DINITROGEN COMPLEXES OF TITANIUM AND VANADIUM STABILIZED BY PHOSPHINE LIGANDS

by

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ABSTRACT

The goal of the work presented in this thesis is to investigate the preparation of dinitrogen complexes of titanium and vanadium from phosphine-based starting materials.

The reactions of TiCl₄, TiCl₃(THF)₃, or VCl₂(TMEDA)₂ with LiN-(SiMe₂CH₂PR₂)₂ (R = isopropyl or methyl) yielded the new phosphine complexes TiCl₃[N(SiMe₂CH₂PPr'₂)₂] (1), TiCl₃[N(SiMe₂CH₂PMe₂)₂] (2), {TiCl₂[N(SiMe₂CH₂PPr'₂)₂]x (x=1 or 2) (3), or [(Pr'₂PCH₂SiMe₂)₂N]V₀.₁-C₁)₂Li(TMEDA) (4), respectively. NMR spectroscopy revealed that complexes 1 and 2 have C₂ᵥ symmetry. The titanium(III) species, 3, is likely to be a dimer as indicated by mass spectrometry. The structure of the vanadium mono(amido-diphosphine) complex, 4, is suggested to be a lithium-chloride adduct.

The reduction of 1 with magnesium powder under dinitrogen resulted in the synthesis of the binuclear titanium dinitrogen complex, {[(Pr'₂PCH₂SiMe₂)₂N]TiCl}(μ-η¹⁻¹:N₂) (5). The unsuccessful reduction of 3 suggests that it is not an intermediate in the synthesis of 5. The most interesting structural feature of 5 is the end-on bound dinitrogen ligand with an N-N bond distance of 1.275(7) Å, typical of other binuclear end-on bound dinitrogen complexes. The ¹H and ³¹P{¹H} NMR spectra indicate that this dinitrogen complex is fluxional at room temperature by a process that is proposed to involve dissociation of the phosphorus atoms of the tridentate ligand and then rotation about the Ti-N (amide) bond, followed by reassociation. The low temperature ³¹P{¹H} NMR spectrum shows an AB quartet which is consistent with the solid state structure. Upon addition of HCl, 0.75 ± 0.04 equivalents of hydrazine and 0.29 ± 0.05 equivalents of dinitrogen were detected.
The reaction between $\text{VCl}_2(\text{TMEDA})_2$ and $\text{LiN(SiMe}_2\text{CH}_2\text{PPr}_2)_2$ under dinitrogen resulted in the formation of a similar vanadium dinitrogen complex, $\{(\text{Pr}_2\text{PCH}_2\text{SiMe}_2)_2\text{N}\}\text{VOCl}_2(\mu-\eta^1:\eta^1-\text{N}_2)$ (7). An alternate synthetic route involves exposure of $\{(\text{Pr}_2\text{PCH}_2\text{SiMe}_2)_2\text{N}\}\text{V(\mu-Cl)}_2\text{Li(TMEDA)}$, 4, in the solid or solution state to one atmosphere of dinitrogen. Complex 7 was also characterized by X-ray crystallography; the end-on dinitrogen bond length is 1.257 (8) Å. Degradation of 7 with HCl produced 0.29 ± 0.04 equivalents of hydrazine.
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\text{at 20°C (top) and at -50°C (bottom)}\}$$

Figure 4.1. Constant pressure gas uptake apparatus
LIST OF ABBREVIATIONS

The following list of abbreviations, most of which are commonly used in the chemical literature, will be employed in this thesis:

Å                  angstrom, 10⁻¹⁰ m
Anal.             analysis
atm               atmosphere
br                 broad
Bu¹               tertiary butyl, (-C(CH₃)₃)
Bz                 benzyl, (-CH₂C₆H₅)
°C                 degree centigrade
Calcd.            calculated
Chem 3D Plus®    molecular modelling program for the Macintosh
cis               cisoidal
Cp                 cyclopentadienyl, (η⁵-C₅H₅)
Cp*               penta(methyl)cyclopentadienyl, (η⁵-C₅Me₅)
δ                  chemical shift
d                 doublet
deg               degree
deepe             1,2-bis(diethylphosphino)ethane, (Et₂P)₂C₂H₄
DIOP              2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane
dippe             1,2-bis(diisopropylphosphino)ethane, (Pr'₂P)₂C₂H₄
DME               1,2-dimethoxyethane, (CH₃O)₂C₂H₄
dmpe              1,2-bis(dimethylphosphino)ethane, (Me₂P)₂C₂H₄
dppe 1,2-bis(diphenylphosphino)ethane, (Ph₂P)₂C₂H₄

e.g. for example
ESR electron spin resonance
Et ethyl, (-C₂H₅)
fac facial


g gram

i.e. that is

⁰_J_{A-B} n-bond coupling constant between A and B atoms

J_{app} apparent coupling constant

kJ kiloJoule

m multiplet

M molar

Me methyl, (-CH₃)

mer meridional

mg milligram

MHz megaHertz

mL millilitre

mm millimetre

mmol millimole

mol mole

MPa megaPascal

μ_{eff} effective magnetic moment

¹⁵N{¹H} observe nitrogen while decoupling proton

NMR nuclear magnetic resonance

pd pentadienyl, (C₅H₇)

Ph phenyl, (-C₆H₅)

ppm parts per million
% percent

%T percent transmittance

$^{31}\text{P}(^1\text{H})$ observe phosphorus while decoupling proton

$\text{Pr}^i$ isopropyl, (-CH(CH$_3$)$_2$)

q quartet

RT room temperature

s singlet

sh shoulder

t triplet

THF tetrahydrofuran, (C$_4$H$_8$O)

TMEDA tetramethylethylenediamine, ((CH$_3$)$_2$N)$_2$C$_2$H$_4$

$trans$ transoidal
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CHAPTER 1

GENERAL INTRODUCTION

1.1 Phosphines in Inorganic and Organometallic Chemistry

Phosphine ligands have played a significant role in the development of inorganic\(^1\) and organometallic\(^2\) chemistry. Many transition metal and some main group elements in various oxidation states form stable complexes with phosphorus derived donors, making them one of the most commonly encountered ancillary ligands in coordination chemistry. For example, there are a number of bulky chelating phosphines such as dippe which allow the isolation of highly reactive, coordinatively unsaturated species.\(^3\) In addition, transition metal complexes incorporating chiral phosphine ligands, e.g. DIOP, act as efficient asymmetric hydrogenation catalysts for a number of ketone or olefinic substrates.\(^4\)\(^-\)\(^6\) Introducing chirality in the backbone of some of the chelating phosphines has enabled the enantioselective synthesis of certain specific drugs, e.g. L-Dopa.\(^7\)

It is important to note that changing substituents on phosphorus ligands can cause changes in the behaviour of the free ligands and their transition metal complexes due to electronic and steric effects. The cone angle of a phosphine ligand is a measure of steric bulk and defined as the apex angle of a cylindrical cone, centered 2.28 Å from the centre of the phosphorus atom, such that the sides of the cone just touch the van der Waals radii of the outermost atoms of the substituent R groups (Figure 1.1).\(^8\) The angle can vary from 87° for PH\(_3\) to 182° for P(t-Bu)\(_3\). In addition, the electron-donating ability of the phosphine ligands may also be varied by changing the substituents on the phosphorus
atoms so that these ligands exhibit $\sigma$-donor (e.g. PMe$_3$) or $\pi$-acceptor (e.g. P(OMe)$_3$) properties.

![Figure 1.1](image)

**Figure 1.1.** Model of a phosphine ligand for cone angle calculation.

One of the most useful methods for characterizing phosphine complexes is by $^{31}$P($^1$H) NMR spectroscopy. The $^{31}$P nucleus has 100% natural abundance with a nuclear spin of one-half, a relative sensitivity of 6.6% to that of the proton, and a large chemical shift window (>600 ppm) making it useful for the study of reaction progress and the characterization of products. Furthermore, this type of NMR spectroscopy has revealed coupling to other NMR active nuclei, e.g. $^{183}$W and $^{195}$Pt, which can give valuable stereochemical information in appropriate instances.

### 1.2 Hybrid Ligand Design

The HSAB (Hard-Soft-Acid-Base) theory classifies donor ligands as either hard or soft donors, and transition metals as hard or soft acids. Hard acids bind most strongly to hard bases, while soft acids and bases bind most strongly together. For example, soft tertiary aryl phosphine ligands, such as PPh$_3$, form complexes with soft, late transition metals. However, as expected, phosphine coordination chemistry with hard early metals
is scarce.\textsuperscript{10} Similarly, the hard amide ligand, \( ^\text{1°} \text{NR}_2 \) (R = alkyl, aryl, or silyl), forms stable complexes with the early metals, but fewer with the soft, late transition elements.\textsuperscript{10}

In an effort to overcome mismatches in coordination, a tridentate hybrid ligand system was developed (Figure 1.2).\textsuperscript{11} The rationale was as follows: the early metals would prefer the amide portion of the ligand and force coordination of the phosphine donor by the chelate effect; alternatively, the late transition metals would prefer the phosphine portion of the ligand which would help stabilize the amide ligation.

![Figure 1.2. The hybrid ligand developed in this laboratory.](image)

The synthesis of the tridentate ligand (Scheme 1.1) with various substituents at the phosphorus atoms such as isopropyl and methyl has provided different steric properties.\textsuperscript{12} The lithium phosphide (LiPR\(_2\)) and starting silylamine (HN(SiMe\(_2\)CH\(_2\)Cl)\(_2\)) are produced by standard procedures;\textsuperscript{12,13} in fact, the silylamine is available commercially (Aldrich). The ligands are obtained as colourless, air- and moisture-sensitive crystalline solids that are soluble in most organic solvents. They are convenient reagents for the incorporation of the ligand onto transition metals by metathesis with suitable metal halide precursors.
Scheme 1.1

1,3-bis(chloromethyl)-tetramethyldisilazane

\[ \text{R} = \text{Ph} \]

\[ \text{R} = \text{Me, Ph, Pr, Bu} \]

\[ \text{L}_{n}M_{X} \]
Since the synthesis of this ligand system just over ten years ago, many complexes with a variety of different metals have been isolated. Figure 1.3 shows a periodic table with the elements highlighted that have been studied with this ligand system. One of the goals of this thesis is to extend this chemistry to titanium and vanadium.

![Periodic Table of the Elements](image)

Figure 1.3. Periodic Table of the elements. Elements in bold have already been studied with this ligand system; the elements Ti and V are the subjects of this thesis.

1.3 Dinitrogen in Inorganic and Organometallic Chemistry

There has been a great deal of interest in the chemistry of dinitrogen, particularly its interaction with transition metals. In certain microorganisms, the enzyme nitrogenase plays a major role in the fixation of atmospheric dinitrogen under mild conditions.\(^3\)\(^,\)\(^{14}\) Initial studies carried out on the nature of nitrogenase indicates that the active site in the enzyme is composed of molybdenum, iron, and sulfur in a cubic array (A, Figure 1.4).\(^{15}\)\(^-\)\(^{18}\) However, recent studies show a different structure for the active site (B, Figure 1.4).\(^{19}\)
Before 1965, the only known reactivity of molecular nitrogen was with lithium to form lithium nitride at ambient temperatures. However in 1965, the synthesis of the first transition metal dinitrogen complex, \([\text{Ru(NH}_3)_5\text{N}_2]^{+2}\), was reported and it represents one of the most prominent discoveries of modern inorganic chemistry, that dinitrogen could act as a ligand.

![Diagram of active site in nitrogenase]

**Figure 1.4.** Two different proposed structures of the active site in nitrogenase.

The simplest molecular orbital description of a transition metal-dinitrogen bond involves one of the metal d-orbitals accepting a pair of electrons from the dinitrogen to

![Molecular orbital diagram]

**Figure 1.5.** Molecular orbital description of the transition metal-dinitrogen \(\pi\) bonds; there is a degenerate set of orbitals perpendicular to the page.
generate a σ-bond; in addition, backbonding from two metal d-orbitals with the correct symmetry to overlap with the π* orbitals of the dinitrogen fragments is also possible (Figure 1.5).\textsuperscript{22}

Dinitrogen can coordinate to a metal in several different modes. In the case of mononuclear complexes, the most prevalent mode of bonding is end-on (A and C, Figure 1.6).\textsuperscript{23} However, there is some spectroscopic evidence for the existence of mononuclear side-on complexes (B and D, Figure 1.6).\textsuperscript{24} The degree of activation of coordinated dinitrogen may be related to the lengthening of the dinitrogen bond distance. The bond length ranges from 1.0975 Å\textsuperscript{25} for free dinitrogen to 1.10-1.16 Å for mononuclear complexes and 1.12-1.36 Å for binuclear complexes.\textsuperscript{26}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{dinitrogen_bonding_modes.png}
\caption{Dinitrogen bonding modes in mononuclear complexes.}
\end{figure}

In the case of binuclear complexes, the end-on bridging dinitrogen form is the most common and can be represented by the two resonance forms shown in A, Figure
1.7. The first example of both terminal and bridging end-on dinitrogen units in the same complex is represented in C, Figure 1.7. Similar to the mononuclear complexes, the side-on form of dinitrogen is even less common in binuclear complexes (B, Figure 1.7). Complex D, Figure 1.7 shows the structure of the first and only planar, side-on bonding between two f-elements and a dinitrogen ligand. In this case the N-N distance is 1.088 (12) Å, not significantly different from that of free N2.

![Diagram of dinitrogen bonding modes in binuclear complexes.]

Figure 1.7. Dinitrogen bonding modes in binuclear complexes.

1.4 The Scope of this Thesis

The focus of this thesis is the syntheses and characterization of dinitrogen complexes of titanium and vanadium and their corresponding precursor derivatives. Chapter 2 describes the syntheses and characterization of various titanium and vanadium mono(amido-diphosphine) complexes. The phosphines were modified by varying the steric bulk of the R groups on the phosphorus atoms of the ligand. It was discovered that
the isopropyl substituted ligand gave the best results in terms of the syntheses of the dinitrogen complexes.

Chapter 3 reports the formation and characterization of two dinitrogen complexes. On the basis of X-ray crystallography both complexes were found to exhibit end-on bound dinitrogen ligands. The reactivity of these complexes, specifically protonation reactions, were also studied.

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CHAPTER 2

MONO(AMIDO-DIPHOSPHINE) COMPLEXES OF TITANIUM AND VANADIUM

2.1 Introduction

This chapter deals with the chemistry of mono(amido-diphosphine) complexes of titanium and vanadium. The syntheses and characterization of the following complexes with variation of the type of phosphorus donor will be described: TiCl₃[N(SiMe₂CH₂PR₂)₂] (R = Pr, Me), {TiCl₂[N(SiMe₂CH₂PPr₂)₂]₀}ₓ (x=1 or 2), and [(Pr₂PCH₂SiMe₂)₂N]V(μ-Cl)₂Li(TMEDA).

Interest in organotitanium compounds dates back to 1861 when Cahours reported reactions involving TiCl₄ and ZnEt₂.⁠¹² Improved procedures for handling air- and thermally-sensitive compounds allowed the isolation of the first organotitanium compound, TiPh(OPr₁)₃, in 1952.³ Since that time, the organometallic chemistry of titanium has been mainly dominated by the work on the cyclopentadienyl derivatives, due to the convenient starting material, Cp₂TiCl₂, and its useful applications in organic syntheses.⁴

Titanium phosphine complexes were initially investigated thirty years ago after the recognition that phosphine-based ligands were the donors of choice for most of the remaining transition series.⁵ According to the HSAB (Hard-Soft-Acid-Base) theory, hard acids such as Ti(IV), are small, electropositive metals that prefer hard bases, i.e. ligands that contain small, non-polarizable donor atoms.⁶ There are fewer titanium phosphine
complexes because there is a mismatch of acceptor and donor: phosphines are considered to be soft bases and the small electron-poor titanium centre is a hard acid. In recent years, the difficulty in this mismatch has been overcome by controlled synthetic techniques, and by elegant hybrid ligand design such as hard and soft bases combined in a chelate array.

The organometallic chemistry of vanadium began with the discovery of vanadocene, Cp₂V, during the 1950’s. Since then it has been found that vanadium can have varying formal oxidation states ranging from -3 to +5. This range of oxidation states has made it possible for the isolation of a wide variety of organovanadium complexes.

Vanadium is unusual among the transition metals because it may form neutral, paramagnetic carbonyl complexes which do not dimerize. Also, low-valent vanadium chemistry has such interesting features such as dinitrogen fixation/activation, multiple metal-metal bond formation, and very negative reduction potentials.

In the following section, examples of the coordination chemistry of phosphine ligands with both titanium and vanadium is summarized to illustrate the wealth and breadth of this area.

### 2.1.1 Titanium(IV) Phosphine Complexes

The simplest tetravalent titanium phosphine complexes are adducts of TiCl₄. A range of mono(phosphine) complexes, TiCl₄L, and the bis(phosphine) complexes, TiCl₄L₂, can be made by controlling the stoichiometry of the starting reagents. Bidentate phosphines also form 1:1 adducts with TiCl₄. Solution studies have indicated that the most common geometry for the complexes, TiCl₄L, is trigonal bipyramidal with C₃ᵥ symmetry. There are also a few examples with C₂ᵥ symmetry. For
the bis(phosphine) complexes, TiCl₄L₂, the geometry is octahedral with C₂ᵥ symmetry when the phosphine ligands are cis disposed.

Titanium(IV) phosphine complexes, Ti(R)X₃Lₙ (n = 1 or 2) and TiR₂X₂L₂, where R = alkyl,²¹-²⁷ aryl,²³ or alkoxy¹⁷,²⁷,²⁸ groups and L = phosphine²¹-²⁴ have also been synthesized. Two particularly interesting examples are Ti(Me)Cl₃(dmpe) and Ti(Et)Cl₃(dmpe);²⁵ these were the first crystallographically characterized examples of secondary bonding between an electropositive metal and the hydrogen atoms of an alkyl moiety, known as an agostic interaction. A neutron diffraction study was carried out on the methyl derivative to confirm this agostic interaction (A, Figure 2.1).²⁶

![Figure 2.1. Examples of titanium(IV) phosphine complexes.](image)

Another major class of titanium(IV) phosphine complexes consists of those incorporating cyclopentadienyl ligands. The mono(cyclopentadienyl) complex, CpTiCl₃ was first synthesized in 1953 and found to be easily derivatized.²⁹ Reactions of CpTiCl₃ with chelating phosphines such as dmpe²⁰ or a monodentate phosphate²⁷ resulted in the formation of CpTiCl₃L (B, Figure 2.1).
2.1.2 Titanium(III) Phosphine Complexes

Analogous to the titanium(IV) phosphine complexes of the formula TiCl₄L₂, the titanium(III) derivatives, TiCl₃L₂, can be made by refluxing titanium trichloride with two equivalents of L where L = monodentate phosphine. However, TiCl₃L₃ complexes have only been synthesized at low temperature.

Diketonate titanium phosphine complexes, TiCl₂(RCOCHCOR)(L)₂ are made by the reaction of TiCl₃(THF)₃ with the anion of the corresponding 1,3-diketone, and the desired phosphine. The trans-dichloro geometry (A, Figure 2.2) was based on spectroscopic analysis.

![Diagram of titanium(III) phosphine complexes](image)

**Figure 2.2.** Examples of titanium(III) phosphine complexes.

Complexes of the type, CpTiCl₂L₂ (L = monodentate phosphine; L₂ = bidentate phosphine) are obtained by the cleavage of [CpTiCl₂]ₓ with phosphines. Also, CpTiCl₃ can be reduced with magnesium in the presence of excess PMe₃ to give CpTiCl₂(PMe₃)₂. The crystal structure of this complex indicates a four-legged piano stool geometry (B, Figure 2.2).
2.1.3 Titanium(II) Phosphine Complexes

Titanium(II) complexes, \( \text{Cp}_2\text{TiL}_2 \) where \( \text{L} \) or \( \text{L}_2 \) = mono- or bidentate phosphines were synthesized by reduction of \( \text{Cp}_2\text{TiCl}_2 \) in the presence of phosphines.\(^{36-38}\) All of these complexes are highly coloured and show pseudotetrahedral geometry. The lability of the coordinated phosphines of A (Figure 2.3) allows for substitution by other donor ligands such as CO, N\(_2\), C\(_2\)H\(_4\), and R\(_2\)CN.\(^{39}\)

\[ \text{Ti} \quad \overset{\text{PMe}_3}{\text{PMe}_3} \quad \text{PMe}_3 \]

**Figure** 2.3. Examples of titanium(II) phosphine complexes.

Mixed cyclopentadienyl-pentadienyl complexes \( \text{CpTi(pd)L} \) (\( \text{L} \) = phosphine) have been formed, but are limited due to the steric requirements of the pentadienyl group.\(^{40}\) However, reduction of \( \text{TiCl}_4(\text{THF})_2 \) with magnesium in the presence of potassium 2,4-dimethylpentadienide and trialkyl phosphine has resulted in the synthesis of the titanium bis(2,4-dimethylpentadienide) phosphine complex (B, Figure 2.3).\(^{41}\)

2.1.4 Low Oxidation States of Titanium Phosphine Complexes

The early work on low valent complexes of titanium resulted in the formation of intractable products. However, recent advances in the understanding of the stability of
titanium-carbon bonded compounds, combined with improved procedures and synthetic methods have allowed for the isolation of these type of complexes.\textsuperscript{42}

In general many zero valent titanium phosphine complexes incorporate 1,3-butadiene or carbon monoxide. For example, Ti(IV) is reduced by magnesium butadiene in the presence of a diphosphine to give Ti(\(\eta^4\)-C\(_4\)H\(_6\))\(_2\)(dppe).\textsuperscript{43-45} Similarly, the carbonyl complexes are formed by the reduction of a titanium(IV) precursor in the presence of a phosphine and then exposure to carbon monoxide, \textit{e.g.} Ti(CO)\(_3\)(dmpe)\(_2\).\textsuperscript{46}

\subsection*{2.1.5 Vanadium(IV) Phosphine Complexes}

Vanadium(IV) chemistry is dominated by the oxovanadium(IV) ion, (VO\(_{2}^+\)) due to its exceptional stability in air and aqueous solution.\textsuperscript{47} Complexes of this ion usually have square pyramidal or trigonal bipyramidal structures with the vanadyl oxygen in an apical position. However VOCl\(_2\)(PR\(_3\))\(_2\), formed by the addition of phosphine to VOCl\(_2\), is trigonal bipyramidal, with the vanadyl oxygen in an equatorial position (A, Figure 2.4).\textsuperscript{48}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{vanadium_complexes.png}
\caption{Examples of vanadium(IV) phosphine complexes.}
\end{figure}
Similar to the titanium(IV) phosphine complexes, vanadium(IV) phosphine complexes of the formula $\text{VCl}_4\text{L}_2$ ($\text{L} = \text{monodentate phosphine}$) can be synthesized by addition of phosphine to $\text{VCl}_4$ at low temperature (B, Figure 2.4).

2.1.6 Vanadium(III) Phosphine Complexes

Vanadium trichloride reacted with trialkyl phosphines results in the formation of trigonal bipyramidal, $\text{VCl}_3(\text{PR}_3)_2$ complexes.\textsuperscript{50,51} For example, $\text{VCl}_3(\text{PMePh}_2)_2$ was made by the reaction of $\text{PMePh}_2$ and $\text{VCl}_3(\text{THF})_3$ (A, Figure 2.5).

![Figure 2.5. Examples of vanadium(III) phosphine complexes.](image)

The low temperature reaction of $\text{VX}_3(\text{PR}_3)_2$ and $\text{CpM}$ ($\text{M} = \text{Na or 1/2 Mg}$) has produced high yields of the mono(cyclopentadienyl) complexes, $\text{CpVX}_2(\text{L})_2$. All these complexes have a characteristic blue colour and are thermally stable.\textsuperscript{52} An X-ray diffraction study shows that the complex, $\text{CpVCl}_2(\text{PMe}_3)_2$, displays square pyramidal geometry (B, Figure 2.5).
2.1.7 Vanadium(II) Phosphine Complexes

Until recently there was a lack of V(II) chemistry due to unsuitable V(II) starting materials,\textsuperscript{53} ease of oxidation of V(II) complexes,\textsuperscript{54} and contamination by species of higher oxidation states. The zinc reduction of VCl\(_3\)(PE\(_3\))\(_2\) gave [VCl\(_2\)(PR\(_3\))\(_2\)]\(_2\) which does not react with dinitrogen or dihydrogen, but reacts with carbon monoxide.\textsuperscript{55} VCl\(_2\)(dmpe)\(_2\) was made by the reaction of VCl\(_2\)(THF)\(_2\) with dmpe and found to be monomeric with octahedral geometry (A, Figure 2.6).\textsuperscript{56}

![Diagram of Vanadium(II) Phosphine Complexes](image)

**Figure 2.6.** Examples of vanadium(II) phosphine complexes.

Reduction of CpVX\(_2\)(PR\(_3\))\(_2\) with Al or Zn in THF gives [CpVX(PR\(_3\))]\(_2\) where X is a halide (B, Figure 2.6).\textsuperscript{57} These complexes are reactive towards many substrates such as dioxygen, alkynes, and carbon monoxide and the dimers can be cleaved to give mononuclear complexes by the addition of phosphines.

2.1.8 Low Oxidation States of Vanadium Phosphine Complexes

The low oxidation states (from -3 to +1) of vanadium complexes are generally limited to those ligands capable of accepting electron density from the reduced vanadium
centre. However, many complexes have been synthesized with ancillary ligands such as carbonyl and cyclopentadienyl.\textsuperscript{58-63} For example, upon irradiation in benzene and addition of PH\textsubscript{3}, CpV(CO)\textsubscript{4} converts to the phosphine derivative CpV(CO)\textsubscript{3}(PH\textsubscript{3}). The neutral, paramagnetic compound, V(CO)\textsubscript{5}PPh\textsubscript{3} was formed from vanadium hexacarbonyl.

The remainder of this chapter describes the syntheses of mono(amido-diphosphine) complexes of titanium and vanadium. These complexes either lead to the synthesis, or are involved in the reactivity studies of the dinitrogen complexes described in Chapter 3. First a review of previously published results from this laboratory on mono(amido-diphosphine) chemistry is presented.

\textbf{2.1.9 Previous Work on Other Group 4 Mono(Amido-Diphosphine) Complexes}

For the mono(amido-diphosphine) complexes of group 4, MCl\textsubscript{3}[N(SiMe\textsubscript{2}CH\textsubscript{2}PR\textsubscript{2})\textsubscript{2}], there are two possible stereoisomers for an octahedral geometry: facial (fac) or meridional (mer). When the central metal is zirconium or hafnium, the long metal-phosphorus bonds combined with the short metal-nitrogen and metal-chloride bonds cause large deviations (Figure 2.7) from pure octahedral geometry.\textsuperscript{64} For example \textit{mer}-ZrCl\textsubscript{3}[N(SiMe\textsubscript{2}CH\textsubscript{2}PP\textsubscript{r}\textsubscript{2})\textsubscript{2}] has a P(1)-Zr-P(2) angle of 159.38 (4)°. The complex HfCl\textsubscript{3}[N(SiMe\textsubscript{2}CH\textsubscript{2}PMe\textsubscript{2})\textsubscript{2}] was found by X-ray crystallography to exist in two isomeric structures in the solid state: monoclinic (P(2)-Hf-Cl(2) = 174.47 (4)°) and orthorhombic (P(2)-Hf-Cl(2) = 163.89 (10)°), both structures have the tridentate ligand bound in a facial mode.
Figure 2.7. Facial and meridional geometries of $\text{MC}_3[\text{N(SiMe}_2\text{CH}_2\text{PR}_2)_2]$, $M = \text{Zr}, \text{Hf}$

It has been established that the mono(amido-diphosphine) derivatives, $\text{MC}_3[\text{N(SiMe}_2\text{CH}_2\text{PR}_2)_2]$ ($R = \text{Me}, \text{Pr}', \text{and Bu}$ and $M = \text{Zr}$ and $\text{Hf}$) exist in solution with the meridional geometry because equivalent environments for each of the different protons on the ligand were indicated by $^1\text{H}$ NMR spectroscopy.\textsuperscript{64}

The zirconium and hafnium mono(amido-diphosphine) trichloride complexes have been quite versatile as starting reagents in the formation of binuclear hydrides,\textsuperscript{65} $\eta^4$-bound butadiene complexes,\textsuperscript{66,67} alkyl derivatives,\textsuperscript{68} side-on and end-on bound dinitrogen complexes.\textsuperscript{69}

The preparation of $\text{TiCl}_3[\text{N(SiMe}_2\text{CH}_2\text{CH}_3\text{PR}_2)_2]$, ($R = \text{CH(CH}_3)_2$, 1 or $\text{CH}_3$, 2) was a logical extension of the syntheses and characterization of the analogous zirconium and hafnium complexes described above.\textsuperscript{64} If this material could be prepared, it was anticipated that it would serve as a useful starting reagent, and allow a direct comparison to be made with the chemistry of the heavier group 4 metal complexes. In addition, the preparation of a titanium dinitrogen complex from 1 was of interest for comparison to a
related zirconium dinitrogen complex which has a bridging side-on bound dinitrogen unit.  

2.2 Syntheses and Characterization of TiCl₃[N(SiMe₂CH₂PR₂)₂], (R = Pr', Me)

The synthesis of TiCl₃[N(SiMe₂CH₂PPr'₂)₂], 1, was straightforward due to the well established procedures for the syntheses of the analogous zirconium and hafnium complexes.  

One equivalent of the lithium amide, LiN(SiMe₂CH₂PPr'₂)₂, was added at low temperature to one equivalent of TiCl₄, which immediately generated the red coloured complex 1 as shown in reaction 2.1.

\[
\text{TiCl}_4 + \text{LiN(SiMe}_2\text{CH}_2\text{PPr'}_2)_2 \xrightarrow{\text{toluene \n- LiCl}} \text{TiCl}_3[\text{N(SiMe}_2\text{CH}_2\text{PPr'}_2)_2]
\]

Complex 1 was characterized by microanalysis, \textsuperscript{1}H and \textsuperscript{31}P{\textsuperscript{1}H} NMR spectroscopy. The \textsuperscript{1}H (Figure 2.8) and \textsuperscript{31}P{\textsuperscript{1}H} (Figure 2.9) NMR spectroscopy both revealed that the reaction was complete with the formation of a single product indicated by a singlet resonance at +32.9 ppm in the \textsuperscript{31}P{\textsuperscript{1}H} NMR spectra. Only one type of environment for each of the different protons on the ligand was indicated by the \textsuperscript{1}H NMR spectrum; thus the geometry can be assumed to be meridional with \textit{C}_2\text{v} symmetry (Figure 2.10). For the meridional geometry the bulky isopropyl groups on the phosphine ligand would undergo fewer unfavourable steric interactions and effectively be \textit{trans} to each other. If the tridentate ligand was in a facial geometry in an octahedral environment, then the \textsuperscript{1}H NMR would indicate two different types of silyl methyl groups (SiCH₃), methylene groups (PCH₂Si), and phosphorus isopropyl groups (PCH(CH₃)₂).
Figure 2.8. 300 MHz $^1$H NMR spectrum of TiCl$_3$[N(SiMe$_2$CH$_2$PPr$_2$)$_2$]. 1, in C$_7$D$_8$.

Solvent and impurity peaks are indicated by an asterisk and a cross, respectively.
Figure 2.9. 121 MHz $^{31}$P($^1$H) NMR spectrum of TiCl$_3$[N(SiMe$_2$CH$_2$PPr$_2$)$_2$]. 1, in C$_7$D$_8$. 

\[
\begin{align*}
\text{Me}_2\text{Si} & \quad \text{Pr}^2 \\
\text{N} & \quad \text{Ti} \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]
Figure 2.10. Solution structure of TiCl₃[N(SiMe₂CH₂PPr₂)₂], 1.

There are some differences between the zirconium, hafnium and titanium complexes of the formula MC₃₃[N(SiMe₂CH₂PPPr₂)₂]. An obvious difference is that the zirconium and hafnium complexes are colourless while the titanium complex is red due to a ligand-to-metal charge-transfer process. Also, in order to obtain high yields, reaction times of at least 12 hours were required for zirconium and hafnium, while the titanium complex reacted immediately. These differences may be attributed to the solubilities of the starting materials: ZrCl₄ and HfCl₄ are rather insoluble in toluene relative to TiCl₄.

The complex, TiCl₃[N(SiMe₂CH₂PMe₂)₂], 2, which has methyl substituents at the phosphorus atoms of the ligand, was synthesized in a similar manner to 1 as shown in reaction 2.2.

\[
\text{TiCl}_4 + \text{LiN(SiMe}_2\text{CH}_2\text{PMe}_2)₂ \xrightarrow{\text{toluene}} \text{TiCl}_3[\text{N(SiMe}_2\text{CH}_2\text{PMe}_2)₂] \quad (2.2)
\]

Formation of 2 was confirmed by microanalysis and \(^1\text{H}\) (Figure 2.11) and \(^{31}\text{P}\{\text{H}\}\) (Figure 2.12) NMR spectroscopy. The geometry was proposed as meridional with \(C_{2v}\) symmetry because the \(^1\text{H}\) NMR displayed only one type of environment for each of the different protons on the ligand. As previously mentioned, both the zirconium and
Figure 2.11. 300 MHz $^1$H NMR spectrum of TiCl$_3$[N(SiMe$_2$CH$_2$PMe$_2$)$_2$, 2, in C$_7$D$_8$.

Solvent peaks are indicated by an asterisk.
Figure 2.12. 121 MHz $^{31}$P($^1$H) NMR spectrum of TiCl$_3$[N(SiMe$_2$CH$_2$PMe$_2$)$_2$], 2, in C$_7$D$_8$. 
hafnium analogues show meridional geometry in solution, but upon crystallization the ligand in HfCl3[N(SiMe2CH2PMe2)2] also binds in a facial mode.\(^{64}\) On the basis of NMR spectroscopy and by analogy to previously published results, it is presumed that TiCl3[N(SiMe2CH2PMe2)2] exists in solution as the meridional geometry (Figure 2.13).

![Figure 2.13. Solution structure of TiCl3[N(SiMe2CH2PMe2)2], 2.](image)

2.3 Reactivity of TiCl3[N(SiMe2CH2PR2)2], (R = Pr\(^{1}\), Me)

One of the first objectives with the new starting materials, TiCl3[N(SiMe2CH2PR2)2] (R = Pr\(^{1}\), Me), was to compare their reactivities to that of the heavier group 4 complexes, MCl3[N(SiMe2CH2PR2)2] (M = Zr, Hf; R = Pr\(^{1}\), Me). However, all the reactions attempted led to uncoordinated ligand or mixtures of intractable products. The reagents used to react with 1 were benzyl potassium (target complex was Ti(CH2Ph)3[N(SiMe2CH2PPr\(^{1}\)2)2]), sodium 2,6-dimethylphenoxide (target complex was TiCl2[N(SiMe2CH2PPr\(^{1}\)2)2][2,6-Me2C6H3O]), ethylene and magnesium (target complex was TiCl(C4H8)[N(SiMe2CH2PPr\(^{1}\)2)2]), methylmagnesium chloride (target complex was TiMe3[N(SiMe2CH2PPr\(^{1}\)2)2]), magnesium butadiene (target complex was TiCl(\(\eta^4\)-C4H6)[N(SiMe2CH2PPr\(^{1}\)2)2]), and sodium cyclopentadiene (target complex was TiCl2Cp[N(SiMe2CH2PPr\(^{1}\)2)2]).
Although none of the above target molecules were isolated, the formation of a dinitrogen complex was achieved (Chapter 3). The reactivity of 2 (R = Me) was also investigated with respect to the dinitrogen chemistry.

2.4 Synthesis and Characterization of \( \{\text{TiCl}_2[\text{N(SiMe}_2\text{CH}_2\text{PPr}_2])_2\}\_x \) (x=1 or 2)

The Ti(III) analogue of 1 was synthesized. The synthesis of \( \{\text{TiCl}_2[\text{N(SiMe}_2\text{CH}_2\text{PPr}_2])_2\}\_x, 3 \), was similar to the preparation of complex 1. One equivalent of the lithium amide, \( \text{LiN(SiMe}_2\text{CH}_2\text{PPr}_2)_2 \), was added at low temperature to one equivalent of the Ti(III) starting material, \( \text{TiCl}_3(\text{THF})_3 \) (reaction 2.3).

\[
\text{TiCl}_3(\text{THF})_3 + \text{LiN(SiMe}_2\text{CH}_2\text{PPr}_2)_2 \rightarrow \text{toluene} - \text{LiCl}
\]

\[
\{\text{TiCl}_2[\text{N(SiMe}_2\text{CH}_2\text{PPr}_2])_2]\}_x \quad 3 \quad (2.3)
\]

Microanalyses could confirm only the empirical formula, not the molecular formula, of 3 therefore, x= 1 or 2. Attempts to ascertain the structure of 3 were unsuccessful using solution molecular weight determination (Signer method)\(^72\) at room temperature because 3 decomposed. However, mass spectrometry provides evidence to suggest that 3 is possibly a dimer. Although the dimer parent ion peak was not observed, the ion peaks of dimer fragments were identified and confirmed by computer generated isotope patterns. Complex 3 is paramagnetic with a magnetic moment as expected for each d\(^1\) metal centre (\( \mu_{\text{eff}} = 1.69 \) BM).

Proton resonances of the paramagnetic complex, 3, could be observed although
Figure 2.14. 300 MHz $^1$H NMR spectrum of ($\text{TiCl}_2[\text{N(SiMe}_2\text{CH}_2\text{PPr}_2^i)_{2x}]_x$ ($x=1$ or 2), 3, in C$_7$D$_8$. Solvent and impurity peaks are indicated by an asterisk and a cross, respectively.
they were broadened and shifted (Figure 2.14). Peak assignments were based on integrated intensities because coupling information could not be obtained. The proton resonances could also be qualitatively assigned based on the isotropic shift phenomenon.\textsuperscript{73} In simple terms, the proton resonances closest to the paramagnetic Ti(III) centre would have greater chemical shift differences than those resonances further from the metal centre. The broad peak at 32.7 ppm was assigned to the methine protons (PCH(CH\textsubscript{3})\textsubscript{2}). Broad singlets at 3.00 and 2.59 ppm were assigned to the isopropyl methyl protons, while the singlet at -0.22 ppm indicates silyl methyl protons. The methylene resonances of the backbone appear at -3.38 ppm.

The \textsuperscript{1}H NMR spectrum at room temperature indicated that the complex is symmetric: one silyl methyl, one methylene, one isopropyl methine and two isopropyl methyl resonances were observed. There are several possible explanations for the observed spectrum. One reason is the fluxionality of the complex in solution is so rapid relative to the NMR time scale that resonances due to the two environments are not resolved. Therefore, two different silyl methyl environments are represented as one resonance in the spectrum (A, B, C, or E, Figure 2.15). A fluxional process could take place whereby a six-coordinate dichloride bridged dimer (A or B) can interconvert to a seven-coordinate tetrachloride bridged dimer (C, D, or E) which could then undergo pseudorotation, a known process for many seven-coordinate complexes.\textsuperscript{74} Alternatively, the complex could be non-fluxional, but symmetric (D, Figure 2.15). Another explanation is that a rapid monomer-dimer equilibrium could be taking place at room temperature or a simple monomer may exist in solution (F, Figure 2.15), but it may become a dimer in the solid state. The low temperature NMR spectra only showed resonances broader than those obtained at room temperature. It is still inconclusive whether complex 3 is a monomer or dimer without the aid of X-ray crystallography due to our inability to grow X-ray quality crystals. The reactivity of 3 was studied with respect to the dinitrogen chemistry of this
Figure 2.15. Some possible structures of \( \{TiCl_2[N(SiMe_2CH_2PPr_2)_2]\}_x \) (x=1 or 2).
system. The results of these studies are presented in Chapter 3.

2.5 Synthesis and Characterization of VCl(TMEDA)[N(SiMe₂CH₂PPr²)₂]

The chelating ligand TMEDA has been used to stabilize low valent titanium and vanadium complexes (e.g. TiCl₂(TMEDA)₂ and VCl₂(TMEDA)₂); these complexes have been versatile starting materials for the preparation of various complexes such as dinitrogen, imido, and amide derivatives. The combination of the mono(amido-diphosphine) and TMEDA ligands was expected to give a vanadium starting reagent which could lead to the preparation of the vanadium dinitrogen complex. A direct comparison could then be made between the titanium and vanadium dinitrogen complexes and their reactivities.

The preparation of VCl(TMEDA)[N(SiMe₂CH₂PPr²)₂] was attempted by the addition of one equivalent of the lithium amide to one equivalent of VCl₂(TMEDA)₂ at -78°C under an atmosphere of argon (reaction 2.4).

\[
\text{VCl}_2\text{(TMEDA)}_2 + \text{LiN(SiMe}_2\text{CH}_2\text{PPr}^\text{i}_2)\text{)}_2 \rightarrow \text{VCl(TMEDA)}[\text{N(SiMe}_2\text{CH}_2\text{PPr}^\text{i}_2)\text{)}_2 \] (2.4)

However, upon characterization using microanalysis, it was determined that the product of reaction 2.4 was not VCl(TMEDA)[N(SiMe₂CH₂PPr²)₂], but some other complex. Attempts to grow X-ray quality crystals were apparently unsuccessful; well formed green crystals were isolated but these did not diffract. \(^1\text{H}\) or \(^31\text{P\{^1\text{H}\}}\) NMR spectroscopy only showed very broad resonances that could not be interpreted.
A different approach was needed to solve the identity of the product therefore, as much information was obtained from other means of characterization. Magnetic susceptibility measurements showed that the vanadium had an oxidation state of +2 as indicated by $\mu_{\text{eff}} = 3.90 \text{ BM}$ as expected for a $d^3$ species. Mass spectrometry indicated many fragments, one of which at 513 was proposed as $\text{VCl}_2[N(\text{SiMe}_2\text{CH}_2\text{PPr_i}_2)_2]$ and later confirmed by computer generated isotope patterns. However, this fragment was not the isolated product from reaction 2.4 because the microanalyses did not match. Also the vanadium oxidation state in $\text{VCl}_2[N(\text{SiMe}_2\text{CH}_2\text{PPr_i}_2)_2]$ is +3, but +2 in the isolated product. Therefore, a partial conclusion can be drawn about the isolated product. It has a partial formula of $\text{VCl}_2[N(\text{SiMe}_2\text{CH}_2\text{PPr_i}_2)_2]$, yet it must contain other ligand(s) to alter the oxidation state of vanadium to +2.

A known amount of the product (reaction 2.4) was dissolved in $\text{C}_7\text{D}_8$, exposed to four atmospheres of dinitrogen and then stirred for one hour. A vanadium dinitrogen complex was formed (Chapter 3) along with TMEDA. The $\text{C}_7\text{D}_8$ and TMEDA were both vacuum transferred to another bomb containing a known amount of ferrocene and subsequently placed into an NMR tube. The TMEDA was quantitatively measured by $^1\text{H}$ NMR spectroscopy using ferrocene as a standard. Given all the above information, the product of reaction 2.4 seems to contain $\text{VCl}_2[N(\text{SiMe}_2\text{CH}_2\text{PPr_i}_2)_2]$ with one equivalent of TMEDA. This would still put the vanadium in a +3 oxidation state, although it doesn't agree with the susceptibility measurements. The above empirical formula must include one or more other ligands which have not yet been identified, giving the +2 oxidation state.

Inductively coupled plasma mass spectrometry (ICP-MS) confirmed that the product of reaction 2.4 also contained lithium. Therefore all the above data indicates a product containing $\text{VCl}_2[N(\text{SiMe}_2\text{CH}_2\text{PPr_i}_2)_2]$, TMEDA, and lithium. This data, plus a recent paper that describes a similar complex as $(\text{PhC}[\text{Me}_3\text{SiN}]_2)_2\text{Ti}(\mu-\text{Cl})_2\text{Li(TMEDA)}$
led to the proposal that \([(\text{Pr}_2\text{PCH}_2\text{SiMe}_2)_2\text{N}]\text{V}(\mu-\text{Cl})_2\text{Li(TMEDA)}, \text{4}, \text{(Figure 2.16) as the formula for the product of reaction 2.4. The measured magnetic susceptibility and the elemental analyses correspond fairly well with this formula. The reactivity studies of 4 are presented in Chapter 3.}

\begin{center}
\textbf{Figure 2.16. Proposed structure of } [(\text{Pr}_2\text{PCH}_2\text{SiMe}_2)_2\text{N}]\text{V}(\mu-\text{Cl})_2\text{Li(TMEDA)}, \text{4.}
\end{center}

\section{2.6 Summary}

The syntheses of new titanium and vanadium phosphine complexes, 1-4, were achieved by complexing an amido-diphosphine ligand to the corresponding halide of titanium or vanadium. NMR spectra indicate meridional geometry with $C_{2v}$ symmetry for both 1 and 2. The Ti(III) analogue, 3, is paramagnetic, but a discernable $^1\text{H NMR}$ spectrum was observed. Mass spectrometry suggests that 3 is a dimer however, with the aid of $^1\text{H NMR}$ spectroscopy, it was proposed that certain solution structures were possible. A vanadium phosphine complex, 4, although not the expected product of the reaction, was found to contain a chloride bridged lithium salt by mass spectrometry, magnetic susceptibility, $^1\text{H NMR}$, ICP-MS, and elemental analysis. All the complexes formed in this chapter are essential to the formation (1 and 4) and reactivity studies (2 and 3) of the titanium and vanadium dinitrogen complexes described in chapter 3.
2.7 References


CHAPTER 3

DINITROGEN COMPLEXES OF TITANIUM AND VANADIUM

3.1 Introduction

This chapter deals with the chemistry of dinitrogen complexes of titanium and vanadium. The syntheses and characterization of the dinitrogen complexes, 

\[ [(\text{Pr}^2\text{PCH}_2\text{SiMe}_2)_2\text{N}]\text{MCl}_2(\mu-\eta^1:\eta^1-\text{N}_2), \quad (\text{M} = \text{Ti}, \text{V}) \]

will be described.

Dinitrogen is generally inert to ordinary reaction conditions. For example, the reduction of dinitrogen to ammonia by the Haber process proceeds fairly efficiently only under extreme conditions of pressure (20 MPa) and temperature (500°C). However, it has been shown that many transition metals can be coordinated to dinitrogen in an effort to find homogeneous catalysts for dinitrogen activation which could eventually lead to changes in the fertilizer industry.

A brief summary of the general dinitrogen coordination chemistry of titanium and vanadium is presented in the next section.

3.1.1 Titanium Dinitrogen Complexes

The original report in 1966 that a mixture of Cp_2TiCl_2 and ethylmagnesium bromide efficiently reduces N_2 at room temperature was the stimulus for extensive
investigation into titanocene-based dinitrogen fixing systems. For example, reduction of 
Cp₂TiCl₂ with sodium sand under an atmosphere of N₂ yielded a blue colored complex, 
{(Cp)₂Ti}₂(μ-N₂).³

The dinitrogen complex \{(Cp^*)₂Ti\}₂(μ-N₂) was characterized by X-ray 
crystallography and found to have an essentially linear Ti-(μ-N₂)-Ti arrangement (A, 
Figure 3.1).⁴ The end-on bound dinitrogen unit has N-N distances of 1.165 (14) and 
1.155 (14) Å for the two molecules in the unit cell. In solution, spectroscopic methods 
showed that the complex is \{(Cp^*)₂TiN₂\}₂(μ-N₂) with one bridging end-on bound 
dinitrogen and two terminal dinitrogen ligands.⁵

![Figure 3.1. Examples of titanium end-on and side-on bound dinitrogen complexes.](image)

The phosphine-substituted titanocene dinitrogen complex, \{Cp₂Ti(PMe₃)\}₂(μ-
N₂), was synthesized by placing Cp₂Ti(PMe₃)₂ under one atmosphere of dinitrogen.⁶
The structure consists of two Cp$_2$Ti(PMe$_3$) fragments bridged by a linear end-on dinitrogen bridge (B, Figure 3.1) with an N-N bond distance of 1.191 (8) Å. The titanocene fragments are twisted with respect to one another such that each phosphine is nearly eclipsed with a ring on the adjacent metal. The lability of the dinitrogen was demonstrated by allowing the complex to stand at room temperature under an atmosphere of CO. The bound dinitrogen was eventually replaced by CO to yield Cp$_2$Ti(CO)$_2$, free dinitrogen, and PMe$_3$.

The reaction of trans-TiCl$_2$(TMEDA)$_2$ with one equivalent of (Me$_3$Si)$_2$NLi under dinitrogen at low temperature produced an end-on bound dinitrogen complex, containing bulky bis(trimethylsilyl) amide ligands. The complex, [((Me$_3$Si)$_2$N)TiCl(TMEDA)]$_2$(μ-N$_2$) (C, Figure 3.1), consists of two titanium fragments which are twisted with respect to each other, and bridged by an N-N bond distance of 1.289 (9) Å. However, reaction of trans-TiCl$_2$(TMEDA)$_2$ with 2.5 equivalents of (Me$_3$Si)$_2$NLi under N$_2$ in the presence of TMEDA resulted in a complex with two bound dinitrogen ligands (D, Figure 3.1). The X-ray diffraction analysis showed that the dinitrogen is bound side-on with a bond length of 1.379 (21) Å, significantly longer than 1.289 (9) Å bond length observed for the end-on bound dinitrogen complex C, Figure 3.1.

3.1.2 Vanadium Dinitrogen Complexes

The first X-ray characterized dinitrogen complex of vanadium, [[V(C$_6$H$_4$CH$_2$NMe$_2$)$_2$(C$_5$H$_5$N)]$_2$(μ-N$_2$)], was reported in 1989. This complex was synthesized by treating trans-VCl$_2$(TMEDA)$_2$ with (o-Me$_2$NCH$_2$)C$_6$H$_4$Li under an atmosphere of dinitrogen. The X-ray structure (A, Figure 3.2) shows the two vanadium fragments linked by an end-on bound dinitrogen ligand with an N-N bond length of 1.228 (4) Å.
Figure 3.2. Examples of vanadium end-on bound dinitrogen complexes.

The reaction of VCl$_3$(THF)$_3$ and dppe in the presence of sodium sand and naphthalene under dinitrogen resulted in the synthesis of [Na(THF)][V(N$_2$)$_2$(dppe)$_2$] (B, Figure 3.2). The X-ray structure of the complex shows terminal end-on bound dinitrogen ligands with an N-N bond length of 1.130 (16) Å.

One of the goals in this research group was to synthesize dinitrogen complexes of the early first row transition metals. Since the first row metals are smaller in size compared to the second and third row transition metals, it would be of interest to compare and establish the end-on versus side-on binding preference of the dinitrogen ligand. The syntheses of two dinitrogen complexes involving titanium and vanadium is presented in the remainder of this chapter, along with a summary of some relevant work done in this laboratory on the coordination chemistry of dinitrogen.

3.1.3 Previous Work on Tantalum and Zirconium Dinitrogen Complexes

One tantalum complex and three zirconium dinitrogen complexes were prepared in this laboratory. These complexes have provided some insight into the nature of
dinitrogen bonding, and the preference of this ligand for side-on versus end-on binding depending on the ligand environment.

The reduction of ZrCl₃[N(SiMe₂CH₂PPPr₂)₂] by sodium amalgam under four atmospheres of dinitrogen resulted in the isolation of {[(Pr₄₂PCH₂SiMe₂)₂N]ZrCl}₂(μ-η²:η²-N₂).¹¹ X-ray crystallography revealed a side-on bound dinitrogen unit (A, Figure 3.3) with an N-N bond length of 1.548 (7) Å. This is the longest N₂ bond distance reported for any dinitrogen complex. This binuclear complex has a planar Zr₂(μ-η²:η²-N₂) core, and each zirconium fragment contains a meridionally coordinated ligand with a chlorine atom lying on the same plane. In order to ascertain the degree of N₂ activation, the complex was degraded with HCl gas. Conversion of the N₂ ligand to hydrazine was quantitative.¹¹

![Figure 3.3. Side-on bound dinitrogen complexes synthesized in this laboratory.¹²,¹³](image)

¹¹ The reduction of ZrCl₃[N(SiMe₂CH₂PPPr₂)₂] by sodium amalgam under four atmospheres of dinitrogen resulted in the isolation of {[(Pr₄₂PCH₂SiMe₂)₂N]ZrCl}₂(μ-η²:η²-N₂). X-ray crystallography revealed a side-on bound dinitrogen unit (A, Figure 3.3) with an N-N bond length of 1.548 (7) Å. This is the longest N₂ bond distance reported for any dinitrogen complex. This binuclear complex has a planar Zr₂(μ-η²:η²-N₂) core, and each zirconium fragment contains a meridionally coordinated ligand with a chlorine atom lying on the same plane. In order to ascertain the degree of N₂ activation, the complex was degraded with HCl gas. Conversion of the N₂ ligand to hydrazine was quantitative.¹¹

![Figure 3.3. Side-on bound dinitrogen complexes synthesized in this laboratory.¹²,¹³](image)
An alkoxide dinitrogen complex was recently synthesized by reducing Zr(2,6-Me_2C_6H_3O)Cl_2[N(SiMe_2CH_2PPr')_2] with Na/Hg amalgam under dinitrogen, giving rise to \([(Pr^i_2PCH_2SiMe_2)N]Zr(2,6-Me_2C_6H_3O)\)]_2(\mu-\eta^2:\eta^2-N_2) (B Figure 3.3).\textsuperscript{13} X-ray crystallography revealed a side-on dinitrogen with a bond length of 1.51 (1) Å. However in this case, the Zr_2(\mu-\eta^2:\eta^2-N_2) unit is twisted and the two phenoxy groups are cis-disposed compared to the trans-disposed chlorine atoms in A, Figure 3.3.

The reduction of the mixed ligand complex, Zr(C_5H_5)Cl_2[N(SiMe_2CH_2PPr')_2] by sodium amalgam under dinitrogen produced \([(Pr^i_2PCH_2SiMe_2)N]Zr(\eta^5-C_5H_5)\)]_2(\mu-\eta^1:\eta^1-N_2) (A, Figure 3.4).\textsuperscript{14} An X-ray crystal structure determination of this complex indicated an end-on bridged dinitrogen ligand having a N-N bond distance of 1.301 (3) Å, much shorter than that observed for the side-on complexes.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.4.png}
\caption{Figure 3.4. End-on bound dinitrogen complexes synthesized in this laboratory.\textsuperscript{10,14}}
\end{figure}
A dinitrogen complex of a group 5 analogue was also synthesized by reducing Ta(=CHR)Cl₂[N(SiMe₂CH₂PPr₂)₂] under dinitrogen to yield {[(Pr₂PCH₂SiMe₂)₂N]Ta=CHR}₂(µ-η¹:η¹-N₂) (R = Bu₁, Ph) (B Figure 3.4). However, in the absence of X-ray crystallography, and based on analogous complexes, it was proposed that the dinitrogen unit is end-on bound.

3.2 Syntheses of {[(Pr₂PCH₂SiMe₂)₂N]MCl}₂(µ-η¹:η¹-N₂), (M = Ti, V)

The reduction of the formally Ti(IV) material, TiCl₃[N(SiMe₂CH₂PPr₂)₂], 1, with excess magnesium powder under four atmospheres of dinitrogen eventually gave the formally Ti(IV) dinitrogen complex, {[(Pr₂PCH₂SiMe₂)₂N]TiCl}₂(µ-η¹:η¹-N₂), 5 (reaction 3.1). Many colours were observed throughout the reduction: starting with the original bright red colour of 1, then dark brown, dark green, grey, dark grey, dark green, and finally dark brown. These colours indicate many intermediates, however no attempt was made to intercept these species.

\[
\begin{align*}
2\text{TiCl}_3[N(SiMe_2CH_2PPr_2)₂] & \xrightarrow{\text{Et}_2O} \text{Et}_2O \quad \text{xsMg} \\
& \quad 4 \text{ atm N}_2 \quad -2\text{MgCl}_2 \\
& \quad \downarrow \\
{[(Pr_2PCH_2SiMe_2)₂N]TiCl}₂(µ-η¹:η¹-N₂) & \quad 5 \\
\end{align*}
\]

Attempts to reduce {TiCl₂[N(SiMe₂CH₂PPr₂)₂]}ₓ (x=1 or 2), 3, under similar reducing conditions did not yield the expected complex 5. Spectroscopic evidence indicated decomposition of the starting material therefore, 3 was probably not an intermediate in the synthesis of the dinitrogen complex. All attempts to reduce the complex TiCl₃[N(SiMe₂CH₂PMe₂)₂], 2, with methyl substituents on phosphorus atoms.
of the ligand were unsuccessful; complete decomposition to intractable products and free
ligand was observed.

The formally vanadium(IV) dinitrogen complex \{[(Pr\textsuperscript{i}2PCH\textsubscript{2}SiMe\textsubscript{2})\textsubscript{2}N]VCl\textsubscript{2}(\mu-\eta\textsuperscript{1}::\eta\textsuperscript{1}-N\textsubscript{2})\}, 7, was prepared by reacting the ligand, LiN(SiMe\textsubscript{2}CH\textsubscript{2}PPPr\textsubscript{i}2), with the V(II) species, VCl\textsubscript{2}(TMEDA)\textsubscript{2}, at low temperature under one atmosphere of dinitrogen (reaction 3.2). As the reaction mixture slowly warmed to room temperature, the colour changed from light blue to dark purple.

\[
\begin{align*}
2\text{LiN(SiMe}_2\text{CH}_2\text{PPPr}_i)_2 & + 2\text{VCl}_2(\text{TMEDA})_2 \\
\text{toluene} & \quad \text{1 atm N}_2 \\
\text{-2LiCl} & \quad \text{-2TMEDA} \\
\implies & \\
\{[(\text{Pr}_i^2\text{PCH}_2\text{SiMe}_2)_2\text{N}]\text{VCl}_2(\mu-\eta^1::\eta^1-N_2)\} \\
\text{7} & \quad \text{(3.2)}
\end{align*}
\]

An alternate synthetic route to 7 was achieved by simply exposing \{[(Pr\textsuperscript{i}2PCH\textsubscript{2}SiMe\textsubscript{2})\textsubscript{2}N]V(\mu-Cl)\textsubscript{2}Li(TMEDA), 4, to four atmospheres of dinitrogen (one atmosphere of dinitrogen is sufficient).

3.3 Molecular Structure of \{[(Pr\textsuperscript{i}2PCH\textsubscript{2}SiMe\textsubscript{2})\textsubscript{2}N]TiCl\textsubscript{2}(\mu-\eta\textsuperscript{1}::\eta\textsuperscript{1}-N\textsubscript{2})\}

The X-ray crystal structure of \{[(Pr\textsuperscript{i}2PCH\textsubscript{2}SiMe\textsubscript{2})\textsubscript{2}N]TiCl\textsubscript{2}(\mu-\eta\textsuperscript{1}::\eta\textsuperscript{1}-N\textsubscript{2})\}, 5, is shown in Figure 3.5 and 3.6. Selected bond angles and bond lengths are given in Tables 3.1 and 3.2.

Complex 5 crystallized in the space group C2/c and the molecule has \textit{C}_2
symmetry, the twofold axis bisecting the central N-N bond. The coordination geometry
Figure 3.5. The molecular structure of \[((\text{Pr}^2\text{PCH}_2\text{SiMe}_2)_2\text{N})\text{TiCl}_2(\mu-\eta^1:\eta^1\cdot\text{N}_2)_2\cdot 5\).
Figure 3.6. Two Chem 3D® views of the molecular structure of 5 showing the symmetric environment about the titanium centres. The top view is looking down the Ti-Ti axis, while the bottom view shows the close contact of the isopropyl groups across the N₂ bridge.
of the titanium atom is distorted square-based pyramidal, where one of the two nitrogen atoms of the dinitrogen ligand occupies the apical position. The two titanium centres are joined by a nearly linear end-on bridging N\(_2\) unit.

In the structure of 5, the two TiCl[N(SiMe\(_2\)CH\(_2\)PPr\(_i\)\(_2\)] fragments each bonded to one of the two nitrogen atoms of the bridging dinitrogen moiety are rotated with respect to each other (torsion angle Cl-Ti1-Ti1'-Cl1' = 76.9°) minimizing the steric repulsion between the bulky isopropyl groups. However, the Ti-(μ-N\(_2\))-Ti moiety is almost linear with an angle of 173.7° (2) for Ti1-N2-N2' (Table 3.1).

<table>
<thead>
<tr>
<th>Bonds</th>
<th>Angle (deg)</th>
<th>Bonds</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1-Ti1-N2</td>
<td>115.3 (2)</td>
<td>P1-Ti1-P2</td>
<td>160.63 (8)</td>
</tr>
<tr>
<td>Ti1-N2-N2'</td>
<td>173.7 (2)</td>
<td>P1-Ti1-N1</td>
<td>82.3 (1)</td>
</tr>
<tr>
<td>Cl1-Ti1-P1</td>
<td>88.91 (8)</td>
<td>P1-Ti1-N2</td>
<td>104.6 (2)</td>
</tr>
<tr>
<td>Cl1-Ti1-P2</td>
<td>93.96 (9)</td>
<td>P2-Ti1-N1</td>
<td>80.8 (1)</td>
</tr>
<tr>
<td>Cl1-Ti1-N1</td>
<td>127.8 (1)</td>
<td>P2-Ti1-N2</td>
<td>91.2 (2)</td>
</tr>
<tr>
<td>Cl1-Ti1-N2</td>
<td>116.7 (2)</td>
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<td></td>
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</table>

The N-N bond distance in the dinitrogen unit of 5 is 1.275 (7) Å (Table 3.2) which is within the range for binuclear end-on dinitrogen complexes of early transition metals (1.12-1.33 Å). This dinitrogen distance is slightly longer than the N-N bond length observed for Ph\(_2\)N\(_2\), 1.255 (16) Å.\(^{14}\) The titanium-amide bond length of 2.035 (5) Å of the ancillary ligand is much longer than the titanium-nitrogen bond of 1.775 (4) Å for the N\(_2\) ligand, but similar to the titanium-amide bond length of 2.023 (5) Å for complex C, Figure 3.1.\(^7\) The Ti-P bond lengths in 5 are 2.630 (2) Å and 2.589 (2) Å,
which are slightly longer than the analogous distances, 2.538 (2) Å and 2.525 (2) Å, found in B, Figure 3.1. A survey of N-N bond lengths of some other titanium end-on dinitrogen complexes is shown in Table 3.3.

### Table 3.2: Selected Bond Lengths for \([(\text{Pr}^2_2\text{PCH}_2\text{SiMe}_2)_2\text{MTiC}]_2(\mu-\eta^1:\eta^1-\text{N}_2)\).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2-N2'</td>
<td>1.275 (7)</td>
<td>Ti1-P2</td>
<td>2.589 (2)</td>
</tr>
<tr>
<td>Ti1-Cl</td>
<td>2.331 (2)</td>
<td>Ti1-N1</td>
<td>2.035 (5)</td>
</tr>
<tr>
<td>Ti1-P1</td>
<td>2.630 (2)</td>
<td>Ti1-N2</td>
<td>1.775 (4)</td>
</tr>
</tbody>
</table>

### Table 3.3: Compilation of N-N Bond Lengths for Some Dinitrogen Complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Bond Length (Å)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>([(\text{Cp})_2\text{Ti}(\text{p-CH}_3\text{C}_6\text{H}_4)]_2(\mu-\eta^1:\eta^1-\text{N}_2))</td>
<td>1.162 (12)</td>
<td>15</td>
</tr>
<tr>
<td>(<a href="">(\text{Cp}^*)_2\text{Ti}</a>)</td>
<td>1.165 (14)</td>
<td>4</td>
</tr>
<tr>
<td>{\text{Cp}_2\text{Ti(PMe}_3\text{)}}_2(\mu-\eta^1:\eta^1-\text{N}_2)</td>
<td>1.191 (8)</td>
<td>6</td>
</tr>
<tr>
<td>{[(\text{Me}_3\text{Si})_2\text{N}]\text{TiCl(py)_2}(\mu-\eta^1:\eta^1-\text{N}_2)}</td>
<td>1.263 (7)</td>
<td>16</td>
</tr>
<tr>
<td>{[(\text{Me}_3\text{Si})_2\text{N}]\text{TiCl(TMEDA)}}_2(\mu-\eta^1:\eta^1-\text{N}_2)</td>
<td>1.289 (9)</td>
<td>7</td>
</tr>
</tbody>
</table>

The traditional view of end-on dinitrogen bonding in a bridging mode is shown in A, Figure 3.7. The N₂ ligand has a bond order of 3 and formal oxidation state of 0 therefore, the predicted N-N bond length should be short and the M-N distances typical of single bonds. With this formalism, each titanium centre in 5 would have an oxidation state of +2.
Another view of end-on dinitrogen bonding is represented as a diimide structure (B, Figure 3.7) in which the N₂ ligand has a formal charge of -4, in other words a hydrazido (-4) unit. The combination of short M-N and long N-N bond lengths is diagnostic of such structures as shown by other N₂ complexes. This formalism is most consistent with the X-ray structure of 5 as evidenced by the bond lengths of Ti-N = 1.775 (4) Å and N-N = 1.275 (7) Å. Therefore, it is reasonable to propose that 5 consists of two Ti(IV) centres.

### 3.4 Molecular Structure of \{[(Pr₂PCH₂SiMe₂)₂N]VCl\}₂(μ-η¹:η¹-N₂)

The X-ray crystal structure of \{[(Pr₂PCH₂SiMe₂)₂N]VCl\}₂(μ-η¹:η¹-N₂), 7, is shown in Figure 3.8 and 3.9. Selected bond angles and bond lengths are given in Tables 3.4 and 3.5.

Complex 7 crystallizes in the space group Fdd2, and the molecule possesses C₂ symmetry. The geometry of the vanadium atom is also distorted square-based pyramidal where one of the two nitrogen atoms of the dinitrogen ligand occupies the apical position. Similar to 5, the two metal centres are joined by a nearly linear end-on bridging N₂ unit.

Structural features similar to those for the titanium dinitrogen complex, 5, prevail.
Figure 3.8. The molecular structure of \(((\text{Pr}^1 \text{PCH}_2 \text{SiMe}_2)_2 \text{N})\text{VCl}_2)(\mu-\eta^1:\eta^1-\text{N}_2)_7\).
Figure 3.9. Two Chem 3D® views of the molecular structure of 7 showing the symmetric environment about the vanadium centres. The top view is looking down the V-V axis, while the bottom view shows the close contact of the isopropyl groups across the N₂ bridge.
for the vanadium complex. The complex consists of two identical VCl[N(SiMe₂CH₂PPr₂)₂] fragments each bonded to one of the two nitrogen atoms of the bridging dinitrogen moiety. The two vanadium fragments are rotated with respect to each other (torsion angle Cl-V1-V1'-Cl1' = 74.4°), again to minimize steric repulsion between the bulky isopropyl groups. The V-(μ-N₂)-V moiety is almost linear with an angle of 174.3 (2) Å for V1-N2-N2' (Table 3.4).

Table 3.4: Selected Bond Angles for \(((\text{Pr}^{i}_2\text{PCH}_2\text{SiMe}_2)_2\text{N})\text{VCl})_2(\mu-\eta^1:\eta^1\text{N}_2)\).

<table>
<thead>
<tr>
<th>Bonds</th>
<th>Angle (deg)</th>
<th>Bonds</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1-V1-N2</td>
<td>127.3 (2)</td>
<td>P1-V1-P2</td>
<td>166.39 (8)</td>
</tr>
<tr>
<td>V1-N2-N2'</td>
<td>174.3 (2)</td>
<td>P1-V1-N1</td>
<td>83.6 (2)</td>
</tr>
<tr>
<td>Cl1-V1-P1</td>
<td>92.70 (9)</td>
<td>P1-V1-N2</td>
<td>93.3 (2)</td>
</tr>
<tr>
<td>Cl1-V1-P2</td>
<td>90.24 (9)</td>
<td>P2-V1-N1</td>
<td>83.5 (2)</td>
</tr>
<tr>
<td>Cl1-V1-N1</td>
<td>121.2 (2)</td>
<td>P2-V1-N2</td>
<td>98.0 (2)</td>
</tr>
<tr>
<td>Cl1-V1-N2</td>
<td>111.5 (2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The N-N bond distance in the end-on dinitrogen unit of 1.257 (8) Å (Table 3.5), is again comparable to other early transition metal complexes containing an end-on dinitrogen ligand, including 5. As in the titanium dinitrogen case, in 7 the vanadium-amide bond length of 2.040 (5) Å for the nitrogen donor in the ancillary ligand is much longer than the vanadium-nitrogen bond of 1.760 (4) Å for the N₂ ligand. To date the only other reported vanadium dinitrogen complexes characterized by X-ray analysis have N-N bond lengths of 1.228 (4) Å and 1.130 (16) Å.⁸,⁹
Table 3.5: Selected Bond Lengths for \([(\text{Pr}_{12}\text{PCH}_2\text{SiMe}_2)_2\text{N}]\text{VC}_{11}\text{2}(1-1-1-1\text{-N}_2)\).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2-N2'</td>
<td>1.257 (8)</td>
<td>V1-P2</td>
<td>2.519 (2)</td>
</tr>
<tr>
<td>V1-C11</td>
<td>2.311 (2)</td>
<td>V1-N1</td>
<td>2.040 (5)</td>
</tr>
<tr>
<td>V1-P1</td>
<td>2.530 (2)</td>
<td>V1-N2</td>
<td>1.760 (4)</td>
</tr>
</tbody>
</table>

Complex 7 is also proposed to have two V(IV) centres by analogy to 5 and other Group 5 dinitrogen complexes.\(^{18}\)

3.5 NMR Spectra of \([(\text{Pr}_{12}\text{PCH}_2\text{SiMe}_2)_2\text{N}]\text{MCl}_2(\mu-\eta^1:\eta^1\text{-N}_2), (M = \text{Ti, V})\)

The \(^1\text{H}\) NMR spectrum of \([(\text{Pr}_{12}\text{PCH}_2\text{SiMe}_2)_2\text{N}]\text{TiCl}_2(\mu-\eta^1:\eta^1\text{-N}_2), 5,\) is shown in Figure 3.10. There is a lack of symmetry on either side of the tridentate mono(amido-diphosphine) plane; however, the X-ray crystal structure indicates a C\(_2\) axis bisecting the dinitrogen ligand relating each silyl methyl group with its counterpart on the alternate ligand making the pair chemically equivalent. Therefore, if we assume the same structure in solution as in the solid state then one would predict four resonances for the silyl methyl protons, but actually two resonances are observed. One possible fluxional process could involve dissociation of the phosphine atoms of the tridentate ligand and then rotation about the Ti-N (amide) bond, followed by reassociation. Another fluxional process could involve the rotation of the two mono(amido-diphosphine) ligands with respect to one another about the Ti-N-N-Ti bonds. However, this process is less likely to occur because the eight isopropyl groups on the phosphorus atoms are so bulky that rotation about the dinitrogen bond would be difficult. The \(^1\text{H}\) NMR spectra recorded from 10°C to -80 °C show only broadened signals that do not decoalesce.
Figure 3.10. 300 MHz $^1$H NMR spectrum of $\left[\left(\text{Pr}^2\text{PCH}_2\text{SiMe}_2\right)\text{N}_{\text{TiCl}_2}\left(\mu-\eta^1.\eta^1.\right.\right.$

$\text{N}_2\right)$, 5, in C$_7$D$_8$. Solvent and impurity peaks are indicated by an asterisk and a cross, respectively.
Figure 3.11. 121 MHz $^{31}P\{^1H\}$ NMR spectra of $\{[(\text{Pr}^2\text{PCH}_2\text{SiMe}_2)\text{N}]\text{TiCl}_2(\mu-\eta^1:\eta^1-\text{N}_2)\}, 5$, in C$_7$D$_8$ recorded at 20°C (top) and at -50°C (bottom).
The $^{31}\text{P}^{(1\text{H})}$ NMR spectrum of 5 at room temperature shows only a singlet at 21.19 ppm (Figure 3.11) indicating four chemically equivalent phosphorus atoms due to the previously invoked fluxional process. However, cooling the sample to -50°C slows the fluxionality enough that the two inequivalent phosphorus sites are discernable on the NMR timescale, resulting in the appearance of an AB quartet ($^2J_{\text{P-P}}$ of 87.9 Hz) (Figure 3.11).

The $^{15}\text{N}^{(1\text{H})}$ NMR spectrum of $\{[(\text{P}r_2\text{PCH}_2\text{SiMe}_2)_2\text{N}]\text{C}_1\}_2{(\mu-\eta^1::\eta^1-\text{N}_2)}$, 6, shows a single resonance at 375.5 ppm which is similar to the chemical shift of other dinitrogen complexes.\textsuperscript{17}

The $^1\text{H}$ and $^{31}\text{P}^{(1\text{H})}$ NMR spectra of $\{[(\text{P}r_2\text{PCH}_2\text{SiMe}_2)_2\text{N}]\text{VCl}_2{(\mu-\eta^1::\text{N}_2)}$, 7, were not fully resolved due to the paramagnetic nature of the complex. However, the $^1\text{H}$ NMR spectra recorded from 10°C to -80 °C show only broadened signals, which could not be assigned. The magnetic moment was determined as $\mu_{\text{eff}} = 1.74$ BM which is expected for each $d^1$ metal centre.

3.6 Reactivity Studies of $\{[(\text{P}r_2\text{PCH}_2\text{SiMe}_2)_2\text{N}]\text{MCl}_2{(\mu-\eta^1::\text{N}_2)}$, (M = Ti, V)

3.6.1 Hydrazine Analysis

In order to probe the degree of N$_2$ activation of 5 and 7, the dinitrogen complexes were degraded with HCl and the products analyzed. In both cases, hydrazine was detected (reaction 3.3). In neither case was one equivalent of hydrazine produced; for the titanium dinitrogen complex, 5, $0.75 \pm 0.04$ equivalents was formed and for the vanadium dinitrogen complex, 7, only $0.29 \pm 0.04$ equivalents of hydrazine was measured. A blank
test performed on TiCl₃[N(SiMe₂CH₂PPr'₂)₂], 1, indicated no interference from the metal or ancillary ligands.

\[ \text{[(Pr}^2\text{PCH}_2\text{SiMe}_2)₂\text{N]}\text{MCi}_2(\mu-\eta^1:\eta^1-\text{N}_2) \xrightarrow{\text{HCl} (g)} \text{N}_2\text{H}_4 + \text{decomposition} \]
\[ M = \text{Ti, 5 or V, 7} \]

(3.3)

Table 3.6: Theoretical and Calculated Hydrazine Concentrations for \{[(Pr}^2\text{PCH}_2\text{SiMe}_2)₂\text{N]}\text{TiCl}_2(\mu-\eta^1:\eta^1-\text{N}_2)\).

<table>
<thead>
<tr>
<th>Trial</th>
<th>5 (mg)</th>
<th>Theoretical [Hydrazine]</th>
<th>%T</th>
<th>Found [Hydrazine]</th>
<th>[Found] [Theoretical]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
<td>3.27 x 10⁻⁶ M</td>
<td>73.8</td>
<td>2.47 x 10⁻⁶ M</td>
<td>0.76</td>
</tr>
<tr>
<td>2</td>
<td>61</td>
<td>4.98 x 10⁻⁶ M</td>
<td>61.0</td>
<td>3.67 x 10⁻⁶ M</td>
<td>0.74</td>
</tr>
<tr>
<td>3</td>
<td>72</td>
<td>5.84 x 10⁻⁶ M</td>
<td>55.1</td>
<td>4.41 x 10⁻⁶ M</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Table 3.7: Theoretical and Calculated Hydrazine Concentrations for \{[(Pr}^2\text{PCH}_2\text{SiMe}_2)₂\text{N]}\text{VCl}_2(\mu-\eta^1:\eta^1-\text{N}_2)\).

<table>
<thead>
<tr>
<th>Trial</th>
<th>7 (mg)</th>
<th>Theoretical [Hydrazine]</th>
<th>%T</th>
<th>Found [Hydrazine]</th>
<th>[Found] [Theoretical]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
<td>3.25 x 10⁻⁶ M</td>
<td>98.2</td>
<td>1.16 x 10⁻⁶ M</td>
<td>0.36</td>
</tr>
<tr>
<td>2</td>
<td>45</td>
<td>3.65 x 10⁻⁶ M</td>
<td>97.9</td>
<td>1.17 x 10⁻⁶ M</td>
<td>0.32</td>
</tr>
<tr>
<td>3</td>
<td>51</td>
<td>4.14 x 10⁻⁶ M</td>
<td>97.9</td>
<td>1.17 x 10⁻⁶ M</td>
<td>0.28</td>
</tr>
<tr>
<td>4</td>
<td>61</td>
<td>4.95 x 10⁻⁶ M</td>
<td>91.8</td>
<td>1.41 x 10⁻⁶ M</td>
<td>0.28</td>
</tr>
<tr>
<td>5</td>
<td>72</td>
<td>5.84 x 10⁻⁶ M</td>
<td>94.0</td>
<td>1.32 x 10⁻⁶ M</td>
<td>0.23</td>
</tr>
</tbody>
</table>
A possible reason for the different amounts of hydrazine produced upon protonation of 5 and 7 is the availability of electrons from each metal centre. For example, 5 (a formally Ti(IV) species) was synthesized from 1 which is a Ti(IV) starting material (reaction 3.1) through a proposed Ti(II) intermediate. Therefore, two electrons are available per titanium centre and, consequently one would expect quantitative formation of hydrazine (reaction 3.4).

\[
\begin{align*}
5 & \quad \quad \quad (((\text{Pr}_2^1\text{PCH}_2\text{SiMe}_2)_2\text{N})\text{TiCl})_2(\mu-\eta^1: \eta^1\text{-N}_2) + 4\text{H}^+ + 4\text{e}^- \\
\downarrow & \\
\text{N}_2\text{H}_4 + \text{decomposition} & \quad (3.4)
\end{align*}
\]

Complex 7 is formed from a V(II) starting material to a V(IV) dinitrogen complex (reaction 3.2). However, one electron is still available on each vanadium centre so in total three electrons are available per vanadium centre allowing quantitative formation of ammonia (reaction 3.5).

\[
\begin{align*}
7 & \quad \quad \quad (((\text{Pr}_2^1\text{PCH}_2\text{SiMe}_2)_2\text{N})\text{VCl})_2(\mu-\eta^1: \eta^1\text{-N}_2) + 6\text{H}^+ + 6\text{e}^- \\
\downarrow & \\
2 \text{NH}_3 + \text{decomposition} & \quad (3.5)
\end{align*}
\]

These proposed mechanisms however, can not explain the actual amounts of hydrazine detected for 5 and 7. A final Ti(III) dinitrogen species would have one electron available per titanium centre and therefore, 0.50 ± 0.04 equivalents of hydrazine and 0.50
equivalents of dinitrogen would be produced. However, if a 50/50 mixture of Ti(IV) and Ti(III) oxidation states are present in 5, 0.75 ± 0.04 equivalents of hydrazine would be expected. Confirmation of these proposals were not performed.

3.6.2 Dinitrogen Analysis

To confirm the hydrazine results, dinitrogen evolution was also measured after degradation of the complexes with aqueous HCl. For the titanium complex 5, the conversion from the dinitrogen ligand to dinitrogen gas was 0.29 ± 0.05 equivalents (an average of two trials, 0.26 and 0.31 equivalents). We can account for all of the dinitrogen ligand in the complex given that 0.75 ± 0.04 equivalents was converted to hydrazine. Despite careful handling of complex 7, a similar determination for the vanadium complex was not achieved due to rapid decomposition prior to any experimental measurements.

3.7 Summary

The new dinitrogen complexes of titanium, 5, and vanadium, 7, were synthesized from their corresponding phosphine precursors. The X-ray crystal structure of 5 consists of two TiCl[N(SiMe₂CH₂PPr')₂] fragments each bonded to one nitrogen atom of a bridging end-on bound dinitrogen unit with an N-N bond length of 1.275 (7) Å. Similarly, the crystal structure of 7 also contains two VCl[N(SiMe₂CH₂PPr')₂] fragments bonded to an end-on bridging dinitrogen ligand (N-N bond length is 1.257 (8) Å). The variable temperature $^{31}$P-$^1$H NMR spectra of 5 could indicate that at room temperature it undergoes a proposed fluxional process involving dissociation of the phosphine atoms of the tridentate ligand and then rotation about the Ti-N (amide) bond, followed by reassociation.
The reactivity of both dinitrogen complexes was investigated with respect to hydrazine and dinitrogen analyses. First, it was found that 5 liberated $0.75 \pm 0.04$ equivalents of hydrazine, while 7 liberated only $0.29 \pm 0.04$ equivalents from the reaction with HCl. Dinitrogen evolution experiments showed that 5 gave off $0.29 \pm 0.05$ equivalents of dinitrogen, close to the expected value.

3.8 References

(14) Fryzuk, M. D.; Haddad, T. S.; Mylvaganam, M.; McConville, D. H.; Rettig, S. J. 


1992, 244.

**112**, 4331.

CHAPTER 4

EXPERIMENTAL PROCEDURES

4.1 General Information

Unless otherwise stated, all manipulations were performed under an atmosphere of prepurified dinitrogen or argon in a Vacuum Atmospheres HE-553-2 glovebox equipped with a MO-40-2H purifier, or in standard Schlenk-type glassware on a vacuum line.

Toluene, hexanes, and THF were predried over CaH₂ for 24 hours, and then dried by refluxing over sodium benzophenone ketyl followed by distillation under argon. Pentane and diethyl ether were treated in a similar manner except that these solvents were not predried over CaH₂. CH₂Cl₂ was predried over CaH₂, then distilled from P₂O₅. Deuterated benzene (C₆D₆) and toluene (C₇D₈) were purchased from Aldrich, dried over activated 4Å molecular sieves, vacuum transferred and "freeze-pump-thawed" three times prior to use.

Microanalyses (C, H, and N) of all air- and moisture-sensitive compounds were performed by Mr. P. Borda of this department. Mr. M. Lapawa of this department acquired all the electron ionization mass spectra.

4.2 Magnetic Susceptibility Measurements

Magnetic susceptibilities were determined in the solid state at ambient temperature
using The Johnson-Matthey Magnetic Susceptibility Balance. The samples were loaded in the glovebox and sealed under dinitrogen. Each run required 30-40 mg of sample ground into a fine powder. Measurements are estimated to be accurate to 10%. The diamagnetic susceptibilities for the ligands were obtained from the literature (e.g. $\chi'_{\text{N(SiMe}_2\text{CH}_2\text{PPr}_2)_2}} = -3.19 \times 10^{-4}$ cgs-emu and $\chi'_{\text{TMEDA}} = -8.71 \times 10^{-5}$ cgs-emu).  

4.3 NMR Spectra

All NMR spectra were recorded at room temperature (20°C) unless otherwise noted. $^1\text{H}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy experiments were done using a Varian XL-300 instrument operating at 300 MHz and 121.4 MHz, respectively. $^1\text{H}$ NMR spectra were referenced to internal $\text{C}_6\text{D}_5\text{H}$ (7.15 ppm) or $\text{C}_6\text{D}_5\text{CD}_2\text{H}$ (2.09 ppm) and $^{31}\text{P}\{^1\text{H}\}$ NMR were referenced to external P(OMe$_3$)$_3$ (141.00 ppm, with respect to 85% H$_3$PO$_4$ at 0.00 ppm). Routine $^1\text{H}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR experiments were done using a Bruker AC-200 instrument operating at 200.1 MHz and 81.1 MHz respectively. Solution $^{15}\text{N}\{^1\text{H}\}$ NMR spectra were recorded on the XL-300, referenced to external formamide set at 0.00 ppm. All chemical shifts (δ) are reported in units of parts per million (ppm).

4.4 X-ray Crystal Structures

The X-ray crystal structures were determined at the UBC Crystallographic Services of the department by Dr. Steve Rettig. The crystals were loaded in 0.3 or 0.5 mm glass capillaries (Charles Supper Co.) in the glove-box, then sealed under dinitrogen. Details of the structure determinations are given in the Appendix.
4.5 Hydrazine Analysis

Hydrazine was analyzed according to the method of Watt and Chrisp.\textsuperscript{2} Three samples of \text{[(Pr\textsubscript{2}PCH\textsubscript{2}SiMe\textsubscript{2})\textsubscript{2}N]TiCl\textsubscript{2}(\mu-\eta\textsuperscript{1}:\eta\textsuperscript{1}-N\textsubscript{2})}, 5, (40, 61, and 72 mg each in 20 mL of toluene) and five samples of \text{[(Pr\textsubscript{2}PCH\textsubscript{2}SiMe\textsubscript{2})\textsubscript{2}N]VCl\textsubscript{2}(\mu-\eta\textsuperscript{1}:\eta\textsuperscript{1}-N\textsubscript{2})}, 7, (40, 45, 51, 61, and 72 mg each in 20 mL of toluene) were loaded into Schlenk tubes, sealed under N\textsubscript{2}, removed from the glovebox and attached to a vacuum line. The dinitrogen was removed and replaced with anhydrous HCl, resulting in an instantaneous loss of brown, 5 or purple, 7 colour to a pale yellow or pale peach colour, respectively. The samples were then exposed to air, extracted with distilled water, and filtered into 500 mL volumetric flasks; 2 mL aliquots of the 500 mL solutions were added to 20 mL aliquots of a colour developer (p-dimethylaminobenzaldehyde, 4.0 g; ethanol, 200 mL; concentrated HCl, 20 mL) and diluted to 50 mL with 1M HCl. After 10 minutes, percent transmittance readings were taken. The spectrometer was set to 100% transmittance using a blank solution consisting of 10 mL of colour developer diluted to 25 mL with 1M HCl. Percent transmittance readings were converted to hydrazine concentrations using equation 5.1 (this equation was determined earlier from solutions of known hydrazine concentration).\textsuperscript{2} The results are tabulated in Tables 3.6 and 3.7.

\[
\log[\text{hydrazine}] = 5.960 + (1.3480 \times 10^{-2})(100 - \%\text{transmittance})
\]  

(5.1)

A 20 mg sample of 1 was treated in a similar manner and it was found to give 100% transmittance. Therefore, there is no interference with this hydrazine test from the titanium, vanadium or the other ancillary ligands.
Figure 4.1. Constant pressure gas uptake apparatus.
4.6 Dinitrogen Evolution Measurements

The constant pressure gas-uptake apparatus (Figure 4.1.) was used to measure the rate of gas evolution at constant gas pressure. 1.0 M HCl was placed in reaction flask A under a strong flow of dinitrogen, and a glass bucket containing the \([(Pr\textsubscript{i\textsubscript{2}}PCH\textsubscript{2}SiMe\textsubscript{2})\textsubscript{2}N]TiCl\textsubscript{2}(\mu-\eta^1:\eta^1-N_2), \text{5} or \([(Pr\textsubscript{i\textsubscript{2}}PCH\textsubscript{2}SiMe\textsubscript{2})\textsubscript{2}N)VCl\textsubscript{2}(\mu-\eta^1:\eta^1-N_2), \text{7} dinitrogen complexes was suspended from a hook inserted through sidearm B. A ground glass joint sealed the hook to the flask while allowing the hook to be rotated to drop the bucket. The flask was attached to coiled glass tubing, which in turn was attached via valve C to valve D. The reaction flask was clamped to a shaker mechanism G and immersed in the oil bath H at the reaction temperature (+ 0.05°C). The section of the system between C and F was evacuated and filled to ~400 mm Hg. Then valve C was opened, the system set to the final reaction pressure, the bucket dropped, and the timer and shaker started. As gas evolved, the height of the liquid (n-dibutyl phthalate) in the left column of manometer J decreased. Gas was withdrawn slowly through needle valve E to restore the balance in manometer J. The resulting dip in the mercury manometer K was measured by a Precision Tool Vernier Microscope Type 2158. Both manometers were suspended in a water bath at 25°C. Calibration permitted the conversion of mercury height measurements to millimoles of gas produced.

4.7 Reagents and Starting Materials

Anhydrous TiCl\textsubscript{3} (Aldrich) and VCl\textsubscript{3} (Strem) were used as received. TiCl\textsubscript{4} (Aldrich) was made up in toluene (0.9640 M). VCl\textsubscript{2}(TMEDA)\textsubscript{2}\textsuperscript{3} and TiCl\textsubscript{3}(THF)\textsubscript{3}\textsuperscript{4} were prepared by published procedures. \textsubscript{N,N,N',N'}-tetramethylethylenediamine (TMEDA) (Aldrich) was distilled over sodium metal and stored under dinitrogen before use.
Magnesium butadiene (MgC\textsubscript{4}H\textsubscript{6}\cdot2THF),\textsuperscript{5} benzyl potassium (KCH\textsubscript{2}C\textsubscript{6}H\textsubscript{5}),\textsuperscript{6} and sodium cyclopentadiene (NaCp•DME)\textsuperscript{7} were all prepared according to the literature procedures.

The organophosphorus ligands, LiN(SiMe\textsubscript{2}CH\textsubscript{2}PPr\textsuperscript{i}\textsubscript{2})\textsubscript{2} and LiN(SiMe\textsubscript{2}CH\textsubscript{2}PMe\textsubscript{2})\textsubscript{2}, were prepared according to literature procedures.\textsuperscript{8} HN(SiMe\textsubscript{2}CH\textsubscript{2}Cl\textsubscript{2} (Aldrich) (50 g) was dissolved in hexanes (50 mL), cooled to -30°C for 24 hours, and then filtered through a fine porosity frit with the aid of Celite. The resulting solution was distilled (42°C) under full vacuum (0.01 mm Hg) and stored under nitrogen.

4.8 Syntheses

4.8.1 TiCl\textsubscript{3}[N(SiMe\textsubscript{2}CH\textsubscript{2}PPr\textsuperscript{i}\textsubscript{2})\textsubscript{2}, (1)

A toluene solution (50 mL) of LiN(SiMe\textsubscript{2}CH\textsubscript{2}PPr\textsuperscript{i}\textsubscript{2})\textsubscript{2} (5.20 g; 13.0 mmol) was added dropwise to a red toluene solution (50 mL) of TiCl\textsubscript{4} (13.5 mL; 13.0 mmol) at -78°C. The reaction mixture became orange coloured, but eventually changed back to deep red. After being warmed to room temperature, the solution was stirred for 18 hours and then brought into the glovebox, where it was filtered through a fine porosity frit with the aid of Celite. The solution volume was reduced under vacuum to 20 mL, and then stored at -30°C for 24 hours. Crystallization gave pure red crystals (6.06 g; 85% yield). Anal. Calcd. for C\textsubscript{18}H\textsubscript{44}Cl\textsubscript{3}NP\textsubscript{2}Si\textsubscript{2}Ti: C, 39.53; H, 8.11; N, 2.56. Found C, 39.90; H, 8.35; N, 2.44. \textsuperscript{1}H NMR (C\textsubscript{7}D\textsubscript{8}, \delta, ppm): 2.09 (br m, 4H, PCH(CH\textsubscript{3})\textsubscript{2}), 1.169 and 1.123 (m, J = 3.3 Hz, 24H, PCH(CH\textsubscript{3})\textsubscript{2}), 0.91 (t, J\textsubscript{app}= 6.9 Hz, 4H, PCH\textsubscript{2}Si), 0.44 (s, 12H, SiCH\textsubscript{3}). \textsuperscript{31}P{\textsuperscript{1}H} NMR (C\textsubscript{7}D\textsubscript{8}, \delta, ppm): +32.9 (s).
4.8.2 TiCl₃[N(SiMe₂CH₂PMe₂)₂], (2)

The same procedure used previously for the preparation of 1 was followed. The reaction of a toluene solution (100 mL) of LiN(SiMe₂CH₂PMe₂)₂ (7.03 g; 24.5 mmol) and a red toluene solution (50 mL) of TiCl₄ (25.6 mL; 24.7 mmol) produced an orange colour that changed to red. Pure red crystals of the product were obtained (10.2 g; 97% yield). Anal. Calcd. for C₁₀H₂₈C₁₃NP₂Si₂Ti: C, 27.61; H, 6.49; N, 3.22. Found: C, 28.22; H, 6.53; N, 2.88. 

¹H NMR (C₇D₈, δ, ppm): 1.06 (t, J= 6.3 Hz, 12H, PCH₃), 0.90 (t, J= 8.7 Hz, 4H, PCH₂Si), 0.28 (s, 12H, SiCH₃).

3¹P {¹H} NMR (C₇D₈, δ, ppm): -1.93 (s).

4.8.3 {TiCl₂[N(SiMe₂CH₂PPr₂)₂]}ₓ, (3)

The same procedure used previously for the preparation of 1 was followed. The reaction of a toluene solution (50 mL) of LiN(SiMe₂CH₂PPr₂)₂ (2.0 g; 5.00 mmol) and a pale blue toluene solution (50 mL) of TiCl₃(THF)₃ (1.88 g; 5.08 mmol) gave a dark green colour. Pure green crystals of the product were obtained (2.20 g; 43% yield). Anal. Calcd. for C₁₈H₄₄Cl₂NP₂Si₂Ti: C, 42.27; H, 8.67. Found: C, 41.46; H, 8.53. 

¹H NMR (C₇D₈, δ, ppm): 32.7 (br m, 8H, PCH(CH₃)₂), 3.00 (br s, 24H, PCH(CH₃)₂), 2.59 (br s, 24H, PCH(CH₃)₂) -0.22 (br s, 24H, SiCH₃), -3.38 (br m, 8H, PCH₂Si).

Magnetic susceptibility measurements, μeff calcd (spin only) 1.73 BM. Found: μeff 1.69 BM/metal centre (κ'_Ti(III) = 1.20 x 10⁻³ cgs·emu).

4.8.4 [(Pr₂PCH₂SiMe₂)_2N]V(μ-Cl)₂Li(TMEDA), (4)

The same procedure used previously for the preparation of 1 was followed, except that the procedure was done under an atmosphere of dry argon instead of dinitrogen. The
reaction of a toluene solution (50 mL) of LiN(SiMe2CH2PPr2)2 (2.05 g; 5.13 mmol) and a pale blue toluene solution (50 mL) of VCl2TMEDA2 (1.78 g; 5.01 mmol) produced a bright green colour. Pure green crystals of the product were obtained (0.88 g; 27% yield). Anal. Calcd. for C24H60Cl2LiN3P2Si2V: C, 45.21; H, 9.48; Cl, 11.13. Found C, 45.01; H, 9.74; Cl, 11.37. 1H (C7D8, δ, ppm): 1.96 (sh), 1.60 (sh), 1.19 (br s, PCH(CH3)2), 1.00 (br s, PCH(CH3)2), 0.86 (br s, PCH2Si), 0.46 (sh), 0.25 (br s, SiCH3). Magnetic susceptibility measurements, μeff calcld (spin only) 3.87 BM. Found: μeff 3.90 BM/ metal centre (χ'V(II) = 6.40 x 10^-3 cgs-emu).

4.8.5 \{[(Pr2PCH2SiMe2)2N]TiCl12(11-111-N2), (5)

Method A: Mg powder (0.111g; 4.57 mmol), TiCl3[N(SiMe2CH2PPr2)2]2 (0.498 g; 0.910 mmol), and 50 mL of diethyl ether were placed into a thick walled reaction flask (300 mL) equipped with a 10 mm Teflon needle valve. The flask was then brought to a vacuum line, cooled to -196°C, filled with N2, sealed, and allowed to warm slowly to room temperature with stirring. The deep red coloured solution slowly became dark brown. After three days of stirring, the N2 was removed and the flask taken into the glovebox for product isolation. The Mg was removed by filtering the solution through a fine porosity frit with Celite. The solution volume was reduced under vacuum to 10 mL and stored at -30°C for 24 hours. Pure brown crystals were formed from diethyl ether (0.40 g; 45% yield). Anal. Calcd. for C36H88Cl2N4P4Si4Ti2: C, 44.12; H, 9.05; N, 5.72; Cl 7.23. Found C, 43.47; H, 9.30; N, 5.30; Cl, 7.50. 1H NMR (C7D8, δ, ppm): 2.63 (br m, 4H, PCH(CH3)2), 2.01 (br m, 4H, PCH(CH3)2), 1.43 (m, 48H, PCH(CH3)2), 0.88 (t, J = 7.5 Hz, 8H, PCH2Si), 0.29 (s, 12H, SiCH3), 0.13 (s, 12H, SiCH3). 31P(1H) NMR (C7D8, δ, ppm): +21.19 (s) and at -50°C: +23.41, +18.35 (AB quartet, Jp-p = 87.9 Hz).
Method B: An alternative to Method A requires the same procedure as previously described except instead of Mg use TMEDA (0.276 mL; 1.83 mmol) and 0.1% Na/Hg amalgam, Na (0.0841 g; 3.66 mmol) in 84 g of Hg. Pure brown crystals were formed (0.37 g; 41%).

4.8.6 \{[(\text{Pr}^i_2\text{PCH}_2\text{SiMe}_2)_2\text{N}]\text{TiCl}}_2(\mu-\eta^1:\eta^1\text{^15N}_2), (6)

The \text{^15N}_2 analogue was prepared similarly (Method A) by introducing \text{^15N}_2 gas into the flask containing the degassed reaction mixture. Workup was carried out under normal N\textsubscript{2}. \text{^15N}{^1H} NMR (C\textsubscript{7}D\textsubscript{8}, \delta, ppm): 375.5 (s).

4.8.7 \{[(\text{Pr}^i_2\text{PCH}_2\text{SiMe}_2)_2\text{N}]\text{VCl}}_2(\mu-\eta^1:\eta^1\text{-N}_2), (7)

A toluene solution (20 mL) of LiN(SiMe\textsubscript{2}CH\textsubscript{2}PPr\textsubscript{i}_2)\textsubscript{2} (0.501 g; 1.25 mmol) was added to the pale blue toluene solution (20 mL) of VC\textsubscript{12}TMEDA\textsubscript{2} (0.453 g; 1.28 mmol) at -78°C. The reaction mixture became a dark purple colour. After being warmed to room temperature, the solution was stirred for 18 hours and then brought into the glovebox, where it was filtered through a fine porosity frit with the aid of Celite. The solution volume was reduced under vacuum to 20 mL, and stored at -30°C for 24 hours. Pure purple crystals of the product were obtained from toluene (0.81g; 66% yield). Anal. Calcd. for C\textsubscript{24}H\textsubscript{60}ClN\textsubscript{3}P\textsubscript{2}Si\textsubscript{2}V: C, 43.85; H, 8.99; N, 5.68. Found C, 43.19; H, 8.97; N, 5.92. \textsuperscript{1}H (C\textsubscript{7}D\textsubscript{8}, \delta, ppm): 1.23 (br s, PCH(CH\textsubscript{3})\textsubscript{2}), 1.03 (br m, PCH(CH\textsubscript{3})\textsubscript{2}), 0.86 (br s, PCH\textsubscript{2}Si), 0.48 (sh), 0.29 (br s, SiCH\textsubscript{3}). Magnetic susceptibility measurements, \mu_{\text{eff}} calcd (spin only) 1.73 BM. Found: \mu_{\text{eff}} 1.74 BM/ metal centre (\chi'_{\text{V(IV)}} = 1.27 \times 10^{-3} \text{cgs-emu}).
4.9. References


FUTURE PROSPECTS

The mono(amido-diphosphine) complexes of titanium and vanadium synthesized in this work are useful precursors. These complexes could lead to other interesting complexes where one or more chlorine atoms can be metathesized with an alkyl or hydride. Since both TiCl$_3$[N(SiMe$_2$CH$_2$PPr$_{1}$)$_2$], 1, and TiCl$_3$[N(SiMe$_2$CH$_2$PMe$_2$)$_2$], 2, are available, a direct comparison of their reactivities could be made based on steric effects in this system. An X-ray crystal structure of the presumed {TiCl$_2$[N(SiMe$_2$CH$_2$PPr$_{1}$)$_2$]}$_x$ (x=1 or 2), 3, was not accomplished, however it remains a viable Ti(III) precursor which should be reactive to many reagents such as ethylene. The solid state structure of [(Pr$_{1}$PCH$_2$SiMe$_2$)$_2$N]V(μ-Cl)$_2$Li(TMEDA), 4, should also be examined by X-ray crystallography. Since it has been shown that this complex can convert to the corresponding dinitrogen complex simply by dissolving it in solvent under one atmosphere of dinitrogen, its reactivity with H$_2$, CO, C$_2$H$_4$, or MeI should be investigated. It should be noted, however, that this complex reacts with N$_2$ even in the solid state.

The dinitrogen complexes should exhibit some interesting chemistry. Again, the possibility exists of substituting chloride ligands and this could affect dinitrogen coordination in the new species generated. A method of recycling the dinitrogen complexes {[(Pr$_{1}$PCH$_2$SiMe$_2$)$_2$N]TiCl)$_2$(μ-η$^1$-η$^1$-N$_2$), 5, and {[(Pr$_{1}$PCH$_2$SiMe$_2$)$_2$N]-VCl)$_2$(μ-η$^1$-η$^1$-N$_2$), 7, back into TiCl$_3$[N(SiMe$_2$CH$_2$PPr$_{1}$)$_2$], 1, and [(Pr$_{1}$PCH$_2$SiMe$_2$)$_2$N]V(μ-Cl)$_2$Li(TMEDA), 4, along with the release of hydrazine, should be studied. The two dinitrogen complexes should also be investigated in terms of production of ammonia after degradation with acid. These results would confirm the results obtained for the hydrazine and dinitrogen measurements. Because the side-on bound dinitrogen seems to be more activated than the end-on form as indicated by the shorter end-on bound
dinitrogen bond lengths, it would be of interest to form side-on dinitrogen complexes by deliberately substituting in various ancillary ligands for their steric and electronic effects.
APPENDIX

A.1 X-ray Crystallographic Analysis of

\{[(Pr_1^2PCH_2SiMe_2)N]TiCl\}_2(\mu-\eta^1:\eta^1-N_2)
Figure A.1.1. Stereoview of \([(\text{Pr}^2\text{PCH}_2\text{SiMe}_2)_2\text{N}]\text{TiCl}_2(\mu-\eta^1:\eta^1-\text{N}_2)\)
A.1.1 Experimental Details for \{[(Pr^{1}2PCH_{2}SiMe_{2})_{2}N]TiCl\}_{2}(\mu-\eta^{1}:\eta^{1}-N_{2})

A.1.1.1 Crystal Data for \{[(Pr^{1}2PCH_{2}SiMe_{2})_{2}N]TiCl\}_{2}(\mu-\eta^{1}:\eta^{1}-N_{2})

- **Empirical Formula**: C_{36}H_{88}N_{4}Cl_{2}P_{4}Si_{4}Ti_{2}
- **Formula Weight**: 980.06
- **Crystal Color, Habit**: dark, plate
- **Crystal Dimensions (mm)**: 0.120 x 0.250 x 0.500
- **Crystal System**: monoclinic
- **No. Reflections Used for Unit Cell Determination (2θ range)**: 25 (22.7 - 28.4°)
- **Omega Scan Peak Width at Half-Height**: 0.39
- **Lattice Parameters**:
  - \(a = 24.541 \text{ (5) Å}\)
  - \(b = 10.690 \text{ (4) Å}\)
  - \(c = 21.641 \text{ (7) Å}\)
  - \(β = 98.17 \text{ (2) Å}\)
  - \(V = 5620 \text{ (3) Å}^3\)
- **Space Group**: C2/c (#15)
- **Z value**: 4
- **\(D_{\text{calc}}\)**: 1.158 g/cm\(^3\)
- **F_{000}**: 2104
- **\(μ(\text{MoKα})\)**: 5.99 cm\(^{-1}\)

A.1.1.2 Intensity Measurements for \{[(Pr^{1}2PCH_{2}SiMe_{2})_{2}N]TiCl\}_{2}(\mu-\eta^{1}:\eta^{1}-N_{2})

- **Diffractometer**: Rigaku AFC6S
- **Radiation**: MoKα (\(λ = 0.71069 \text{ Å}\))
Temperature 21°C
Take-Off Angle 6.0°
Detector Aperture 6.0 mm horizontal
6.0 mm vertical
Crystal to Detector Distance 285 mm
Scan Type \( \omega - 2\theta \)
Scan Rate 16.0°/min (in omega) (8 rescans)
Scan Width \((1.26 + 0.35 \tan \theta)^*\)
\( 2\theta_{\text{max}} \) 45.1°
No. of Reflections Measured Total: 4034
Unique: 3923 \( (R_{\text{int}} = 0.045) \)
Corrections Lorentz-polarization
Absorption (trans. factors: 0.76 - 1.00)

A.1.1.3 Structure Solution and Refinement for
\{[(\text{Pr}^2\text{PCH}_2\text{SiMe}_2)_2\text{N}]\text{TiCl}_2(1.-\text{N}_2) \}

Structure Solution Patterson Method
Refinement Full-matrix least-squares
Function Minimized \( \Sigma w (|F_{\text{O}}| - |F_{\text{C}}|)^2 \)
Least-squares Weights \( 4F_o^2/\sigma^2(F_o^2) \)
p-factor 0.01
Anomalous Dispersion All non-hydrogen atoms
No. Observations \((I>3.00\sigma(I))\) 1775
No. Variables 253
Reflection/Parameter Ratio 7.02
Residuals: \( R;R_w \) 0.045; 0.044
Goodness of Fit Indicator 2.56
Max Shift/Error in Final Cycle 0.30
Maximum Peak in Final Diff. Map 0.23 e/Å³
Minimum Peak in Final Diff. Map - 0.18 e/Å³

A.1.2 Tabulated Data for \{[(Pr_i^2PCH_2SiMe_2)_2N]TiCl_2(μ-η^1:η^1-N_2)\}

Table A.1.1  Final atomic coordinates (fractional) and \(B_{eq}(Å^2)\)⁺ for

\{[(Pr_i^2PCH_2SiMe_2)_2N]TiCl_2(μ-η^1:η^1-N_2)\}

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*B_{eq} = \frac{8}{3} \pi \sum \sum U_{ij} a_i^* a_j^* (a_i \cdot a_j)
Table A.1.2  Bond lengths (Å) with estimated standard deviations for
\{[(Pr\textsuperscript{1}2PCH\textsubscript{2}SiMe\textsubscript{2})\textsubscript{2}N]TiCl\textsubscript{2}(\mu-\eta\textsuperscript{1}:\eta\textsuperscript{1}-N\textsubscript{2}). *

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*The symbol ' refers to the symmetry operation: 1-x, y, 1/2-z.*
Table A.1.3  Bond angles (\(^\circ\)) with standard deviations for

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A.2 X-ray Crystallographic Analysis of

\[ \{[(\text{Pr}^1_2\text{PCH}_2\text{SiMe}_2)_2\text{N}]\text{VCl}\}_2(\mu-\eta^1:\eta^1-\text{N}_2) \]
Figure A.2.1. Stereoview of \(((\text{Pr}^2\text{PCH}_2\text{SiMe}_2)_2\text{NNVCl})_2(\mu-\eta^1:\eta^1-\text{N}_2)\)
A.2.1 Experimental Details for \(\{(\text{Pr}^2\text{PCH}_2\text{SiMe}_2)_2\text{N}^\text{VCi}\}_2(\mu-\eta^1_1:\eta^1_1-\text{N}_2)\).

A.2.1.1 Crystal Data for \(\{(\text{Pr}^2\text{PCH}_2\text{SiMe}_2)_2\text{N}^\text{VCi}\}_2(\mu-\eta^1_1:\eta^1_1-\text{N}_2)\)

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<td>Formula Weight</td>
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<td>Crystal Color, Habit</td>
<td>purple, prism</td>
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<tr>
<td>Crystal Dimensions (mm)</td>
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<td>Determination (2θ range)</td>
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<tr>
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<td>(\mu(\text{MoK}\alpha))</td>
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A.2.1.2 Intensity Measurements for \(\{(\text{Pr}^2\text{PCH}_2\text{SiMe}_2)_2\text{N}^\text{VCi}\}_2(\mu-\eta^1_1:\eta^1_1-\text{N}_2)\)

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<th>Instrument</th>
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<tr>
<td>Temperature</td>
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</table>
Take-Off Angle: 6.0°
Detector Aperture: 6.0 mm horizontal
6.0 mm vertical
Crystal to Detector Distance: 285 mm
Scan Type: ω - 2θ
Scan Rate: 16.0°/min (in omega) (8 rescans)
Scan Width: (1.10 + 0.35 tanθ)*
2θ_{max}: 60.0°
No. of Reflections Measured: Total (Unique): 4253
Corrections: Lorentz-polarization
Absorption (trans. factors: 0.93 - 1.00)
Secondary Extinction (coefficient: 0.36 (3) E-07)

A.2.1.3 Structure Solution and Refinement for
{[(Pr^{1}_{2}PCH_{2}SiMe_{2})_{2}N]VCl}_{2}(μ-η^{1}:η^{1}-N_{2})

Structure Solution: Patterson Method
Refinement: Full-matrix least-squares
Function Minimized: Σ w (|F_{o}l - |F_{c}l|)^2
Least-squares Weights: 4F_{o}^2/σ^2(F_{o}^2)
p-factor: 0.00
Anomalous Dispersion: All non-hydrogen atoms
No. Observations (I>3.00σ(I)): 1565
No. Variables: 244
Reflection/Parameter Ratio: 6.41
Residuals: R;R_w: 0.038; 0.031
Goodness of Fit Indicator: 1.94
Max Shift/Error in Final Cycle: 0.14
Maximum Peak in Final Diff. Map: 0.20 e/Å^3
Minimum Peak in Final Diff. Map  
- 0.28 e^−/Å^3

A.2.2 Tabulated Data

Table A.2.1  Final atomic coordinates (fractional) and $B_{eq}$ ($Å^2$)* for  

$\{[(Pr^{2}PCH_{2}SiMe_{2})_{2}N]VCl\}_{2}(\mu-\eta^{1}:\eta^{1}-N_{2})$

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*B<sub>eq</sub> = (8/3)π<sup>2</sup>∑∑U<sub>ijkl</sub>*a<sub>i</sub>*a<sub>j</sub>(a<sub>i</sub>*a<sub>j</sub>)"
**Table A.2.2** Bond lengths (Å) with estimated standard deviations for
\(((\text{Pr}^1_2\text{PCH}_2\text{SiMe}_2)\_2\text{N}^1\text{VCl}_2)(\mu-\eta^1:\eta^1-\text{N}_2)\). *

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*The symbol ' refers to the symmetry operation: \(1/2-x, 1/2-y, z\).*
Table A.2.3  Bond angles (°) with standard deviations for 
\{([Pr\textsubscript{12}PCH\textsubscript{2}SiMe\textsubscript{2}N]VCl\textsubscript{2}(μ-η\textsuperscript{5}:η\textsuperscript{5}-N\textsubscript{2})).

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