to yield white crystals.

¹H NMR (CDCl₃, 300 MHz): δ = 7.40 (d, 1H, 8 Hz), 6.79 (t, 1H, 8 Hz), 6.77 (s, 2H), 6.37 (t, 1H, 8 Hz), and 6.19 (d, 1H, 7 Hz) (ArH), 5.49 (bs, 1H, NH), 2.15 (s, 3H), and 2.00 (s, 6H) (ArCH₃).

¹³C{¹H} NMR (C₆D₆, 75 MHz): δ = 143.5, 136.0, 132.2, 129.0, 127.6, 127.4, 127.1, 118.2, 112.1, and 109.0 (ArC), 20.4, and 17.4 (ArCH₃).

GC-MS: 17.6 min (m/z): 291 (100, [M + H]⁺).


PhMes[NPN]⁺Li⁺(p-C₄H₈O₂) (6.2·(p-C₄H₈O₂)). To a stirred solution of 6.1 (8.7 g, 30.0 mmol) in Et₂O (250 mL) at −35 °C was added "BuLi (1.6 M, 37.5 mL, 60 mmol) dropwise over 15 min. The clear yellow solution was warmed to rt and stirred for 3 h. The solution
was chilled (—35 °C), and PhPCL₂ (2.58 g, 14.4 mmol) in Et₂O (20 mL) was added dropwise over 2 h at this temperature. The reaction mixture turned dark orange throughout the addition. The orange solution was warmed slowly to rt and stirred for 24 h to obtain an orange-yellow suspension. The suspension was taken to dryness under vacuum to obtain an orange foam. Hexanes (100 mL) was added to the foam to obtain a translucent pale orange solution. Upon addition of 1,4-dioxane (5 mL) a yellow precipitate formed. The yellow suspension was filtered through Celite in a frit, and the yellow solids and Celite were rinsed with hexanes (3 × 10 mL). The yellow solids were then transferred to an Erlenmeyer flask along with some of the Celite. The yellow filtrate was allowed to concentrate overnight in the glovebox atmosphere to obtain small yellow crystals that were collected on a frit and dried. Meanwhile, the yellow solids mixed with Celite were suspended in toluene (150 mL) with THF added (2 mL), and the suspension was filtered through Celite (~3 cm deep in a glass frit). The yellow filtrate was taken to dryness to obtain a yellow powder. The combined solids (6.60 g, 10.5 mmol, 73%) were stored at —35 °C. Single crystals of 6.2·(p-C₄H₈O₂) were grown by slow evaporation of a concentrated benzene solution of the compound.

¹H{³¹P} NMR (C₆D₆, 300 MHz): δ = 7.81 (m, 4H), 7.05 - 6.99 (m, 5H), 6.97 (s, 2H), 6.89 (s, 2H), 6.60 (d, 2H, 8 Hz), and 6.58 (d, 2H, 8 Hz) (ArH), 3.35 (bs, 4H, dioxane), 2.34 (s, 6H), 2.32 (s, 6H), and 2.29 (s, 6H) (ArCH₃), 1.25 (bs, 4H, dioxane).

³¹P{¹H} (C₆D₆, 121 MHz): δ = —35.2 (q, ⁴J_Pₗi = 41 Hz).

⁷Li{¹H} (156 MHz, C₆D₆): δ = 0.05 (d, 1Li, ⁷J_Lₗ = 41 Hz), —1.89 (s, 1Li).

Ph,Mes [NPN]H₂ (6.3). Trimethylammonium chloride (0.836 g, 8.75 mmol) was added all at once to a stirred solution of 6.2·(p-C₄H₈O₂) (1.10 g, 1.75 mmol) in THF (15 mL). The yellow suspension immediately became colourless. After 1 h, the white suspension was taken to
dryness to obtain white solids. The solids were extracted with hot toluene (20 mL, ~50 °C) and the extracts were filtered through Celite in a glass frit. The colourless filtrate was taken to dryness to obtain a white powder that was collected on a frit, washed with cold pentane (3 mL, −35 °C), and dried (0.88 g, 1.7 mmol, 95%). Compound 6.3 is air-stable as a solid for weeks and in solution for days, although in our laboratory it is stored in the glovebox to keep it water-free. Single crystals of 6.3 suitable for X-ray analysis were grown by slow evaporation of a benzene solution of the compound.

$^1H\{^{31}P\}$ NMR (C$_6$D$_6$, 300 MHz): δ = 7.59 (t, 2H, 7 Hz), 7.35 (d, 2H), 7.16-6.98 (m, 5H), 6.77 (bs, 2H), 6.72 (bs, 2H), 6.65 (t, 2H, 7 Hz), and 6.37 (d, 2H, 8 Hz) (ArH), 6.11 (s, 2H, NH), 2.14 (s, 6H), 2.06 (bs, 6H), and 1.92 (bs, 6H) (ArCH$_3$).

$^{31}P\{^1H\}$ NMR (C$_6$D$_6$, 121 MHz): δ = −34.3 (s).

$^{13}C\{^1H\}$ NMR (C$_6$D$_6$, 300 MHz): δ = 149.9 (d, 18 Hz), 136.0, 135.9 (bs), 135.8 (bs), 135.3, 134.9 (4 Hz), 134.6, 134.4, 134.1 (5 Hz), 131.2, 129.6, 129.1, 129.0 (7 Hz), 118.8, 117.8 (d, 6 Hz), and 112.3 (ArC), 21.4, 18.2 (bs), and 18.0 (bs) (ArCH$_3$).

(4-PrC$_6$H$_4$)(2-BrC$_6$H$_4$)NH (6.4). In an N$_2$ glovebox, rac-BINAP (1.74 g, 2.8 mmol) and Pd$_2$(dba)$_3$ (1.28 g, 1.4 mmol) were suspended in toluene (200 mL) in a 500-mL Teflon-sealed bomb and stirred for 10 min. 1,2-Dibromobenzene (35.4 g, 17.9 mL, 0.15 mol) and NaO'Bu (20.2 g, 0.21 mol) were added to the solution, and the flask removed to the Schlenk line. Under N$_2$, 4-isopropylaniline (22.4 g, 23.4 mL, 0.17 mol) was added to the reaction. The puce suspension was stirred and heated at 80 °C for 5 d under N$_2$. The brown reaction mixture was cooled, and extracted with H$_2$O (3 × 200 mL). The organic phase was separated, dried with Na$_2$SO$_4$, filtered, and concentrated under vacuum to obtain a dark
purple residue. The residue was purified by flash column chromatography on silica gel (pet ether, \( R_f = 0.6 \)) to obtain 6.4 as a colourless liquid (27.1 g, 62%).

\( ^1\)H NMR (C\(_6\)D\(_6\), 500 MHz): \( \delta = 7.37 \) (d, 1H, 8 Hz), 7.07 (d, 1H, 8 Hz), 6.97 (d, 2H, 8 Hz), 6.85 (d, 2H, 8 Hz), 6.84 (t, 1H, 8 Hz), and 6.43 (t, 1H, 8 Hz) (ArH), 5.94 (bs, 1H, NH), 2.70 (m, 1H, 7 Hz, CH\(_2\)), 1.15 (d, 6H, 7 Hz, CH\(_3\)).

\( ^{13}\)C\({ }^1\)H NMR (CDCl\(_3\), 75 MHz): \( \delta = 143.7, 142.0, 139.0, 132.8, 128.0, 127.3, 121.1, 120.2, 115.1, \) and 111.5 (ArC), 33.5 (CH), 24.1 (CH\(_3\)).

Anal. Calcd. for C\(_{15}\)H\(_{16}\)NBr: C, 62.08; H, 5.56; N, 4.83; Found: C, 62.35; H, 5.66; N, 4.70.

EI-MS (m/z): 289 (40, [M]+), 274 (100, [M — Me]+), 195 (40, [M — (Me + Br)]+).

**Ph-Ar[NPN]Li₂(p-C\(_4\)H\(_8\)O\(_2\)) (6.5(p-C\(_4\)H\(_8\)O\(_2\))) (Ar = 4-'PrC\(_6\)H\(_4\))**. To a stirred solution of (4-'PrC\(_6\)H\(_4\))NH(2-BrC\(_6\)H\(_4\)) (10.4 g, 35.8 mmol) in Et\(_2\)O (300 mL) at \(-35 \) °C was added \({ }^6\)BuLi (1.55 M in hexanes, 46 mL, 71.7 mmol), dropwise over 30 min. The clear yellow solution was warmed to room temperature and stirred for 3 h. The solution was chilled \((-35\) °C) and PhPC\(_1\) (3.20 g, 17.9 mmol) in Et\(_2\)O (50 mL) was added dropwise over 2 h to obtain an orange suspension. The reaction mixture was warmed slowly to room temperature and stirred for 24 h to obtain a yellow suspension. The reaction mixture was taken to dryness under vacuum to obtain a pale yellow foam. Hexanes (75 mL) was added to the foam to obtain a translucent yellow solution. Upon addition of 1,4-dioxane (5 mL) a yellow precipitate formed. The yellow suspension was filtered through Celite (\(-3 \) cm deep) in a glass frit, and the solids and Celite were washed with hexanes (20 mL). The yellow filtrate was transferred to a second Erlenmeyer flask, and was concentrated and chilled to obtain a yellow crystalline solid that was collected on a frit. Meanwhile, the yellow solids trapped on Celite in the frit were eluted with toluene (50 mL) into the Erlenmeyer flask. The yellow
Toluene filtrate was taken to dryness to obtain a yellow powder. This powder was combined with the crystals from the hexanes filtrate and the solids were dried under vacuum (7.4 g, 11.8 mmol, 66% yield based on PhPCl₂). A portion (4 g) of the powder was recrystallized from THF/hexanes at -35 °C (1.50 g, 38%). Single crystals of 6.5·(p-C₄H₈O₂) were grown by slow evaporation of a benzene solution of the compound.

NMR data for yellow crystals of 6.5·2THF grown from THF/hexanes:

1H NMR (C₆D₆, 500 MHz): δ = 7.79 (t, 2H, 8 Hz), 7.72 (t, 2H, 7 Hz), 7.65 (t, 2H, 7 Hz), 7.41 (d, 4H, 8 Hz), 7.17 (d, 4H, 8 Hz), 7.12 (t, 4H), 7.02 (t, 1H, 7 Hz) and 6.67 (t, 2H, 7 Hz) (ArH), 3.10 (m, 8H, THF), 2.83 (m, 2H, 7 Hz, CH), 1.26 (d, 6H, 7 Hz, CH₃), 1.25 (d, 6H, 7 Hz, CH₃), 1.06 (m, 8H, THF).

31P{1H} NMR (C₆D₆, 202 MHz): δ = -34.8 (q, δP₁L₁ = 42 Hz).

7Li{1H} NMR (C₆D₆, 194 MHz): δ = -0.36 (d, 1Li, δP₁L₁ = 42 Hz), -1.70 (s, 1Li).

13C{1H} NMR (C₆D₆, 126 MHz): δ = 161.6 (d, 28 Hz), 154.7, 138.8, 137.2, 135.4, 132.6 (d, 14 Hz), 130.3, 128.2, 127.6, 126.8, 126.0, 120.6, 119.3 (d, 5 Hz), and 117.0 (ArC), 67.9 (THF), 33.8 (CH), 25.2 (THF), 24.66, and 24.69 (CH₃).

Ph₄f[NPN]Zr(NMe₂)₂ (6.6). Trimethylammonium chloride (0.518 g, 5.42 mmol) was added all at once to a stirred solution of 6.5·p-C₄H₈O₂ (1.06 g, 1.69 mmol) in THF (30 mL). The reaction mixture became an off-white suspension after 15 min. After 1 h, the reaction mixture was taken to dryness to obtain white solids. The solids were extracted with hot toluene (20 mL, ~ 50 °C), and the extracts were filtered through Celite in a glass frit. The filtrate was taken to dryness to obtain a translucent white residue (0.85 g, 1.61 mmol, 95%).
$^1$H NMR (C$_6$D$_6$, 500 MHz): $\delta = 7.50$ (t, 2H, 7 Hz), 7.29 (m, 4H), 7.05 (m, 5H), 6.91 (d, 4H, 7 Hz), 6.82 (d, 4H, 7 Hz), and 6.72 (t, 2H, 7 Hz) (ArH), 6.39 (d, 2H, $J_{HP} = 6$ Hz, NH), 2.66 (m, 2H, 7 Hz, CH), 1.13 (d, 12H, 7 Hz), and 1.12 (d, 12H, 7 Hz) (CH$_3$)

$^{31}$P{$^1$H} NMR (C$_6$D$_6$, 202 MHz): $\delta = -32.4$ (s).

$^{13}$C{$^1$H} NMR (C$_6$D$_6$, 126 MHz): $\delta = 160.0, 148.4$ (d, 18 Hz), 142.7, 140.8, 135.0, 134.2 (d, 19 Hz), 130.7, 129.2, 129.1 (d, 8 Hz), 127.4, 122.5 (d, 6 Hz), 121.2, 120.5, and 116.7 (ArC), 33.8 (CH), 24.2 (CH$_3$).

Zr(NMe$_2$)$_4$ (0.430 g, 1.61 mmol) and PhAr[NpN]H$_2$ (0.85 g, 1.61 mmol) were mixed together, and toluene (15 mL) was added. The lemon yellow solution was stirred for 2 h, and the solvent was removed to obtain a yellow residue. The addition of pentane (5 mL) to the residue provided a clear yellow solution. After about 30 s a light yellow precipitate formed that was collected on a frit and dried (1.07 g, 1.52 mmol, 94%). Single crystals of 6.6 suitable for X-ray analysis were grown by slow evaporation of a benzene solution of the compound.

$^1$H NMR (C$_6$D$_6$, 500 MHz): $\delta = 7.48$ (t, 2H, 7 Hz), 7.44 (t, 2H, 8 Hz), 7.17 (m, 7H), 7.07 (m, 4H), 7.00 (dd, 2H, $J_{HP} = 6$ Hz, $J_{HH} = 8$ Hz), 6.75 (dd, 2H, $J_{HH} = 8$ Hz, $J_{HP} = 6$ Hz), and 6.65 (t, 2H, 7 Hz) (ArH), 2.84 (s, 6H, N(CH$_3$)$_2$), 2.76 (m, 2H, 7 Hz, CH), 2.51 (s, 6H, N(CH$_3$)$_2$), 1.19 (d, 12H, 7 Hz, CH$_3$).

$^{31}$P{$^1$H} NMR (C$_6$D$_6$, 202 MHz): $\delta = -10.0$ (s).

$^{13}$C{$^1$H} NMR (C$_6$D$_6$, 126 MHz): $\delta = 163.7$ (d, 29 Hz), 149.2, 143.2, 134.9, 133.2, 133.0 (d, 25 Hz), 132.2 (d, 13 Hz), 129.3, 129.0, 127.6, 126.1, 119.3 (d, 5 Hz), 117.7 (d, 8 Hz), and 116.4 (d, 34 Hz) (ArC), 41.5, and 40.7 (N(CH$_3$)$_2$), 34.0 (CH(CH$_3$)$_2$), 24.3, and 24.2 (CH(CH$_3$)$_2$).
6.5. References.


9 Wohlfart, M.; MacLachlan, E. A. unpublished results.


13 Fiona Hess, personal communication.


17 MacKay, B. A.; Munha, R. unpublished work.


19 Yandulov, D.V.; Schrock, R. R. Science 2003, 301, 76.


Appendix One

X-ray Crystal Structure Data

Table A1.1. Crystal Data and Structure Refinement for [NPN]*Li2(THF)2 (2.7-2THF), [NPN]*ZrCl2 (2.10) and [NPN]*ZrCl2(Py) (2.13).

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R₁ (F², I>2σ(I)) = Σ|F₁ - |F_c||/Σ|F_c|; R_w (all data) = (Σw(|F₀|² - |F_c|²)²)/Σw|F₀|² ²)¹/²
Table A1.2. Crystal Data and Structure Refinement for \([\text{NPN}]^\text{Hf}(\text{NMe})_2\) (2.14), \([\text{NPN}]^\text{HfCl}_2\) (2.15), \([\text{NPN}]^\text{HfI}_2\) (2.17).

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<th>2.17·1.5C(_6)H(_6)</th>
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<tbody>
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<td>formula</td>
<td>(\text{C}<em>{42}\text{H}</em>{45}\text{N}_{4}\text{HfP})</td>
<td>(\text{C}<em>{53}\text{H}</em>{54}\text{Cl}<em>{2}\text{N}</em>{2}\text{PHf})</td>
<td>(\text{C}<em>{47}\text{H}</em>{48}\text{I}<em>{2}\text{N}</em>{2}\text{PHf})</td>
</tr>
<tr>
<td>fw</td>
<td>821.33</td>
<td>999.34</td>
<td>736.09</td>
</tr>
<tr>
<td>colour, habit</td>
<td>pale yellow, needle</td>
<td>pale yellow, plate</td>
<td>yellow, prism</td>
</tr>
<tr>
<td>cryst size, mm</td>
<td>(0.35 \times 0.15 \times 0.07)</td>
<td>(0.30 \times 0.13 \times 0.07)</td>
<td>(0.35 \times 0.15 \times 0.10)</td>
</tr>
<tr>
<td>cryst syst</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>(\text{P}_{2_1}/c)</td>
<td>(\text{C}_{2}/c)</td>
<td>(\text{P}_{2_1}/n)</td>
</tr>
<tr>
<td>(a, \AA)</td>
<td>11.5176(2)</td>
<td>44.7205(16)</td>
<td>10.5510(6)</td>
</tr>
<tr>
<td>(b, \AA)</td>
<td>19.3137(4)</td>
<td>11.0406(4)</td>
<td>17.2009(9)</td>
</tr>
<tr>
<td>(c, \AA)</td>
<td>17.9531(4)</td>
<td>19.4718(5)</td>
<td>24.6184(13)</td>
</tr>
<tr>
<td>(\alpha, \text{deg})</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>(\beta, \text{deg})</td>
<td>105.0270(10)</td>
<td>94.1910(10)</td>
<td>95.214(5)</td>
</tr>
<tr>
<td>(\gamma, \text{deg})</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>(V, \AA^3)</td>
<td>3857.05(14)</td>
<td>9588.3(5)</td>
<td>4449.4(4)</td>
</tr>
<tr>
<td>(Z)</td>
<td>4</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td>(T, \text{°C})</td>
<td>173</td>
<td>173</td>
<td>173</td>
</tr>
<tr>
<td>(\rho_{\text{calc}}, \text{g/cm}^3)</td>
<td>1.414</td>
<td>1.385</td>
<td>1.648</td>
</tr>
<tr>
<td>(F(000))</td>
<td>1672</td>
<td>4056</td>
<td>2148</td>
</tr>
<tr>
<td>radiation</td>
<td>Mo</td>
<td>Mo</td>
<td>Mo</td>
</tr>
<tr>
<td>(\mu, \text{cm}^{-1})</td>
<td>2.78</td>
<td>2.357</td>
<td>3.801</td>
</tr>
<tr>
<td>Trans. factors</td>
<td>0.5382 – 0.8529</td>
<td>0.4060 – 0.6838</td>
<td></td>
</tr>
<tr>
<td>(2\theta_{\text{max}}, \text{deg})</td>
<td>55.416</td>
<td>45.392</td>
<td>54.77</td>
</tr>
<tr>
<td>total no. of reflns</td>
<td>80641</td>
<td>72405</td>
<td>16781</td>
</tr>
<tr>
<td>no. of unique reflns</td>
<td>9136</td>
<td>10472</td>
<td>9455</td>
</tr>
<tr>
<td>(R_{\text{merge}})</td>
<td>0.07</td>
<td>0.103</td>
<td>0.153</td>
</tr>
<tr>
<td>no. with (I \geq n\theta(I))</td>
<td>7398</td>
<td>7378</td>
<td>6559</td>
</tr>
<tr>
<td>no. of parameters</td>
<td>445</td>
<td>541</td>
<td>486</td>
</tr>
<tr>
<td>(R)</td>
<td>0.0296</td>
<td>0.0357</td>
<td>0.0367</td>
</tr>
<tr>
<td>(R_w)</td>
<td>0.049</td>
<td>0.0753</td>
<td>0.0774</td>
</tr>
<tr>
<td>gof</td>
<td>1.059</td>
<td>1.018</td>
<td>0.907</td>
</tr>
<tr>
<td>residual dens, e/(\AA^3)</td>
<td>1.172, -0.699</td>
<td>1.110, -1.004</td>
<td>1.685, -2.085</td>
</tr>
</tbody>
</table>

\[
R_1 (F^2; I>2\sigma(I)) = \frac{\Sigma |F_o| - |F_c|}{\Sigma |F_o|} ; R_w (all data) = (\Sigma w(\Sigma F_o^4 - F_c^4)^2/\Sigma wF_o^4)^{1/2}
\]
Table A1.3. Crystal Data and Structure Refinement for [NPNJ*HfMe₂ (3.2), [NPNC]*Zr(η²-CH₂C₆H₅) (3.4).

<table>
<thead>
<tr>
<th>Compound</th>
<th>3.2 C₆H₅</th>
<th>3.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₄₆H₅₁N₂HfP</td>
<td>C₄₅H₄₅N₂PZr</td>
</tr>
<tr>
<td>Mw</td>
<td>841.35</td>
<td>736.02</td>
</tr>
<tr>
<td>Colour, Habit</td>
<td>pale yellow, needle</td>
<td>orange, irregular</td>
</tr>
<tr>
<td>Crystal Size, mm</td>
<td>0.50 × 0.35 × 0.05</td>
<td>0.25 × 0.15 × 0.10</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space Group</td>
<td>P-I</td>
<td>P-I</td>
</tr>
<tr>
<td>a, Å</td>
<td>11.6308(11)</td>
<td>11.2260(3)</td>
</tr>
<tr>
<td>b, Å</td>
<td>12.7965(10)</td>
<td>15.3120(4)</td>
</tr>
<tr>
<td>c, Å</td>
<td>13.6170(11)</td>
<td>15.5773(4)</td>
</tr>
<tr>
<td>α, deg</td>
<td>84.039(7)</td>
<td>64.7420(10)</td>
</tr>
<tr>
<td>β, deg</td>
<td>80.881(7)</td>
<td>70.8540(10)</td>
</tr>
<tr>
<td>γ, deg</td>
<td>87.582(8)</td>
<td>70.5370(10)</td>
</tr>
<tr>
<td>V, Å³</td>
<td>1989.5(3)</td>
<td>2228.39(10)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>T, °C</td>
<td>173</td>
<td>173</td>
</tr>
<tr>
<td>ρcalc, g/cm³</td>
<td>1.404</td>
<td>1.097</td>
</tr>
<tr>
<td>F(000)</td>
<td>856</td>
<td>768</td>
</tr>
<tr>
<td>Radiation</td>
<td>Mo</td>
<td>Mo</td>
</tr>
<tr>
<td>μ, cm⁻¹</td>
<td>2.695</td>
<td>0.311</td>
</tr>
<tr>
<td>Transmission Factors</td>
<td>0.3305-0.8739</td>
<td>0.8774-0.9694</td>
</tr>
<tr>
<td>2θmax, deg</td>
<td>54.15</td>
<td>55.64</td>
</tr>
<tr>
<td>Total No. of Reflins</td>
<td>12008</td>
<td>46139</td>
</tr>
<tr>
<td>No. of Unique Reflins</td>
<td>6580</td>
<td>10215</td>
</tr>
<tr>
<td>Rmerge</td>
<td>0.137</td>
<td>0.058</td>
</tr>
<tr>
<td>No. with I ≥ nσ(I)</td>
<td>5611</td>
<td>7857</td>
</tr>
<tr>
<td>No. of Parameters</td>
<td>461</td>
<td>465</td>
</tr>
<tr>
<td>R</td>
<td>0.0367</td>
<td>0.0346</td>
</tr>
<tr>
<td>R_within</td>
<td>0.0908</td>
<td>0.0892</td>
</tr>
<tr>
<td>GoF</td>
<td>1.014</td>
<td>1.026</td>
</tr>
<tr>
<td>Residual Density, e/Å³</td>
<td>1.568, -1.653</td>
<td>0.481, -0.314</td>
</tr>
</tbody>
</table>

R₁(2σᵢ(I)) = Σ|Fᵢ - Fᵢ|/Σ|Fᵢ|; R_within (all data) = (Σw[Fᵢ|² - [Fᵢ|²]²)/Σw[Fᵢ|²]²)⁰.₅

Residual electron density consistent with disordered solvent was evident, however, no reasonable model could be established. Instead, the program SQUEEZE was used to generate a data set that corrects for the scattering contribution from this disordered solvent.

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Table A1.4. Crystal Data and Structure Refinement for [NPN]*Hf(η^1-CH_2C_6H_5)_2 (3.5), [NPNC]*Zr(CH_2SiMe_3) (3.7).

<table>
<thead>
<tr>
<th>compound</th>
<th>3.5·C_6H_6</th>
<th>3.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
<td>C_{58}H_{59}N_2PHf</td>
<td>C_{42}H_{49}N_2PSiZr</td>
</tr>
<tr>
<td>fw</td>
<td>993.53</td>
<td>732.11</td>
</tr>
<tr>
<td>colour, habit</td>
<td>pale yellow, chip</td>
<td>red, plate</td>
</tr>
<tr>
<td>cryst size, mm</td>
<td>0.35 × 0.12 × 0.05</td>
<td>0.50 × 0.40 × 0.08</td>
</tr>
<tr>
<td>cryst syst</td>
<td>triclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td>space group</td>
<td>P-1</td>
<td>P-1</td>
</tr>
<tr>
<td>a, Å</td>
<td>11.268(2)</td>
<td>9.22160(10)</td>
</tr>
<tr>
<td>b, Å</td>
<td>12.550(2)</td>
<td>11.5343(2)</td>
</tr>
<tr>
<td>c, Å</td>
<td>17.847(3)</td>
<td>19.5329(3)</td>
</tr>
<tr>
<td>α, deg</td>
<td>93.0410(10)</td>
<td>86.9080(10)</td>
</tr>
<tr>
<td>β, deg</td>
<td>93.5840(10)</td>
<td>78.1770(10)</td>
</tr>
<tr>
<td>γ, deg</td>
<td>103.1290(10)</td>
<td>76.0500(10)</td>
</tr>
<tr>
<td>V, Å^3</td>
<td>2447.1(7)</td>
<td>1973.54(5)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>T, °C</td>
<td>173</td>
<td>173</td>
</tr>
<tr>
<td>ρ calc, g/cm^3</td>
<td>1.348</td>
<td>1.232</td>
</tr>
<tr>
<td>F(000)</td>
<td>1016</td>
<td>768</td>
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<tr>
<td>radiation</td>
<td>Mo</td>
<td>Mo</td>
</tr>
<tr>
<td>μ, cm^-1</td>
<td>2.203</td>
<td>0.379</td>
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<tr>
<td>transmission factors</td>
<td>0.590-0.896</td>
<td>0.8609-0.9701</td>
</tr>
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<td>2θ max, deg</td>
<td>46.75</td>
<td>51.932</td>
</tr>
<tr>
<td>no. of reflns</td>
<td>87588</td>
<td>43622</td>
</tr>
<tr>
<td>no. of unique reflns</td>
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<td>9436</td>
</tr>
<tr>
<td>R_merge</td>
<td>0.087</td>
<td>0.06</td>
</tr>
<tr>
<td>no. with I ≥ nθ(I)</td>
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<td>7340</td>
</tr>
<tr>
<td>no. of parameters</td>
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<td>434</td>
</tr>
<tr>
<td>R</td>
<td>0.0284</td>
<td>0.0349</td>
</tr>
<tr>
<td>R_w</td>
<td>0.0599</td>
<td>0.0973</td>
</tr>
<tr>
<td>gof</td>
<td>1.013</td>
<td>1.109</td>
</tr>
<tr>
<td>residual dens, e/Å^3</td>
<td>0.985, -0.519</td>
<td>0.495, -0.313</td>
</tr>
</tbody>
</table>

R = \left( \sum F_o^2 - F_c^2 \right)^{1/2} / \sum F_o^2; R_w (all data) = \left( \sum w(F_o^2 - F_c^2)^2 \right)^{1/2} / \sum w(F_o^2)^{1/2}
Table A1.5. Crystal Data and Structure Refinement for $\{[\text{NPN}]^*[\text{Zr(THF)}]_2(\mu-\eta^2:\eta^2-\text{N}_2)^*\}$ (4.1), $\{[\text{NPN}]^*[\text{Zr(Py)}]_2(\mu-\eta^2:\eta^2-\text{N}_2)^*\}$ (4.2), and $\{[\text{NPN}]^*[\text{Zr(PMe}_2\text{Ph)}]_2(\mu-\eta^2:\eta^2-\text{N}_2\text{)}_2\}^*$ (4.4).

<table>
<thead>
<tr>
<th>Compound</th>
<th>4.1 (Sol)</th>
<th>4.2</th>
<th>4.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C$<em>{98}$H$</em>{120}$N$_6$O$_3$P$_2$Zr$_2$</td>
<td>C$<em>{86}$H$</em>{88}$N$_8$P$_2$Zr$_2$</td>
<td>C$<em>{85}$H$</em>{88}$N$_6$P$_3$Zr$_2$</td>
</tr>
<tr>
<td>fw</td>
<td>1674.38</td>
<td>1478</td>
<td>1456.95</td>
</tr>
<tr>
<td>Colour, habit</td>
<td>black, prism</td>
<td>black, prism</td>
<td>black, rectangular</td>
</tr>
<tr>
<td>Cryst size, mm</td>
<td>0.30 × 0.15 × 0.10</td>
<td>0.50 × 0.40 × 0.30</td>
<td>0.30 × 0.10 × 0.10</td>
</tr>
<tr>
<td>Cryst syst</td>
<td>trigonal</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>R-3c</td>
<td>P2$_1$/n</td>
<td>P2$_1$/c</td>
</tr>
<tr>
<td>a, Å</td>
<td>27.3381(7)</td>
<td>19.6395(7)</td>
<td>23.7417(8)</td>
</tr>
<tr>
<td>b, Å</td>
<td>27.3381</td>
<td>19.7497(8)</td>
<td>15.2378(5)</td>
</tr>
<tr>
<td>c, Å</td>
<td>59.1867(16)</td>
<td>27.0757(12)</td>
<td>23.7851(8)</td>
</tr>
<tr>
<td>$\alpha$, deg</td>
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<td>90.00</td>
<td>90.00</td>
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<tr>
<td>$\beta$, deg</td>
<td>90.00</td>
<td>91.7900(10)</td>
<td>98.896(2)</td>
</tr>
<tr>
<td>$\gamma$, deg</td>
<td>120.00</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>$V$, Å$^3$</td>
<td>38308.2(14)</td>
<td>10496.8(7)</td>
<td>8501.3(5)</td>
</tr>
<tr>
<td>Z</td>
<td>18</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>T, °C</td>
<td>173</td>
<td>173</td>
<td>173</td>
</tr>
<tr>
<td>$\rho_{calc}$, g/cm$^3$</td>
<td>1.306</td>
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</tr>
<tr>
<td>F(000)</td>
<td>15912</td>
<td>3080</td>
<td>3036</td>
</tr>
<tr>
<td>Radiation</td>
<td>Mo</td>
<td>Mo</td>
<td>Mo</td>
</tr>
<tr>
<td>$\mu$, cm$^{-1}$</td>
<td>0.337</td>
<td>0.265</td>
<td>0.344</td>
</tr>
<tr>
<td>Transmission factors</td>
<td>0.839-0.967</td>
<td>0.8580-0.9241</td>
<td>0.812-0.966</td>
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<td>$2\theta_{max}$, deg</td>
<td>40.48</td>
<td>44.892</td>
<td>53.038</td>
</tr>
<tr>
<td>Total no. of refinls</td>
<td>210263</td>
<td>35075</td>
<td>88103</td>
</tr>
<tr>
<td>No. of unique refinls</td>
<td>7426</td>
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<td>20097</td>
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<tr>
<td>$R_{merge}$</td>
<td>0.080</td>
<td>0.088</td>
<td>0.063</td>
</tr>
<tr>
<td>No. with $I \geq n\sigma(I)$</td>
<td>5613</td>
<td>9468</td>
<td>14389</td>
</tr>
<tr>
<td>No. of parameters</td>
<td>467</td>
<td>899</td>
<td>873</td>
</tr>
<tr>
<td>R</td>
<td>0.0481</td>
<td>0.0561</td>
<td>0.0396</td>
</tr>
<tr>
<td>$R_w$</td>
<td>0.1429</td>
<td>0.1630</td>
<td>0.1045</td>
</tr>
<tr>
<td>GoF</td>
<td>1.043</td>
<td>1.020</td>
<td>1.017</td>
</tr>
<tr>
<td>Residual dens, e/Å$^3$</td>
<td>1.174, -0.522</td>
<td>0.971, -0.548</td>
<td>0.779, -0.282</td>
</tr>
</tbody>
</table>

$R_w(F^2; I>2\sigma(I)) = \Sigma || F_o^2 || F_c^2 || / \Sigma F_c^2$; $R_w$ (all data) = $(\Sigma w(F_o^4 - F_c^4)^2 / \Sigma w F_o^4)^{1/2}$

Sol = (C$_6$H$_8$+THF+0.67(C$_6$H$_{14}$))

---

*See note on Squeeze (Table A1.3)*
**Table A1.6.** Crystal Data and Structure Refinement for \{[NPN]⁺Zr(PMe₃)}(µ-H)(µ-η²:η²-NNH){Zr[NPN]⁺}⁺ (5.1), \{[NPN]⁺Zr(Py)}(µ-H)(µ-NNSiH₂Ph){Zr[NPN]⁺}⁻ (5.3).

<table>
<thead>
<tr>
<th>Compound</th>
<th>5.1</th>
<th>5.3·C₆H₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₇₉H₸₉N₆P₃Zr₂</td>
<td>C₉₃H₹₆N₇P₂SiZr₂</td>
</tr>
<tr>
<td>fw</td>
<td>1397.91</td>
<td>1585.32</td>
</tr>
<tr>
<td>Colour, habit</td>
<td>yellow, rod</td>
<td>red, plate</td>
</tr>
<tr>
<td>Cryst size, mm</td>
<td>0.5 × 0.1 × 0.1</td>
<td>0.5 × 0.3 × 0.1</td>
</tr>
<tr>
<td>Cryst syst</td>
<td>triclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
<td>P-1</td>
</tr>
<tr>
<td>a, Å</td>
<td>13.418</td>
<td>12.8123(4)</td>
</tr>
<tr>
<td>b, Å</td>
<td>19.268</td>
<td>13.1606(5)</td>
</tr>
<tr>
<td>c, Å</td>
<td>20.788</td>
<td>25.1766(11)</td>
</tr>
<tr>
<td>α, deg</td>
<td>67.54</td>
<td>85.4180(10)</td>
</tr>
<tr>
<td>β, deg</td>
<td>75.49</td>
<td>84.5970(10)</td>
</tr>
<tr>
<td>γ, deg</td>
<td>86.02</td>
<td>74.8280(10)</td>
</tr>
<tr>
<td>V, Å³</td>
<td>4806.3</td>
<td>4072.3(3)</td>
</tr>
<tr>
<td>Z</td>
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<td>2</td>
</tr>
<tr>
<td>T, °C</td>
<td>173</td>
<td>173</td>
</tr>
<tr>
<td>(\rho_{\text{calo}}) g/cm³</td>
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<td>1.292</td>
</tr>
<tr>
<td>(F(000))</td>
<td>1460</td>
<td>1654</td>
</tr>
<tr>
<td>Radiation</td>
<td>Mo</td>
<td>Mo</td>
</tr>
<tr>
<td>(\mu, \text{cm}^{-1})</td>
<td>0.302</td>
<td>0.360</td>
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<tr>
<td>Transmission factors</td>
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<td>0.773-0.982</td>
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<tr>
<td>(2\theta_{\text{max}}, \text{deg})</td>
<td>45.537</td>
<td>44.91</td>
</tr>
<tr>
<td>Total no. of reflns</td>
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<td>43112</td>
</tr>
<tr>
<td>No. of unique reflns</td>
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<td>10446</td>
</tr>
<tr>
<td>(R_{\text{merge}})</td>
<td>0.324</td>
<td>0.065</td>
</tr>
<tr>
<td>No. with (I \geq n\theta(I))</td>
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<td>7593</td>
</tr>
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<td>No. of parameters</td>
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<td>959</td>
</tr>
<tr>
<td>(R)</td>
<td>0.1663</td>
<td>0.0413</td>
</tr>
<tr>
<td>(R_{\text{wp}})</td>
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<td>0.1020</td>
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<td>GoF</td>
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<td>1.002</td>
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<tr>
<td>Residual dens, e/Å³</td>
<td>6.601, -2.132</td>
<td>0.470, -0.344</td>
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</tbody>
</table>

\[R_1(F^2, I > 2\sigma(I)) = \frac{\sum |F_o| - |F_c|/\Sigma |F_o|}{\sum |F_o|^2/\Sigma |F_o|^2}^{1/2}\]

\[R_w (\text{all data}) = (\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^2)^{1/2}\]

---

† See note on Squeeze (Table A1.3)

† H1 (bridging hydride) and H1Si, H2Si were located from the electron density map and refined normally.
### Table A1.7. Crystal Data and Structure Refinement for \(\{\text{NPN}^*\text{Zr}\}_2(\mu-\eta^1:\eta^2-\text{NNC}(4-\text{MeC}_6\text{H}_4)\}_2\) (5.4), \(\{\text{NPN}^*\text{Zr} (\text{NCPh}_2)\}_2(\mu-\eta^1:\eta^2-\text{N}_2\text{H}_2)\)_2 (5.5), and \(\{\text{NPN}^*\text{Zr}\}_2(\mu-\text{O})_2\) (5.6).

| Compound | Formula | \(m\) | Colour, Habit | Cryst Size, mm | Cryst Syst | Space Group | \(a, \text{Å}\) | \(b, \text{Å}\) | \(c, \text{Å}\) | \(\alpha, \text{deg}\) | \(\beta, \text{deg}\) | \(\gamma, \text{deg}\) | \(V, \text{Å}^3\) | \(Z\) | \(T, ^\circ\text{C}\) | \(\rho_{\text{calc}}, \text{g/cm}^3\) | \(F(000)\) | \(\mu, \text{cm}^{-1}\) | Transmission Factors | \(2\theta_{\text{max}}, \text{deg}\) | Total No. of Reflns | No. of Unique Reflns | \(R_{\text{merge}}\) | No. with \(I \geq n\theta(I)\) | No. of Parameters | GOF | Residual Dens, e/Å\(^3\) |
|----------|---------|-------|--------------|---------------|-----------|-------------|------------|----------|----------|------------|----------|----------|-------------|--------|---------|----------------|--------------|-------------|----------------|----------------|------------|----------------|--------|----------------|
| 5.4      | \(\text{C}_{91}\text{H}_{92}\text{N}_6\text{OP}_2\text{Zr}_2\) | 1530.09 | Orange, Platelet | 0.3 \(\times\) 0.1 \(\times\) 0.1 | Monoclinic | \(P2_1\) | 13.875(2) | 13.3465(3) | 23.3359(6) | 90.00 | 104.983(10) | 90.00 | 4544.0(14) | 2 | 173 | 1.118 | 1596 | 0.309 | 0.793-0.970 | 46.61 | 30481 | 13553 | 0.107 | 9195 | 937 | 0.049 | 0.561, -0.503, |
| 5.5      | \(\text{C}_{112}\text{H}_{113}\text{N}_8\text{P}_2\text{Zr}_2\) | 1839.48 | Red, Platelet | 0.35 \(\times\) 0.20 \(\times\) 0.05 | Monoclinic | \(P2_1\) | 14.394(3) | 23.3359(6) | 16.1975(4) | 90.00 | 107.4220(10) | 90.00 | 4813.3(2) | 3 | 173 | 1.267 | 1920 | 0.303 | 0.856-0.985 | 44.632 | 29776 | 6478 | 0.046 | 6359 | 1149 | 0.049 | 0.856-0.985 |
| 5.6      | \(\text{C}_{82}\text{H}_{84}\text{N}_4\text{P}_2\text{Zr}_2\text{O}_2\) | 1401.91 | Yellow, Platelet | 0.21 \(\times\) 0.17 \(\times\) 0.15 | Monoclinic | \(C2/c\) | 22.298(5) | 14.064(3) | 23.800(5) | 93.884(4) | 90.00 | 90.00 | 7446(3) | 4 | 296 | 1.250 | 2920 | 0.371 | 0.881-0.945 | 46.52 | 29927 | 5350 | 0.049 | 4612 | 415 | 0.1125 | 0.881-0.945 |

\(R_1 = \sum \left| \frac{F_o - F_c}{F_o} \right| / \sum |F_o| ; R_w (all data) = \left( \sum w(F_o^2 - F_c^2)^2 / \sum wF_o^2 \right)^{1/2}\)

\(^1\) See note on Squeeze (Table A1.3)
<table>
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<th>6.3</th>
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<td>C₃₆H₃₇N₂P</td>
</tr>
<tr>
<td>fw</td>
<td>784.83</td>
<td>528.65</td>
</tr>
<tr>
<td>Colour, habit</td>
<td>yellow, prism</td>
<td>colourless, prism</td>
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<td>Cryst size, mm</td>
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<td>0.50 × 0.30 × 0.20</td>
</tr>
<tr>
<td>Cryst syst</td>
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<td>triclinic</td>
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<tr>
<td>Space group</td>
<td>P2₁/c</td>
<td>P-1</td>
</tr>
<tr>
<td>a, Å</td>
<td>17.0576(13)</td>
<td>7.9830(8)</td>
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<tr>
<td>b, Å</td>
<td>25.018(2)</td>
<td>13.3300(13)</td>
</tr>
<tr>
<td>c, Å</td>
<td>11.3813(9)</td>
<td>14.4770(14)</td>
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<tr>
<td>α, deg</td>
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<td>97.374(5)</td>
</tr>
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<td>β, deg</td>
<td>71.743(5)</td>
<td>105.276(5)</td>
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<tr>
<td>γ, deg</td>
<td>90.00</td>
<td>91.745(5)</td>
</tr>
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<td>V, Å³</td>
<td>4612.5(6)</td>
<td>1470.5(3)</td>
</tr>
<tr>
<td>Z</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>T, °C</td>
<td>173</td>
<td>173</td>
</tr>
<tr>
<td>ρ calc, g/cm³</td>
<td>1.130</td>
<td>1.194</td>
</tr>
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<td>F(000)</td>
<td>1672</td>
<td>564</td>
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<td>Radiation</td>
<td>Mo</td>
<td>Mo</td>
</tr>
<tr>
<td>μ, cm⁻¹</td>
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<td>0.121</td>
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<td>Transmission factors</td>
<td>0.837-0.970</td>
<td>0.854-0.976</td>
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<tr>
<td>θ max, deg</td>
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<td>59.32</td>
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<td>Total no. of reflns</td>
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<td>11151</td>
</tr>
<tr>
<td>No. of unique reflns</td>
<td>9059</td>
<td>7659</td>
</tr>
<tr>
<td>R merge</td>
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<td>0.060</td>
</tr>
<tr>
<td>No. with I ≥ nθ(I)</td>
<td>5871</td>
<td>5370</td>
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<td>No. of parameters</td>
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<td>360</td>
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<tr>
<td>R</td>
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<td>0.0541</td>
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<tr>
<td>Rw</td>
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<td>0.1607</td>
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<tr>
<td>Gof</td>
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<td>1.031</td>
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<td>Residual dens, e/Å³</td>
<td>0.461, -0.339</td>
<td>0.511, -0.451</td>
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</tbody>
</table>

\[
R_1(F^2, I>2σ(I)) = \frac{\sum |F_o| - |F_c| / \sum |F_o|}{\sum w|F_o|^2 / \sum w|F_c|^2}^{1/2}
\]

\[
R_\text{w} \text{ (all data)} = \left( \sum w(|F_o|^4 - |F_c|^4)^2 / \sum w |F_o|^4 \right)^{1/2}
\]
Table A1.9. Crystal Data and Structure Refinement for $^{4}$PrC$_{6}$H$_{4}$ (6.5), $^{4}$PrC$_{6}$H$_{4}$ (6.6).

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<th>Compound</th>
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<th>6.6:1.5C$<em>{6}$H$</em>{6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C$<em>{49}$H$</em>{52}$Li$<em>{2}$N$</em>{2}$O$_{2}$P</td>
<td>C$<em>{49}$H$</em>{52}$N$_{4}$PZr</td>
</tr>
<tr>
<td>fw</td>
<td>745.78</td>
<td>706.01</td>
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<td>Colour, Habit</td>
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<td>yellow, irregular</td>
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<td>Cryst size, mm</td>
<td>0.35 x 0.15 x 0.05</td>
<td>0.50 x 0.20 x 0.15</td>
</tr>
<tr>
<td>Cryst syst</td>
<td>triclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
<td>P2$_{1}$/c</td>
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<tr>
<td>a, Å</td>
<td>11.5372(7)</td>
<td>19.7201(5)</td>
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<tr>
<td>b, Å</td>
<td>13.4014(8)</td>
<td>11.5343(2)</td>
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<tr>
<td>c, Å</td>
<td>16.1799(9)</td>
<td>17.3982(5)</td>
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<tr>
<td>α, deg</td>
<td>107.995(2)</td>
<td>90.00</td>
</tr>
<tr>
<td>β, deg</td>
<td>109.297(2)</td>
<td>66.3300(10)</td>
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<td>γ, deg</td>
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<td>90.00</td>
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<td>V, Å$^{3}$</td>
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<td>3687.69(17)</td>
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<td>173</td>
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<td>Mo</td>
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<td>μ, cm$^{-1}$</td>
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<td>GoF</td>
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<td>Residual dens, e/Å$^{3}$</td>
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<td>1.109, -0.294</td>
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</tbody>
</table>

$R_1 (F^2, I>2σ(I)) = \Sigma ||F_o| - |F_e|| / \Sigma |F_o| ; R_w$ (all data) = $(\Sigma w(|F_o|^2 - |F_e|^2))^2 / \Sigma w|F_o|^2)^{1/2}$

**X-ray Crystal Structure Analysis**

Selected crystals were coated in oil, mounted on a glass fiber, and placed under an N$_{2}$ stream. Measurements for compounds were made on a Bruker X8 Apex diffractometer or a Rigaku AFC-7 diffractometer, both with graphite-monochromated Mo Kα radiation ($λ=0.71073$ Å). The data were collected at a temperature of $-100 ± 1$ °C. Data were collected
and integrated using the Bruker SAINT software package.\textsuperscript{1} Data were corrected for absorption effects using the multiscan technique (SADABS)\textsuperscript{2} and for Lorentz and polarization effects. Neutral atom scattering factors were taken from Cromer and Waber.\textsuperscript{3} Anomalous dispersion effects were included in $F_{\text{calc}}$;\textsuperscript{4} the values for $\Delta f''$ and $\Delta f'''$ were those of Creagh and McAuley.\textsuperscript{5} The values for the mass attenuation coefficients are those of Creagh and Hubbell.\textsuperscript{6} All refinements were performed using the SHELXTL crystallographic software package of Bruker-AXS. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically using SHELXL-97. Except where noted, hydrogen atoms were included in fixed positions. Structures were solved and refined using the WinGX software package version 1.64.05.

Crystals for structure 5.6 were sent to the University of Windsor. Data collection and refinement were performed by Greg Welch and Prof. Douglas Stephan in the Department of Chemistry.
Table A1.10. Crystallographic Data Collection and Structure Solution Information.

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<th>Diffractometer</th>
<th>Data Collection</th>
<th>Structure solution</th>
<th>Special details</th>
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<tr>
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<td>BP, EM</td>
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<td>EM</td>
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<td>EM</td>
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<tr>
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<td>BP</td>
<td>EM, BP</td>
<td>S, M</td>
<td></td>
</tr>
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<td>-</td>
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<td>HJ</td>
<td>EM, BP</td>
<td>S</td>
</tr>
<tr>
<td>4.4</td>
<td>666</td>
<td>-</td>
<td>BX8</td>
<td>HJ</td>
<td>HJ, EM</td>
<td>S</td>
</tr>
<tr>
<td>5.1</td>
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<td>-</td>
<td>BX8</td>
<td>HJ</td>
<td>HJ, EM</td>
<td>S, LR</td>
</tr>
<tr>
<td>5.3</td>
<td>671</td>
<td>C₆H₆</td>
<td>BX8</td>
<td>BP</td>
<td>EM</td>
<td>H, M</td>
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<td>652</td>
<td>-</td>
<td>RAFC7</td>
<td>HJ</td>
<td>EM</td>
<td>S</td>
</tr>
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<td>5.5</td>
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<td>2C₆H₆</td>
<td>BX8</td>
<td>BP</td>
<td>EM</td>
<td></td>
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<td>C₆H₆</td>
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<td>GW</td>
<td>GW, DS</td>
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<td>6.2</td>
<td>646</td>
<td>2C₆H₆</td>
<td>RAFC7</td>
<td>HJ</td>
<td>MW, EM</td>
<td></td>
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<tr>
<td>6.3</td>
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<td>-</td>
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<td>HJ</td>
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<td>H</td>
</tr>
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<td>-</td>
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<td>BP</td>
<td>EM</td>
<td></td>
</tr>
</tbody>
</table>

BX8 = Bruker Apex X8 Diffractometer, RAFC7 = Rigaku AFC-7 Diffractometer, SSS = Siemens SMART System CCD Diffractometer; BP = Dr. Brian Patrick, HJ = Howard Jong, GW = Greg Welch, DS = Prof. Doug Stephan, MW = Malte Wohlfahrt; S = Squeeze, H = Hydrogen atoms of interest located from electron density and stable to refinement, LR = low resolution structure, M = solvent modeled.


2 SADABS. Bruker Nonius area detector scaling and absorption correction - V2.05, Bruker AXS Inc., Madison, Wisconsin, USA.


Appendix Two
Spectroscopic Supporting Information

A2.2 Variable-temperature NMR investigation of [NPN]⁺H₂ (2.8).

A stacked plot of the ¹H NMR spectra of 2.8 in toluene-d₈ at 300 MHz acquired every 10K from 300 to 370 K is shown in Figure A2.1. At 300 K, the two ortho-methyl resonances on MesN are broad singlets. ¹H NMR spectra were acquired at 5 K increments between 300 K and 340 K, and at 10 K increments between 240K and 300 K, and between 340 K and 370 K. Coalescence is observed at 320 K, and the two ortho-methyl resonances are separated by 75 Hz at 273 K. The exchange of the two ortho-methyl groups on each MesN substituent of 2.8 due to rotation about the N–C₉₅ is depicted in Equation A2.1.

The rate constant for the exchange reaction at the coalescence temperature is (Equation A2.2):

\[ k_c = \frac{\pi \Delta \nu}{\sqrt{2}} = 2.22 \Delta \nu \]

\[ (A2.2) \]

\( k_c \) is the rate constant at the coalescence temperature, \( T_c \), and \( \Delta \nu \) is the separation between the two peaks at a temperature well below the coalescence temperature. In this case, \( \Delta \nu \) did not increase below 273 K (spectra acquired to 240 K).¹ In this experiment, \( k_c = 166.5 \pm 2 \text{ s}^{-1} \).
\[ \Delta G^\dagger = -RT_c \ln \left( \frac{k_c h}{k_B T_c} \right) \]  

(A2.3)

\( R \) is the gas constant, \( T_c \) is the coalescence temperature, \( k_c \) is the rate constant, \( h \) is Planck's constant, and \( k_B \) is the Boltzmann constant.

Equation A2.3 can be restated (Equation A2.4):

\[ \Delta G^\dagger = 4.58T_c \left( 10.32 + \log \left( \frac{T_c}{k_c} \right) \right) \text{cal mol}^{-1} \]  

(A2.4)

The main sources of error in this experiment are those associated with measuring the coalescence temperature; this error will be much greater than the error in determining the peak separation at low temperature. For \( T_c \), a value of 320 ± 5 K has been used to determine \( \Delta G^\dagger \). In this experiment, \( \Delta G^\dagger \) is 15.5 ± 0.3 kcal mol\(^{-1}\).
Figure A2.1. $^1$H NMR spectra of $[\text{NPN}]^+\text{H}_2$ (2.8) in toluene-$d_8$ from 300 K (bottom) to 370 K (top) in 10 K increments.

A2.2. Kinetics of Decomposition of $[\text{NPN}]^+\text{Zr(CH}_2\text{Ph)}_2$ (3.3).

At room temperature, the decomposition of $[\text{NPN}]^+\text{Zr(CH}_2\text{Ph)}_2$ (3.3) occurs over 2 d to yield $[\text{NPNC}]^+\text{Zr(\eta}^2\text{-CH}_2\text{Ph)}$ (3.4) as a red-orange complex. The decomposition reaction was followed by $^1$H NMR spectroscopy. The decrease in the concentration of 3.3 was taken as the integral measured for Zr$\text{CH}_2\text{Ph}$ in 3.3 ($\delta$ 2.92), divided by the sum of that integral plus two times the integral for CH$_2$H$_3$Mes in 3.4 ($\delta$ 2.70), according to Equation A2.5, where int. is the integral value. Thus, the fraction of 3.3 relative to an initial value of 1.0 was used, rather than the molar concentration. These resonances were chosen because they did not overlap with any other resonances in the spectrum. The values obtained were similar to those from other related combinations of integrals taken from other parts of the spectrum, and their values were standardized to a peak of unchanging concentration.
\[
- \frac{d[3.3]}{dt} = -k_{\text{obs}}[3.3] = \frac{-k_{\text{obs}}[\text{int CH}_2\text{Ph}(3.3)]}{[\text{int CH}_2\text{Ph}(3.3)] + 2[\text{int CH}_4\text{H}_6\text{Mes}(3.4)]}
\]

\[\text{(A2.5)}\]

The thermal decomposition reaction was determined to be first order in 3.3 (spectra not shown) by determining the rate of decomposition for three solutions of different concentration at room temperature. The rate constants \(k_{\text{obs}}\) at five different temperatures (298, 328, 338, 348, and 358 K) were then determined from the plots of \(\ln[3.3]\) vs. time, for which a representative plot is shown in Figure A2.2 (338 K).

\[\ln[3.3] \text{ vs. time at 328 K}\]

![Graph](image)

**Figure A2.2.** Plot of \(\ln[3.3]\) vs. \(t\) at 338 K. From the slope of the line, \(k_{338} = 1.403 \times 10^{-3} \pm 1.0 \times 10^{-3}\) s\(^{-1}\).
Thus, the values of $k_{\text{obs}}$ at 5 different temperatures were obtained:

\[ k_{298} = 1.80 \times 10^{-5} \pm 6 \times 10^{-7} \text{ s}^{-1} \]

\[ k_{223} = 4.33 \times 10^{-4} \pm 1 \times 10^{-5} \text{ s}^{-1} \]

\[ k_{238} = 1.40 \times 10^{-3} \pm 1 \times 10^{-5} \text{ s}^{-1} \]

\[ k_{248} = 3.44 \times 10^{-3} \pm 2 \times 10^{-4} \text{ s}^{-1} \]

\[ k_{258} = 7.35 \times 10^{-3} \pm 5 \times 10^{-4} \text{ s}^{-1} \]

The free energy of activation ($\Delta G^\ddagger$) is related to the enthalpy of activation ($\Delta H^\ddagger$) and entropy of activation ($\Delta S^\ddagger$) (Equation A2.6).

\[ \Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \]  

(A2.6)

By inserting equation A2.6 into the Eyring equation (A2.3), Equation A2.7 is obtained:

\[ \ln \left( \frac{k_e \hbar}{k_B T_c} \right) = \frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R} \]  

(A2.7)

This expression can be simplified to (Equation A2.8):

\[ \log \frac{k}{T} = 10.32 - \frac{\Delta H^\ddagger}{19.14T} + \frac{\Delta S^\ddagger}{19.14} \]  

(A2.8)
From the Eyring plot of $\ln(k_{\text{obs}}/T)$ vs. $1/T$ (Figure 3.7), the enthalpy ($\Delta H^\ddagger$) and entropy ($\Delta S^\ddagger$) of activation were determined according to Equation A2.8 from the y-intercept and the slope of the line. Thus:

$$\Delta H^\ddagger = 20.8 \pm 0.4 \text{ kcal mol}^{-1}, \text{ and } \Delta S^\ddagger = -10.3 \pm 1.3 \text{ cal K}^{-1} \text{ mol}^{-1}$$

The two main sources of error in this experiment are due to temperature measurement and integration of resonances in the $^1$H NMR spectrum. The error in temperature is estimated to be $\pm 1$K, and the error is estimated to be $\pm 5\%$ for the fractions of 3.3 and 3.4 in solution based on integration of the $^1$H NMR spectrum. The error in $k_{\text{obs}}$ was determined statistically.

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