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## DEDICATION

Mwen voye remesie papa'm Fritz Desmangles,  
manman'm Gladys Barbot Desmangles  
ak fre mwen Laurent Desmangles,  
pou sipò yo, ancourajman yo, e sitou pou renmen yo  
ki te toujou la pou gide'm nan tout sa m'ap fe

## ABSTRACT

The chemistry of low-valent vanadium was extensively investigated especially in the organometallic field. Apart from cyclopentadienyl and alkoxides (or aryloxides) derivatives, its chemistry is poorly developed.

Among the supporting ligands for the stabilization of low-valent vanadium, alkylamides need to be studied in more details. By introducing bulky amides such as  $R_2N^-$  ( $R = iPr, Cy, SiMe_3, C_6H_5, 3,5-Me_2Ph$  and  $Ad$ ) in chemistry of vanadium(III) and vanadium(IV), we have opened a new field in the coordination of this early transition metal.

Synthetic methodology is focused on the preparation of novel tris(amide) vanadium(III) complexes via transmetallation reaction of  $VCl_3(THF)_3$  with  $R_2NLi$ , using the stoichiometry ratio 1:3 and the same reaction conditions.

Reaction of  $VCl_3(THF)_3$  with  $[(CH_3)_3Si]NPhLi$  led to the formation of the corresponding tetrahedral  $\{[(CH_3)_3Si]NPh\}_3V(THF)$  complex. Conversely, the reaction of  $CH_3C[(CH_2)N(iPr)Li]_3(TIAME)$  with  $VCl_3(THF)_3$  gave the new dinitrogen complex  $(TIAME)V-N_2-V(TIAME)$  whose structure was determined by X-ray analysis.

The reaction of  $VCl_3(THF)_3$  with  $(3,5-Me_2Ph)AdNLi.Et_2O$  [ $Ad = adamantyl$ ] yielded the homoleptic vanadium(III) complex  $[(3,5-Me_2Ph)AdN]_3V$  which reacts with chalcogens  $E$  [ $E = S, Se$ ] to yield diamagnetic terminal chalcogenide derivatives.

The use of low-valent vanadium in the polymerization of olefins is poorly developed apart from acetylacetonato derivatives and chloride derivatives. The complexes of formula  $(R_2N)_2VCl_2$  ( $R = iPr, Cy$ ) provide a unique example of oxidative disproportionation. The formation of dicyclohexyl and diisopropyl derivatives is the result of oxidative coupling of two low-valent vanadium entities. The first to be formed is the bis(amido) $V^{IV}Cl_2$  followed by the unstable " $V^{II}Cl_2$ ".

The stability of the novel vanadium(IV) bisamido complexes allowed us to investigate their reactivity towards olefin polymerization.

## PUBLICATIONS

**N. Desmangles, H. Jenkins, K. B. Rupp, S. Gambarotta.** Preparation and characterization of vanadium(III) dinitrogen complex supported by a tripodal anionic amide ligand. *Inorganica Chimica Acta*, 250, (1996) 1-4.

**K. B. Rupp, N. Desmangles, S. Gambarotta, G. Yap and A. Rheingold.** Preparation and characterization of a homoleptic vanadium(III) amide complex and its transformation into terminal chalcogenide derivatives  $[(3,5\text{-Me}_2\text{Ph})\text{AdN}]_3\text{V}(=\text{E})$  [E = S, Se; Ad = adamantyl]. *Inorganic Chemistry*, 36, (1997), 1194-97.

**N. Desmangles and S. Gambarotta.** Preparation and Characterization of  $(\text{R}_2\text{N})_2\text{VCl}_2$  [R = Cy, i-Pr] and its Activity as Olefin Polymerization Catalyst. *Journal of Inorganic Chemistry*, (in press).

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Last but not least, I would like to say a special thanks to my fellow lab mates, for all the help and skilled guidance throughout this work. In particular, I would like to thank Dr. H. Jenkins, Dr. M. Moore, Dr. K. B. Rupp, Dr. A. Kasani, Dr. I. Kovacs, K. Feghali, M. Tayebani, T. Dube, and Y. Ma.

## TABLE OF CONTENT

<b>DEDICATION</b>	2
<b>ABSTRACT</b>	3
<b>PUBLICATIONS</b>	5
<b>ACKNOWLEDGEMENTS</b>	6
<b>TABLE OF CONTENT</b>	7
<b>LIST OF ABBREVIATIONS</b>	10
<b>LIST OF FIGURES</b>	11
<b>LIST OF SCHEMES</b>	12
<b>LIST OF TABLES</b>	13
<b>Summary</b>	14
<b>Chapter 1</b>	15
<b>Introduction</b>	15
Dinitrogen Fixation/Activation	17
Bonding mode of Dinitrogen	26
Dinitrogen Complexes of Vanadium	28
Vanadium Amides	35
Conclusions	43
References	44

**Preparation and Characterization of a Vanadium (III) Dinitrogen****Complex Supported by a Tripodal Anionic Amide Ligand**

Introduction	51
Results and Discussion	52
Experimental section	55
Preparation of $\text{Me}_3\text{Si}(\text{Ph})\text{NLi}(\text{Et}_2\text{O})$	55
Preparation of $\{[(\text{CH}_3)_3\text{Si}]\text{NPh}\}_3\text{V}(\text{THF})$	55
Preparation of $(\text{TIAME})\text{V}-\text{N}_2-\text{V}(\text{TIAME})$	56
<u>Method A,B.</u>	
References	61

**Chapter 3****Preparation and Characterization of a Homoleptic Vanadium(III) Amide****Complex and its Transformation into Terminal Chalcogenide Derivatives** **$[(3,5\text{-Me}_2\text{Ph})\text{AdN}]_3\text{V}(=\text{E})$  [E = S, Se; Ad = adamantyl].**

Introduction	64
Results and Discussion	65
Experimental section	71
Preparation of $3,5\text{-Me}_2\text{PhN}(\text{Ad})\text{H}$ [Ad = adamantyl]	71
Preparation of $3,5\text{-Me}_2\text{PhN}(\text{Ad})\text{Li}\cdot\text{Et}_2\text{O}$	72
Preparation of $[3,5\text{-Me}_2\text{PhN}(\text{Ad})]_3\text{V}$	73
Preparation of $[3,5\text{-Me}_2\text{PhN}(\text{Ad})]_3\text{V}[\text{CN}(\text{t-Bu})]\cdot\text{Et}_2\text{O}$	73
Preparation of $[3,5\text{-Me}_2\text{PhN}(\text{Ad})]_3\text{V}(\text{E})\cdot 0.5\text{Et}_2\text{O}$ [E = S, Se]	74

X-ray Crystallography	75
References	79
<b>Chapter 4</b>	<b>82</b>
<b>Preparation and Characterization of <math>(R_2N)_2VCl_2</math> [R = Cy, i-Pr] and its Activity as Olefin Polymerization Catalyst.</b>	
Introduction	82
Results and Discussion	83
Experimental section	89
Synthesis of $(i\text{-Pr}_2N)_2VCl_2$	90
Synthesis of $(Cy_2N)_2VCl_2$	90
Method A, B, C.	
Isolation of $VCl_2(TMEDA)_2$	91
Method A, B.	
Synthesis of $(Cy_2N)_2VNp_2 \cdot 1/4\text{hexane}$	92
Synthesis of $(Cy_2N)_2VPh_2$	93
Synthesis of $(Cy_2N)_2VBz_2$	93
X-ray crystallography	94
References	99
Aim for further research	104
Appendix	105

## LIST OF ABBREVIATIONS

Ad	Adamantyl
Å	Angstroms
$\delta$	Chemical shift
$\nu$	Frequency
$\eta$	Hapto
$\mu_{\text{eff}}$	Effective magnetic moment in Bohr magnetons
Bz	Benzyl
$\text{cm}^{-1}$	Wave number
$\text{Cp}^{\cdot}$	Trimethylcyclopentadienyl anion
$\text{Cp}^{\cdot}$	Pentamethylcyclopentadienyl anion
Cy	Cyclohexyl
DIFABS	Absorbtion corrections
EPR	Electron Paramagnetic Resonance Spectroscopy
g	grams
iBu	Isobutyl
iPr	Isopropyl
L/Ln	Sum of ligands
M	Metal
Me	Methyl
Mhz	Frequency in megahertz
mL	milliliter
mmol	millimole
m.p.	Melting point
NMR	Nuclear Magnetic Resonance
Np	Neopentyl - $\text{CH}_2\text{CMe}_3$
Nf	Neophyl - $\text{CH}_2\text{CMe}_2\text{Ph}$
OEPG	Octaethylporphyrinogen
ORTEP	Oak Ridge Thermal Ellipsoid Program
Ph	Phenyl
ppm	Parts per million
R	Alkyls
TMEDA	N,N,N',N'-tetramethylethylenediamine
THF	Tetrahydrofuran

## LIST OF FIGURES

## Figure

1.1	Side-on dinitrogen coordination by a lithium counteraction of [Cp <sub>2</sub> ZrPPh <sub>2</sub> ][Li(THF) <sub>3</sub> ] <sub>2</sub> (μ -N <sub>2</sub> )	24
1.2	Side-on dinitrogen coordination of dinitrogen by Samarium [(THF) <sub>2</sub> Li(OEPG)Sm] <sub>2</sub> (N <sub>2</sub> Li <sub>4</sub> )	25
1.3	Bonding modes of dinitrogen	26
1.4	Vanadium dinitrogen complexes	29
1.5	Formation of a M-N π-bond between a metal center and an amido ligand	30
<b>Figure 1</b>	Thermal ellipsoid plot of $\{[(CH_3)_3Si]NPh\}_3V(THF)$	59
<b>Figure 2</b>	Thermal ellipsoid plot of (TIAME)V-N <sub>2</sub> -V(TIAME)	60
<b>Figure 3</b>	ORTEP plot of [3,5-Me <sub>2</sub> PhN(Ad)] <sub>3</sub> V	77
<b>Figure 4</b>	ORTEP plot of [3,5-Me <sub>2</sub> PhN(Ad)] <sub>3</sub> V(E).0.5Et <sub>2</sub> O [E = S(3a)]	78
<b>Figure 5.</b>	Thermal ellipsoid plot of (Cy <sub>2</sub> N) <sub>2</sub> VCl <sub>2</sub> <b>1b</b> .	96
<b>Figure 6.</b>	Thermal ellipsoid plot of (Cy <sub>2</sub> N) <sub>2</sub> VNp <sub>2</sub> <b>2a</b> .	97
<b>Figure 7.</b>	FTIR of the EP copolymer.	98

## LIST OF SCHEMES

### Scheme

1.1	The Haber-Bosch process	17
1.2	Dinitrogen reduction	19
1.3	Dinitrogen cleavage by a molybdenum(III) complex	20
1.4	Reaction of $VCl_3(THF)_3$ with 2 equiv. of $^iPr_2NLi$	21
1.5	Synthesis of N-aminopyrrole from dinitrogen using transition metals	23
1.6	First vanadium dinitrogen complex	29
1.7	Reduction of $V(mes)_3(THF)$ by metallic sodium in diglyme	30
1.8	First non-organometallic dinitrogen vanadium complex	32
1.9	Nitrido-bridged complex $\{[(OEPG)V]_2(\mu-N)(\mu-Li)_4\}[Li(TMEDA)_2]$	33
1.10	Reactivity of $[N_3N]V$	36
1.11	Reaction of $VCl_2(TMEDA)_2$ with $Ph_2NNa$	38
1.12	Reaction of $VCl_3(THF)_3$ with 2 equiv. of $LiN(SiMe_3)_2$	40
1.13	Reaction of $VCl_3(THF)_3$ with an excess of $^iPr_2NLi$	42
2.1	Preparation of vanadium(III) supported by anionic amides	53
3.1	Preparation of $[3,5-Me_2PhN(Ad)]_3V$ and its chalcogenide derivatives	67
4.1	Preparation of $(Cy_2N)_2VCl_2$ and its alkyl derivatives	85

## LIST OF TABLES

### Tables

3.1	Crystal Data and Structure Analysis Results of $[3,5\text{-Me}_2\text{PhN(Ad)}]_3\text{V}$ and $[3,5\text{-Me}_2\text{PhN(Ad)}]_3\text{V=S}$	105
3.2	Selected Bond Distances (Å) and Angles (deg) of $[3,5\text{-Me}_2\text{PhN(Ad)}]_3\text{V}$ ( <b>1</b> ) and $[3,5\text{-Me}_2\text{PhN(Ad)}]_3\text{V=S}$ ( <b>3a</b> ).	106
4.1	Ethylene-Propylene Copolymerization Activity of $(\text{Ph}_2\text{N})_3\text{V(THF)}$	108
4.2	Crystal Data and Structure Analysis Resultsof $(\text{Cy}_2\text{N})_2\text{VCl}_2$ ( <b>1b</b> ) and $(\text{Cy}_2\text{N})_2\text{VNp}_2$ ( <b>2a</b> )	109
4.3	Selected Bond Distances (Å) and Angles (deg) of of $(\text{Cy}_2\text{N})_2\text{VCl}_2$ ( <b>1b</b> ) and $(\text{Cy}_2\text{N})_2\text{VNp}_2$ ( <b>2a</b> )	110

## Summary

Low and medium valent vanadium amide complexes display a promising and diversified reactivity (C-H bond activation, activation of small molecules such as N<sub>2</sub> and CO and catalysis). The nature of the organic substituent of the amide seems to play an important role in the reactivity of the amide complex. However, in spite of these promising features, the chemistry of low-medium vanadium amide derivatives is not entirely understood. More research is necessary to fully understand the factors which promote the chemical behavior of vanadium amides.

During this work we have prepared and characterized a series of vanadium(III) amide derivatives where the nature of the amide organic substituents was systematically varied. This was done with the hope to gain some insight on the factors that favor dinitrogen fixation/activation. In the following two chapters we describe our preliminary results on this line of research. The last chapter is a preliminary study on the ability of vanadium(III) and (IV) amido complexes to work as olefin polymerization catalysts.

## Chapter 1

### Introduction

Vanadium complexes have been used successfully to promote a wide variety of transformations<sup>1</sup> which span from insertion reactions<sup>2</sup>, to reductive coupling<sup>3</sup> and Ziegler-Natta polymerization<sup>4</sup>. This, in addition to the observation made about 20 years ago that vanadium plays an important role in biological systems<sup>5</sup> such as nitrogenase<sup>6</sup>, has served as a powerful *stimulus* to develop the organometallic and coordination chemistry of the low and medium oxidation states of this metal.

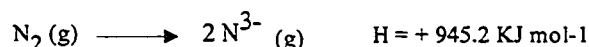
My interest in this field was prompted by the observation that the coordination chemistry of low-valent vanadium consists of several unrelated systems which promote remarkable and diversified transformations. However, on the basis of the information available to date, it is virtually impossible to rationalize the factors intrinsic to the nature of the ligand that are responsible for the behavior of the metal center. Therefore, in an attempt to gain some insight into the role played by the ligand in determining both the reactivity of the metal and its ability to interact with N<sub>2</sub>, I undertook a synthetic work to develop the chemistry of medium valent vanadium with several classes of ligands (alkoxides, alkyls, carboxylates, etc.). The preliminary conclusion that could be drawn from a literature survey was that carbon donor based ligands are versatile for dinitrogen fixation<sup>28,29,30</sup>. In contrast to former literature<sup>9a,d,e</sup> reports showing that oxygen-donor based ligands are able to catalyze dinitrogen reduction, more recent work has shown that vanadium alkoxides and aryloxides (with the only exception of vanadium catecholate) do not react with N<sub>2</sub>. We thus became interested in using nitrogen donor based ligands (amides, amidinates) which show electronic features and basicity properties somewhat

intermediate between those of alkyls and alkoxides. It was hoped that this ligand system would help to shed some light onto the factors which promote dinitrogen fixation/activation. The use of amide ligands was advised due to their electronic and steric properties. An important aspect of these properties, is the ability of alkylamido ligands to participate in single and multiple bonding with the metal center. The  $\sigma$ -bond shows a pyramidal  $sp^3$  nitrogen (M-N distances 1.981-2.157 Å). For the early transition metals, the  $d\pi-p\pi$  interactions between metal and nitrogen can occur when nitrogen lone pairs are available to interact with empty d orbitals, resulting in multiple bonding thus shorter M-N distances (1.85-1.98 Å) and trigonal planar nitrogen atom. From a structural point of view this family of ligands give rise to a rich chemistry in their transition metal complexes. Both electronic (strong  $\pi$ -donor ability) and steric factors (steric congestion around the metal center) have been suggested as major contributors to the activation barriers (11-24 kcal/mol) for the rotation about the M-N bond.

The initial goal of this thesis was to prepare vanadium(III) amide derivatives and to test their reactivity with particular emphasis to dinitrogen activation. However, during the course of this research we incidentally found that these species act as powerful Ziegler Natta catalysts for olefin polymerization. A preliminary study on olefin homo and copolymerization is reported in Chapter four

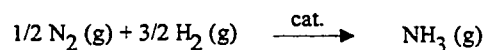
## Dinitrogen Fixation/Activation

Dinitrogen is the most abundant element in the atmosphere and is an essential ingredient for life. The main characteristic of dinitrogen lies on its remarkable inertness. Due to its stability, dinitrogen is typically used as an inert gas to protect air-sensitive chemicals, to blanket reaction vessels and to fill dry-boxes. In industry it is commonly used to prevent degradation of foods and merchandises.



The stability of the dinitrogen molecule can be ascribed to two factors: (1) the presence of the N-N triple bond (1.10 Å) and (2) the exceedingly low redox potential ( $E_{\text{red}} = -7.8 \text{ eV}$ ). The oxidation of  $\text{N}_2$  to form nitrogen oxides ( $E_{\text{ox}} = 0.8 \text{ eV}$ ) is a more viable process. However, it still requires high temperatures and typically occurs under combustion type conditions. Although more difficult to achieve, the reduction of  $\text{N}_2$  is more promising because of the realistic possibility of controlling the extent of reduction and because of the high reactivity of the species produced (e.g. hydrazides, nitrides).

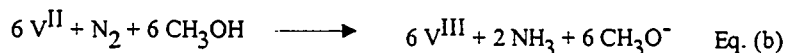
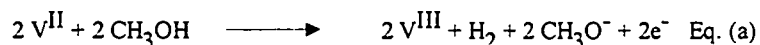
So far, the most popular method employed to reduce dinitrogen on an industrial scale is the Haber-Bosch process (Scheme 1.1). This reaction employs severe conditions such as high temperatures (400-500 °C) and pressures (200 atm). In a convenient variation, the utilization of a ruthenium-based catalyst (Kellogg process), allows to use substantially milder reaction conditions ( $T = 250 \text{ °C}$ ,  $P = 50 \text{ atm}$ ).



**Scheme 1.1**

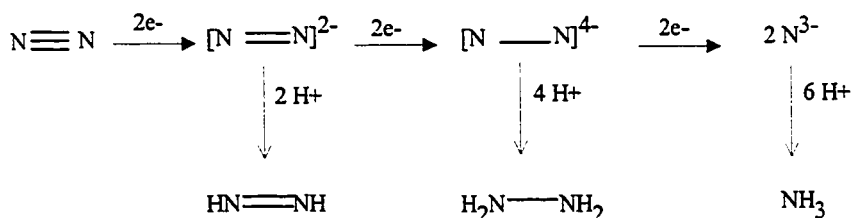
The importance of the reduction of N<sub>2</sub> becomes apparent when considering that 23 million tons of NH<sub>3</sub> are produced each year in the US only. The severity of the conditions used in these processes contrasts strikingly with the ability of naturally occurring systems, such as nitrogenase, to perform catalytic reduction of N<sub>2</sub> under exceptionally mild reaction conditions (1 atm, aqueous medium, neutral pH, room temperature)<sup>7</sup>.

Among the early transition metals involved in dinitrogen fixation/activation, vanadium is particularly promising. As mentioned above, its chemistry is particularly rich and diversified. For example, catalytic activation of dinitrogen was reported to be promoted by in situ generated vanadium(II) hydroxide in a protic medium<sup>8</sup>. The mixed-valence tetranuclear V<sup>II</sup>/V<sup>III</sup> complex [Na<sub>2</sub>V<sub>4</sub>(OMe)<sub>2</sub>{O<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(<sup>t</sup>Bu)<sub>2</sub>}<sub>4</sub>{OC<sub>6</sub>H<sub>2</sub>(OH)(<sup>t</sup>Bu)<sub>2</sub>}<sub>2</sub>(MeOH)<sub>2</sub>] isolated from a methanol solution containing VCl<sub>2</sub>, 3,5-di-tert-butylcatechol (dbcat) and NaOCH<sub>3</sub>, also proved to be a powerful reducing agent. It evolves H<sub>2</sub> from the protic solvent in approximately 3-4 hours [Eq.(a)] and reduces dinitrogen [Eq.(b)]. Unfortunately, the reduction of N<sub>2</sub> is competitive with that of methanol.



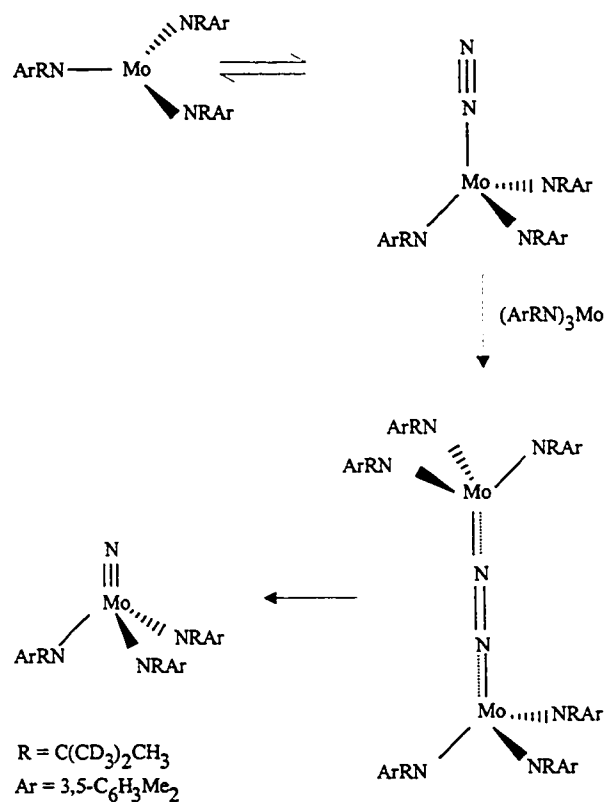
Vanadium is an important component of some metalloenzymes<sup>9</sup> (for example, the nitrogenase of *Azotobacter vinelandii* which contains an iron-vanadium protein) and therefore, the development of vanadium chemistry will be beneficial for understanding the mechanism of action of nitrogenase in living systems. In spite of these promising features, information about the chemistry of low-medium valent vanadium complexes remains rather scarce.

In 1986, the existence of vanadium nitrogenase was demonstrated<sup>10</sup>. This particular form of nitrogenase is another natural system capable of fixing nitrogen. In this system, the molybdenum-iron cofactor is simply replaced by a vanadaprotein<sup>11</sup>. The vanadium present in this particular protein is probably in a relatively high oxidation state, which implies that even medium-high valent vanadium complexes can incorporate dinitrogen in their coordination sphere. This strikingly contrasts with the synthetic systems where catalytic N<sub>2</sub> activation is mainly prompted by divalent vanadium species. In addition, the d<sup>3</sup> electronic configuration of vanadium(II) makes this oxidation state particularly promising for this purpose, since a simple dinuclear vanadium(II) system possesses the six electrons necessary for the cleavage of the N-N triple bond. In fact, for N<sub>2</sub> to be entirely reduced, six electrons are necessary (Scheme 1.2).



**Scheme 1.2**

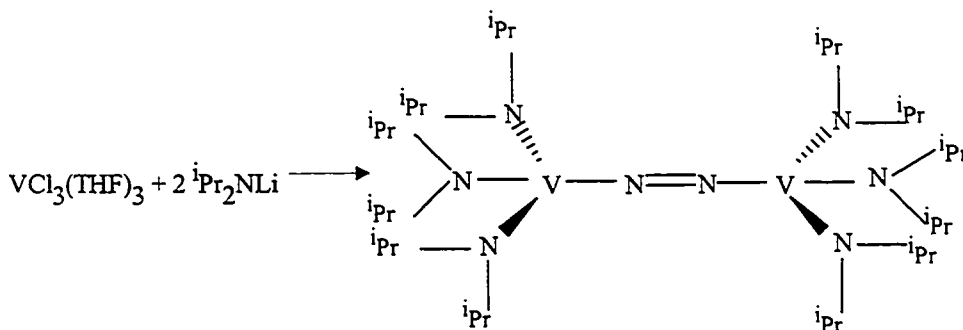
The ability of a d<sup>3</sup> system to cleave N<sub>2</sub> was recently demonstrated in the case of a molybdenum(III) complex. The complex Mo(NRAr)<sub>3</sub> [Ar = 3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, R = C(CD<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>] reacts with N<sub>2</sub> to give an end-on dinitrogen complex which further evolved into a terminal Mo-N species<sup>12</sup> (Scheme 1.3).



**Scheme 1.3**

The observation that  $d^2$  zirconium(II) and titanium(II) complexes supported by anionic amides are capable of reducing dinitrogen to a considerable extent (hydrazido tetraanion) arises the question whether a  $d^2$  vanadium(III) system might be able to perform a similar transformation. Even though the reduction potential of V(III) ( $E_{\text{red}} = -0.25$  V), is lower than that of V(II), and a  $d^2$  configuration is sufficient for only partial reduction of  $\text{N}_2$  recent work in our group has demonstrated that complexes in which vanadium exists in the oxidation state +3 are able to reduce dinitrogen. The reaction of  $\text{VCl}_3(\text{THF})_3$  with 3 equivalents of  ${}^i\text{Pr}_2\text{NLi}$  gave a dinuclear end-on bridged dinitrogen complex  $\{[{}^i\text{Pr}_2\text{N}]_3\text{V}\}_2$

(N<sub>2</sub>)<sup>13</sup> (Scheme 1.4). In contrast to the majority of end-on bridged dinitrogen complexes of transition metals from which N<sub>2</sub> can be easily removed by ligand exchange reaction or in some cases simply by applying vacuo, the V- N<sub>2</sub>-V frame was surprisingly robust. The coordinated N<sub>2</sub> could not be replaced by conventional reagents such as pyridine, nitriles or even upon treatment with preferential reagents such as azides, diazo etc.



**Scheme 1.4**

The V- N<sub>2</sub>-V moiety was attacked only by destructive reagents such as MeI and HCl. Cyclic voltammograms of complex {[iPr<sub>2</sub>N]<sub>3</sub>V}<sub>2</sub>(N<sub>2</sub>) showed a reversible one-electron reduction at -0.6 V. Given that no oxidation wave could be detected and the fact that the complex is diamagnetic, one could reasonably assume that vanadium is in the formal oxidation state +5. However, the N-N bond distance [1.27(1) Å] indicated only partial reduction of the N-N triple bond. Therefore, the formal oxidation state of vanadium remains uncertain in this particular complex.

Recent structural studies on nitrogenase have shown the presence of two different proteins with molecular weight of about 260,000 (the iron-protein) and 240,000 (the molybdenum-protein). The iron containing protein consists of two identical subunits that coordinate a single FeS<sub>4</sub> cuboid cluster. The MoFe protein consists of a tetramer. The tetramer is formed by two cuboid subunits linked together by bridging sulfur atoms. In

both proteins, sulfide ions are present in a number approximately equal to that of the iron atoms. Unfortunately, the crystal structures do not provide any suggestion on which metal center the dinitrogen fixation might occur<sup>14</sup>. The X-ray structure of the MoFe protein also shows that the two cuboid moieties are linked by an additional atom, whose nature (O or N) remains undefined.

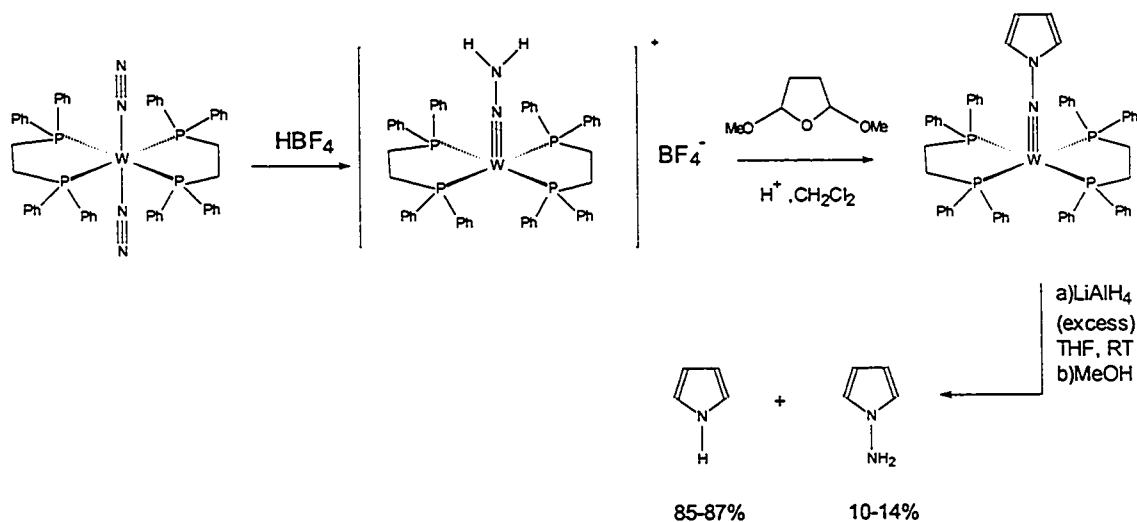
It is believed that nitrogen is first coordinated to one of the metal centers and is reduced in a multi-step process. Electrons are carried from a reducing agent to the protein and the energy required for the transfer of each electron is supplied by the ATP/ADP system. The coordinated dinitrogen is reduced stepwise by nitrogenase, sequentially forming several intermediates such as diazenido, hydrazido and nitride anions which, in the presence of a protic solvent liberate hydrazine and ammonia.

The efficiency of nitrogenase to perform dinitrogen reduction under mild reaction conditions has posed fascinating mechanistic questions and has stimulated considerable research in this field. The main goal has always been the understanding of the detailed mechanism of action of nitrogenase and of course a better understanding of the reactivity of transition metals with N<sub>2</sub>. This was not only in the view of finding alternatives to the Haber/Kellogg processes, but also to enable the utilization of N<sub>2</sub> as a source of nitrogen atoms for the preparation of basic commodity chemicals such as heterocycles, ureas and carbamates.

Historically, the first dinitrogen complex was isolated and characterized by Allen and Senoff<sup>15</sup> in 1965. Since the discovery that [Ru(NH<sub>3</sub>)<sub>5</sub>]<sup>2+</sup> could coordinate dinitrogen,

intensive efforts were directed towards the development and synthesis of dinitrogen complexes. As a result, many dinitrogen complexes have been discovered for a number of transition metals<sup>16</sup> and in a variety of oxidation states and bonding modes.

Preliminary results from Hidai showed that the ambitious goal of using N<sub>2</sub> as a raw material for incorporation into organic substrates is indeed a realistic goal. N-aminopyrrole was prepared from dinitrogen via the series of transformations outlined in scheme 1.5<sup>17</sup>. The reduction of M(N<sub>2</sub>)<sub>2</sub>(dpe)<sub>2</sub> [M = Mo or W, dpe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>] with HBF<sub>4</sub> gave the complexes [MF(NNH<sub>2</sub>)<sub>2</sub>(dpe)<sub>2</sub>][BF<sub>4</sub>]. In presence of 2,5-dimethoxytetrahydrofuran, the same procedure gave 1-pyrrolylimido complexes [MF(NNCH=CHCH=CH)(dpe)<sub>2</sub>][BF<sub>4</sub>]. Following reduction with LiAlH<sub>4</sub> the pyrrole ring was disanchored from the pyrrolimido complexes.



**Scheme 1.5**

As mentioned above, the first step of dinitrogen reduction is the coordination with a strongly reducing metal<sup>18</sup>. The presence of d electrons is commonly regarded as an essential prerequisite for the sformation of stable dinitrogen complexes. tabilization of the

resultant coordination complex where the  $N_2$  moiety gives variable extent of back-bonding depending on the nature of the metal. Until now, there is no evidence that dinitrogen fixation may occur directly on a  $d^0$  transition metal. However, in one case dinitrogen was found to be attached to the lithium counteranion of a zirconium(III) complex<sup>19</sup>  $[Cp_2ZrPPh]_2[Li(THF)_3]_2(\mu-N_2)_2$  (Figure 1.1). In this complex, the N-N bond distance (1.06 Å) is shorter than in free  $N_2$ , thus suggesting that no reduction has taken place. Should this result be confirmed, it will certainly open new perspectives for the reactivity of dinitrogen with high valent transition metals.

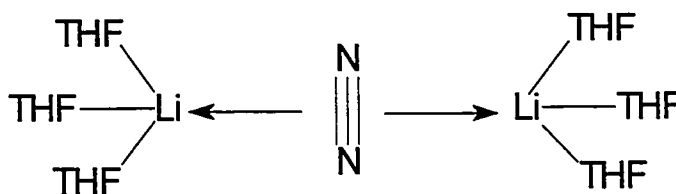
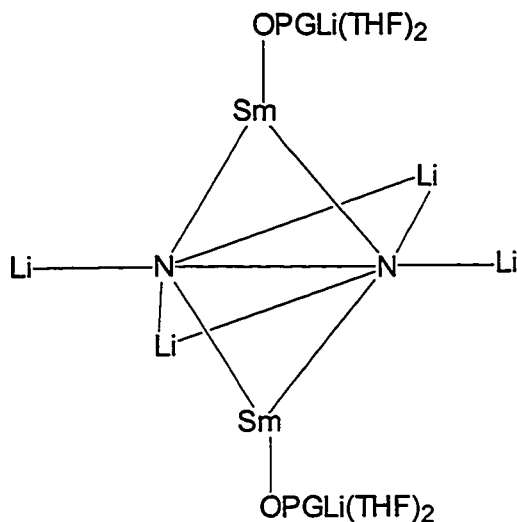


Figure 1.1

In 1988, Evans reported the first example of dinitrogen fixation on an f-block metal. The crystal structure of samarocene showed a dinuclear complex  $[Cp^*_2Sm]_2(\mu-N_2)$ <sup>20</sup> containing a side-on bonded dinitrogen ligand. The strikingly short N-N bond distance and the easy dissociation of  $N_2$  in toluene solutions to form  $Cp_2Sm$ , suggests a minimal degree of  $N_2$  reduction. Recent work from our lab showed that dinitrogen can be attached to a samarium(II) center even in a non-cyclopentadienyl ligand system. The reaction of the macrocyclic porphyrinogen  $OEPG(THF)_4Li_4$  with  $SmCl_3(THF)_3$  under

argon, followed by reduction of the product with metallic lithium, and subsequent exposure to  $N_2$  gave a dinuclear complex containing side-on bonded dinitrogen  $[(THF)_2Li(OEPG)Sm]_2(N_2Li_4)^{21}$ . The complex is formed by two  $(THF)_2Li(OEPG)Sm$  units which are bridged by a planar  $N_2Li_4$  moiety (Figure 1.2). The dinitrogen molecule is encapsulated in a  $Sm_2Li_4$  octahedron and is coaxial with a Li-Li diagonal with the Sm atoms symmetrically placed above and below the  $N_2Li_4$  plane. In this complex, the long N-N bond distance of 1.525 Å suggests that dinitrogen had undergone a four electron reduction to form a hydrazido tetraanion.

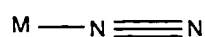


**Figure 1.2**

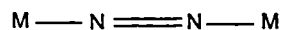
## Bonding modes of Dinitrogen

The comparison of the N-N distance in dinitrogen complexes with respect to free  $N_2$  is commonly used as a probe to assess the degree of reduction. In free  $N_2$ , the N-N bond distance is 1.098 Å. When  $N_2$  is coordinated to a metal center, the N-N bond distance of the  $N_2$  moiety falls in the range 1.10-1.16 Å for mononuclear end-on complexes and 1.12-1.36 Å for bridging dinuclear complexes or clusters. In the only case mentioned above of a side-on complex, a distance as long as 1.5 Å was determined. According the literature, dinitrogen can be attached to transition metals by adopting the four different bonding modes depicted in Figure 1.3.

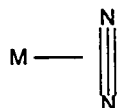
### Bonding Mode



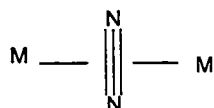
End-on



Bridging end-on



Side-on



Bridging side-on

**Figure 1.3**

The terminal end-on and bridging end-on bonding modes of dinitrogen are widely documented in the chemistry of low-valent mononuclear molybdenum, rhenium and tungsten<sup>22</sup>. In these complexes, the coordination of N<sub>2</sub> is the result of two basic processes: (1) the  $\sigma$  donation (M $\leftarrow$  N<sub>2</sub>) and (2) the  $\pi$ -back donation (M  $\rightarrow$  N<sub>2</sub>). The  $\sigma$  donation is accomplished by using a populated antibonding orbital of the nitrogen molecule which donates electron density into an empty metal orbital of suitable symmetry. The back-bonding from the metal to N<sub>2</sub> is also possible because the dinitrogen ligand possesses empty  $\pi^*$  orbitals of appropriate symmetry to overlap with filled metal d orbitals. The result of the back-bonding is a partial population of the nitrogen antibonding orbital with consequent decrease of N-N bond order. In the bridging end-on coordination mode<sup>23</sup>, the two metals lie on the opposite ends of the N-N vector, forming a linear M-N-N-M array. In the side-on coordination mode, the metal coordinates to dinitrogen perpendicularly to the N-N vector. From the theoretical point of view, the side-on bonding mode implies better back-donation from the metal to the  $\pi^*$  orbital of dinitrogen, because of a more favorable orientation of the N<sub>2</sub> orbitals. The result is a higher degree of reduction of the N-N bond<sup>24</sup>. The side-on bridging coordination of dinitrogen is rare<sup>25</sup>. Besides the case of the Sm complex described above, it was determined in only two cases of low-valent group IV transition metals<sup>26</sup>. In these cases, the N-N distance is particularly long thus indicating that the reduction of the N-N triple bond is indeed rather substantial.

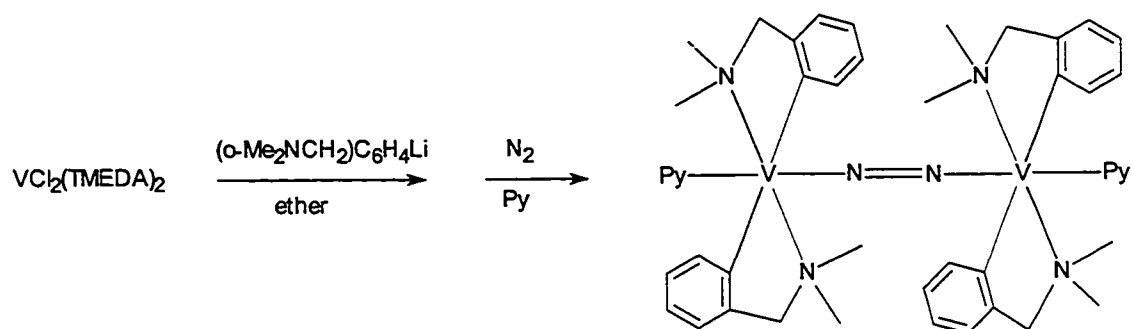
Upon reduction of ZrCl<sub>2</sub>[N(SiMe<sub>2</sub>CH<sub>2</sub>PR<sub>2</sub>) where R is <sup>t</sup>Pr or <sup>t</sup>Bu, Fryzuk and coworkers<sup>27</sup> have obtained the side-on dinitrogen complex {ZrCl[N(SiMe<sub>2</sub>CH<sub>2</sub>PR<sub>2</sub>)}

${}_{2}(\mu-\eta^{2}:\eta^{2}-N_{2})$ . With a N-N distance of 1.548 Å, this bond length is the longest ever reported for a side-on complex. Theoretical calculations have been carried out to clarify the bonding. The metal center possesses three d orbitals ( $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$ ) oriented diagonally and directed towards  $N_{2}$  which are involved in  $\pi$  bonding with dinitrogen. The other d orbitals ( $d_{x^2-y^2}$ ,  $d_z$ ) are involved in  $\sigma$  bonding with  $N_{2}$ . One is bonding with respect to the M-N bond and the other is antibonding with respect to the N-N bond. For the bridging side-on mode, the  $\pi$  orbital is exceedingly stable and contributes more to the bond order than does the  $\pi$  orbital of the end-on form.

Since the type of bonding adopted by  $N_{2}$  is expected to be a crucial factor for further activation, the attention of researchers was mainly focused on understanding the factors which determine the particular type of bonding mode adopted by  $N_{2}$ . This is probably the key to understanding the continuous efforts towards preparing large series of new complexes containing dinitrogen bonded in a variety of modes.

### **Dinitrogen Complexes of Vanadium**

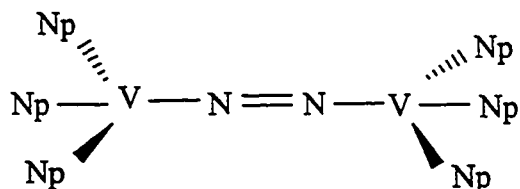
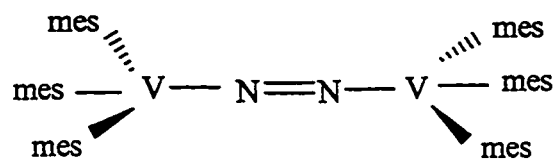
The first example of fixation of dinitrogen on a vanadium center was observed when  $VCl_{2}(TMEDA)_{2}$ <sup>28</sup> was reacted with two equivalents of  $[o-C_{6}H_{4}CH_{2}N(CH_{3})_{2}]Li$ , followed by addition of one equivalent of pyridine to give  $(\mu-N_{2})\{[o-C_{6}H_{4}CH_{2}N(CH_{3})_{2}]_{2}V(py)\}(THF)_{2}$  as product (Scheme 1.6).



**Scheme 1.6**

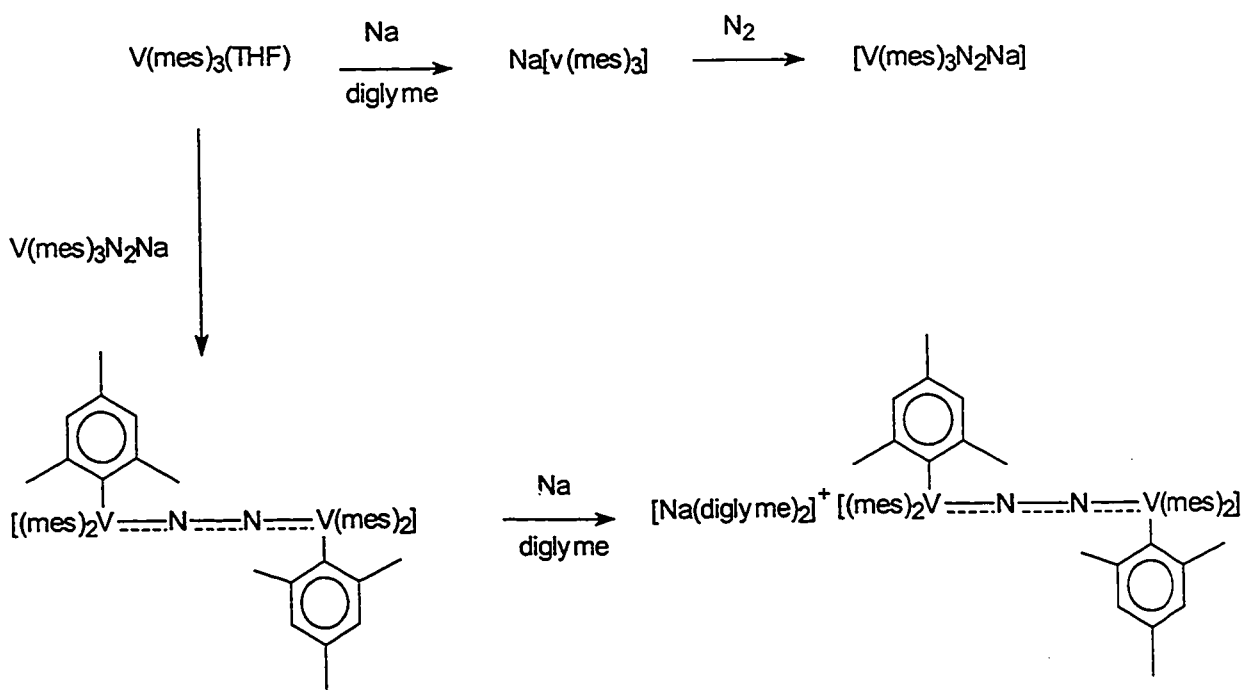
The reaction initially formed an unidentified intermediate, which upon treatment with pyridine reacted with dinitrogen to form the final complex. The magnetic moment ( $\mu_{\text{eff}} = 3.47 \mu_{\text{B}}$ ) is slightly lower than expected for a  $d^3$  electronic configuration, thus indicating that only a minimal reduction of dinitrogen occurred. Nevertheless, the coordination of dinitrogen appears to be rather robust, since exposure to vacuum did not remove nitrogen. However, simple treatment with Lewis bases such as CO, alkynes or pyridine, released  $\text{N}_2$  to form a monomeric vanadium(II) complexes. In the case of pyridine the mononuclear  $[\text{o-C}_6\text{H}_4\text{CH}_2\text{N}(\text{CH}_3)_2]_2\text{V}(\text{py})_2$  was isolated and fully characterized.

Following these findings, other dinitrogen complexes of vanadium(II)<sup>29</sup> and (III)<sup>30</sup> were synthesized and characterized (Figure 1.5).



**Figure 1.4**

The reduction of  $V(\text{mes})_3(\text{THF})$  [ $\text{mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ ] by sodium metal in the presence of nitrogen in diglyme, produces the dinuclear complex  $(\mu\text{-N}_2)\text{N}[(\text{mes})_2\text{Me}_3\text{C}_6\text{H}_2]^- [\text{Na}(\text{diglyme})_2]^+$  (Scheme 1.7)<sup>31</sup>.



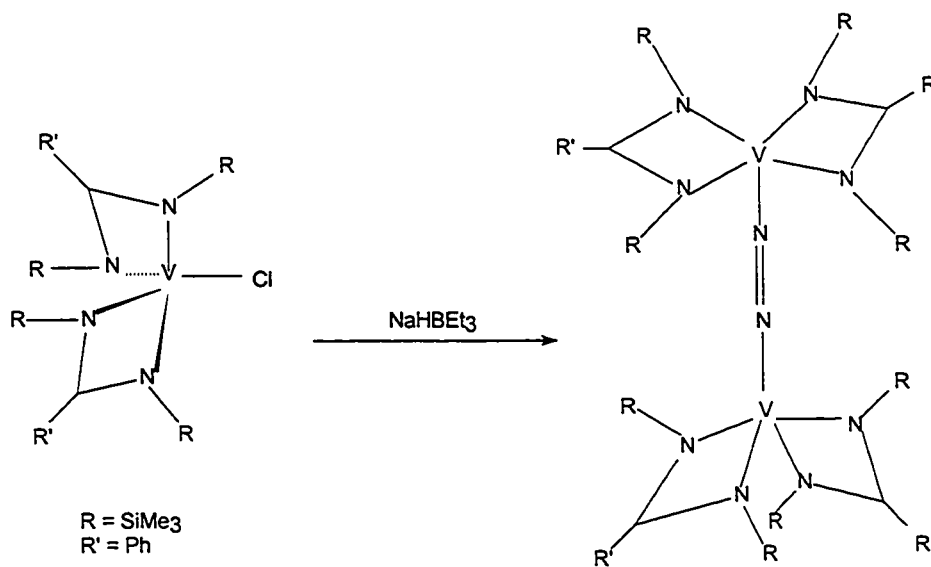
**Scheme 1.7**

The V-N distance at 1.763(15) Å is very short and suggests multiple bond character, while the N-N bond length of 1.280(21) Å is longer than the bond distance in the free dinitrogen molecule (1.098 Å). These two bond distances suggest that dinitrogen was reduced to some extent in this species. The magnetic moment of 1.69  $\mu_B$  per metal center is significantly lower than expected for a  $d^3-d^3$  system. Usually, coordination of  $N_2$  does not change the magnetic properties of the original metal ion<sup>32</sup>. The lowering of the magnetic moment can either be a consequence of a strong electronic coupling of the two vanadium atoms through the dinitrogen bridge, or may reflect a change in the oxidation state of the metal atom.

A trivalent vanadium(III) dinitrogen bridged complex  $[(Me_3CCH_2)_3V]_2(\mu-N_2)$  was obtained when  $VCl_3(THF)_3$  was treated with 3 equivalents of  $Me_3CCH_2Li$  in diethyl ether under nitrogen<sup>33</sup>. The red-brown diamagnetic complex consists of two identical tris(neopentyl)vanadium fragments linked by a bridging end-on dinitrogen ligand. The vanadium atoms are tetrahedral with three sites occupied by neopentyl groups and the fourth site by the  $\mu-N_2$  moiety. In spite of the diamagnetism, which might suggest large extent of reduction of dinitrogen, the N-N distance of 1.250(3) Å is not particularly long. Moreover, release of dinitrogen is observed when  $[(Me_3CCH_2)_3V]_2(\mu-N_2)$  is dissolved in THF, thus indicating that  $N_2$  is only weakly bound.

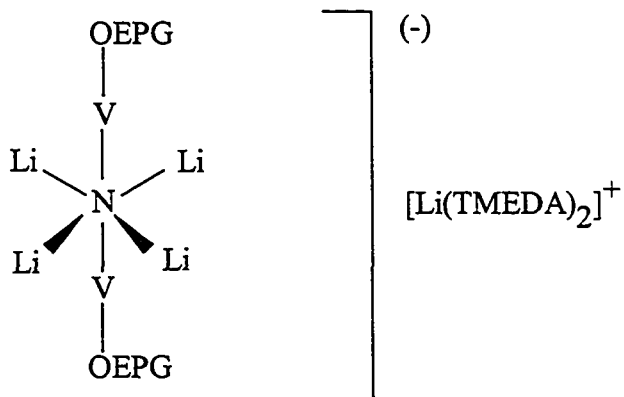
With exception of  $[(iPrN)_3V]_2(\mu-N_2)$ <sup>34</sup>, examples of dinitrogen fixation by vanadium has been observed only on organometallic systems. The first example of dinitrogen fixation by a non-organometallic vanadium complex was obtained by treating

$[\text{RNC}(\text{R}')\text{NR}]_2\text{VCl}$  (where  $\text{R} = \text{SiMe}_3$  and  $\text{R}' = \text{Ph}$ ) with  $\text{NaHBET}_3$  in toluene. The reaction yielded a new dinuclear paramagnetic ( $\mu_{\text{eff}} = 0.91 \mu_{\text{B}}$  per dimer) dinitrogen complex  $\{[\text{Me}_3\text{Si}]\text{NC}(\text{Ph})\text{N}(\text{SiMe}_3)_2\text{V}\}_2 (\mu\text{-N}_2)^{35}$  (Scheme 1.8). During a Toepler pump experiment, 87% of  $\text{N}_2$  was recovered upon treatment of the complex with THF, thus indicating weak ligation. The short N-N bond distance [1.235(6) Å] and the relative lability of dinitrogen also indicates minimal degree of dinitrogen reduction.



**Scheme 1.8**

The employment of a macrocyclic ligand enhanced the ability of vanadium to interact with dinitrogen. The reaction of  $\text{VCl}_2(\text{TMEDA})_2$  with the tetralithium salt of octaethylporphyrinogen (OEPG) under nitrogen, yielded the paramagnetic ( $\mu_{\text{eff}} = 2.85 \mu_{\text{B}}$  per dimer) nitrido-bridged dinuclear complex  $[\{(\text{OEPG})\text{V}\}_2 (\mu\text{-N})(\mu\text{-Li})_4] [\text{Li}(\text{TMEDA})_2]$  (Scheme 1.9)<sup>36</sup>.



Scheme 1.9

The structure is formed by two parallel planar V(OEPG) units linked by a nitride function. The magnetic moment, lower than expected for a  $d^2$  electronic configuration, can be explained by the presence of a magnetic coupling between the two vanadium centers. The formation of the nitrido-bridged complex arises from a complicated series of reactions. The first complex formed from the reaction between (OEPG)Li<sub>4</sub> and VCl<sub>2</sub>(TMEDA)<sub>2</sub> is the divalent vanadium species [(OEPG)VLi<sub>4</sub>Cl<sub>2</sub>(THF)<sub>4</sub>]. In an attempt to remove LiCl, the complex was treated with excess of TMEDA. The reaction led to the trivalent [(OEPG)V(THF)<sub>2</sub>][Li(TMEDA)<sub>2</sub>] which was isolated and characterized. The formation this species was accompanied by formation of a nitrido-bridged complex. This species probably arose from the cleavage of dinitrogen performed by the low-valent OEPG-vanadium complex [(OEPG)VLi<sub>4</sub>Cl<sub>2</sub>(THF)<sub>4</sub>].

Another example of formation of nitride via dinitrogen cleavage was obtained during attempts to prepare (amide)<sub>2</sub>V-H via hydrogenolysis of the V-V bond of a dinuclear amido vanadacyclobutane<sup>37</sup>. The reaction of the dinuclear vanadacyclobutane with either pyridine or PMe<sub>3</sub> cleaved the complex to form the corresponding monomeric

species  $[\{\text{Me}_3\text{Si}\}_2\text{N}\}\text{V}\{\text{CH}_2(\text{SiMe}_2)_2\text{N}(\text{SiMe}_3)\}\text{(L)}$  where  $\text{L} = \text{pyridine}$  or  $\text{PMe}_3$ . The cleavage of the dinuclear structure did not affect the stability of the metallocyclobutane, but enhanced its reactivity. The hydrogenolysis of the  $\text{PMe}_3$  monomeric adduct gave a mixed valent complex composed of two fragments. The first unit is a cationic trihydridodivanium moiety  $[\{(\text{Me}_3\text{P})_3\text{V}\}_2(\mu\text{-H})_3]^+$ , while the second is an anionic nitrido-bridged  $[\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{V}\}_2(\mu\text{-N})_2]^-$  unit. The fact that no traces of methane or silanes ( $\text{Me}_3\text{SiH}$ ,  $\text{Me}_2\text{SiH}_2$ ,  $\text{SiH}_4$ ) were detected in the reaction mixture, suggests that the nitrido bridged atoms did not originate from the hydrogenolysis of the N-Si bond but instead from the reduction of dinitrogen.

### Vanadium Amides

Given the literature scenario described above, the employment of ligands with nitrogen-based donor atoms such as anionic organic amides ( $\text{R}_2\text{N}^-$ ) seems particularly promising for the stabilization of low-valent vanadium complexes and to study their reactivity with dinitrogen. Anionic organic amides as a ligand system display some attractive and unique characteristics. First of all, they are readily accessible by simple deprotonation of secondary and primary amines. Secondly, they are widely available due to the unlimited selection of amines available from commercial sources or via simple organic preparation. Thirdly, they are sterically tunable via the appropriate selection of the organic substituents connected to the nitrogen donor atom. Fourth, they are versatile in terms of bonding modes, since they may act as both monodentate, end-on bidentate

bridged or bridging. Fifth, amides are electronically flexible participating when necessary in extensive  $\mu$ -donation from nitrogen to the metal center (Figure 1.6). Finally, the alkyl substituents may be selected to adjust the solubility of the complex in the desired manner.

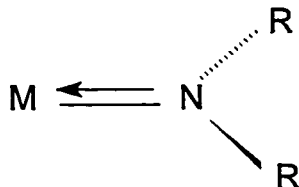
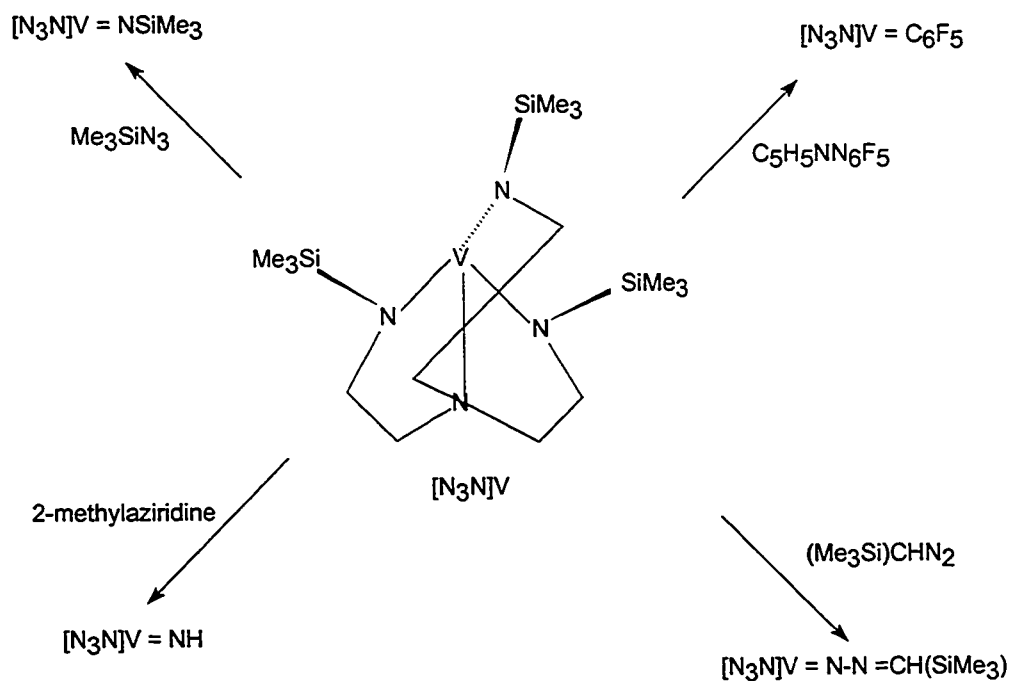


Figure 1.5

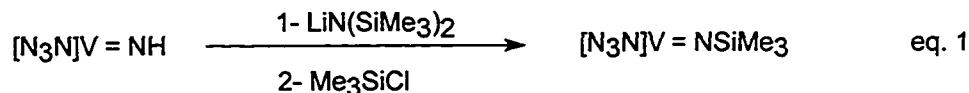
The chemistry of amido vanadium complexes is poorly developed. Early studies<sup>38</sup> mainly focused on the synthesis of amido vanadium(IV) complexes. In 1957 the synthesis of what was assumed to be  $\text{VCl}_2(\text{NMe}_2)_2$  was achieved<sup>39</sup> from  $\text{VCl}_4$  and gaseous  $\text{HNMe}_2$ . Even though the nature of the final product was never conclusively demonstrated, this methodology can be extended to other primary amines<sup>40</sup>. Substitution of more than two chlorides is commonly achieved by using the amide lithium salt<sup>41</sup>. The majority of vanadium amide derivatives characterized so far was prepared by using the salt method<sup>42</sup>, or by reduction of amido vanadium(IV) compounds<sup>43</sup>. Cummins and Schrock have reported the preparation of a few vanadium amido complexes. The tetradentate tripodal amide  $\text{Li}_3[\text{N}_3\text{N}]$  ( $\text{N}_3\text{N} = [(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]_3$ ) was reacted with  $\text{VCl}_4(\text{DME})$  (DME = 1,2-dimethoxyethane) to give the corresponding  $[\text{N}_3\text{N}]\text{VCl}$  derivative<sup>44</sup>. The reduction of  $[\text{N}_3\text{N}]\text{VCl}$  with Na/Hg gave trigonal pyramidal  $[\text{N}_3\text{N}]\text{V}$  (Scheme 1.10). Tertiary amines, phosphines and weak donors such as ether and THF have no tendency to coordinate to the

empty coordination site in  $[\text{N}_3\text{N}]\text{V}$ , possibly because of the large steric hindrance of the amide ligand which is protecting the coordination site. Nevertheless, the addition of  $\text{Me}_3\text{SiN}_3$  to the blue  $[\text{N}_3\text{N}]\text{V}$  yielded the orange-yellow silylimido complex  $[\text{N}_3\text{N}]\text{V}=\text{NSiMe}_3$  (Scheme 1.10). The treatment of  $[\text{N}_3\text{N}]\text{V}$  compound with perfluorinated pyridine (Scheme 1.10) gave the imido derivative  $[\text{N}_3\text{N}]\text{V}=\text{NC}_6\text{F}_5$ . When  $\text{Me}_3\text{SiCH}_2\text{N}_2$  was added to  $[\text{N}_3\text{N}]\text{V}$ , the pentavalent  $[\text{N}_3\text{N}]\text{V}=\text{N}-\text{N}=\text{CH}(\text{SiMe}_3)$  was formed instantaneously (Scheme 1.10). This complex is remarkably robust and does not eliminate dinitrogen even upon photolysis. Interestingly, the reaction of  $[\text{N}_3\text{N}]\text{V}$  with 2-methylaziridine in ether or benzene yielded the diamagnetic  $[\text{N}_3\text{N}]\text{V}=\text{NH}$  and propylene as by-product. The imido moiety in this complex is regarded as particularly interesting and was considered to be an important intermediate towards the reduction of dinitrogen to ammonia.



**Scheme 1.10**

The treatment of  $[\text{N}_3\text{N}]\text{V}=\text{NH}$  with  $\text{LiN}(\text{SiMe}_3)_2$  followed by an excess of  $\text{Me}_3\text{SiCl}$  gave the complex  $[\text{N}_3\text{N}]\text{V}=\text{NSiMe}_3$  (eq 1).



The addition of excess sodium azide to  $[\text{N}_3\text{N}]\text{VCl}$  yielded the black crystalline  $[\text{N}_3\text{N}]\text{VN}_3$ . Further reduction by sodium amalgam produced a yellow-green solution which when treated with excess  $\text{Me}_3\text{SiCl}$  produced  $[\text{N}_3\text{N}]\text{V}=\text{NSiMe}_3$  (eq. 2).

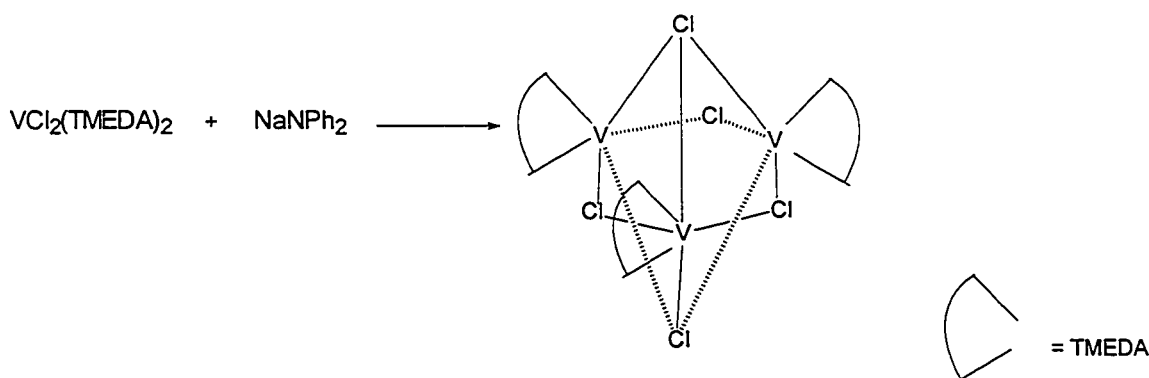


On the basis of these observations, Cummins suggested that  $[\text{N}_3\text{N}]\text{VN}^\cdot$  was formed during the reduction.

In spite of producing promising model systems to study crucial intermediates in the dinitrogen reduction process, all the systems described above did not participate in any direct dinitrogen fixation or activation. Although vanadium(II) amide shows great potential for dinitrogen activation, these species remain elusive so far. There are only a few reports in the literature describing attempts to prepare homoleptic V(II) amide. Reaction of  $\text{VCl}_2(\text{TMEDA})_2$  with  $\text{Cy}_2\text{NLi}$  yielded an unprecedented ethylidyne vanadium cluster where the organic moiety was provided by the fragmentation of THF<sup>45</sup>. The cleavage of THF could be either the result of the reaction of a vanadium(II) intermediate with THF or of its ability to work as a “scavenger” of reactive fragments produced such as  $\text{Cy}_2\text{NLi}$ . The crystal structure of the ethylidyne vanadium cluster showed a *nido* trigonal bipyramidal configuration with a  $\text{V}_2\text{LiC}(\text{CMe})$  core and with the apical position

occupied by the lithium atom. The rather short V-V distance [2.640 Å] and the low magnetic moment ( $\mu_{\text{eff}} = 2.53 \mu_{\text{B}}$ ) indicate the presence of a metal-metal interaction.

Replacement of the cyclohexyl substituents with aromatic ring such as in the case of  $\text{Ph}_2\text{N}^-$  anion, gave a completely different behavior. Treatment of  $\text{VCl}_2(\text{TMEDA})_2$  with  $\text{Ph}_2\text{NNa}$  (Scheme 1.11) in THF gave the olive green ionic complex  $[\text{V}_3\text{Cl}_5(\text{TMEDA})_3][\text{V}(\text{NPh}_2)_4]$ . The cationic unit is composed of a triangular trivanadium cluster with three bridging chlorine coplanar with the  $\text{V}_3$  unit with the other two symmetrically placed above and below the molecular plane. The mononuclear anionic unit features a vanadium atom placed in the center of a tetrahedron bound by the nitrogen atoms of four amido ligands.

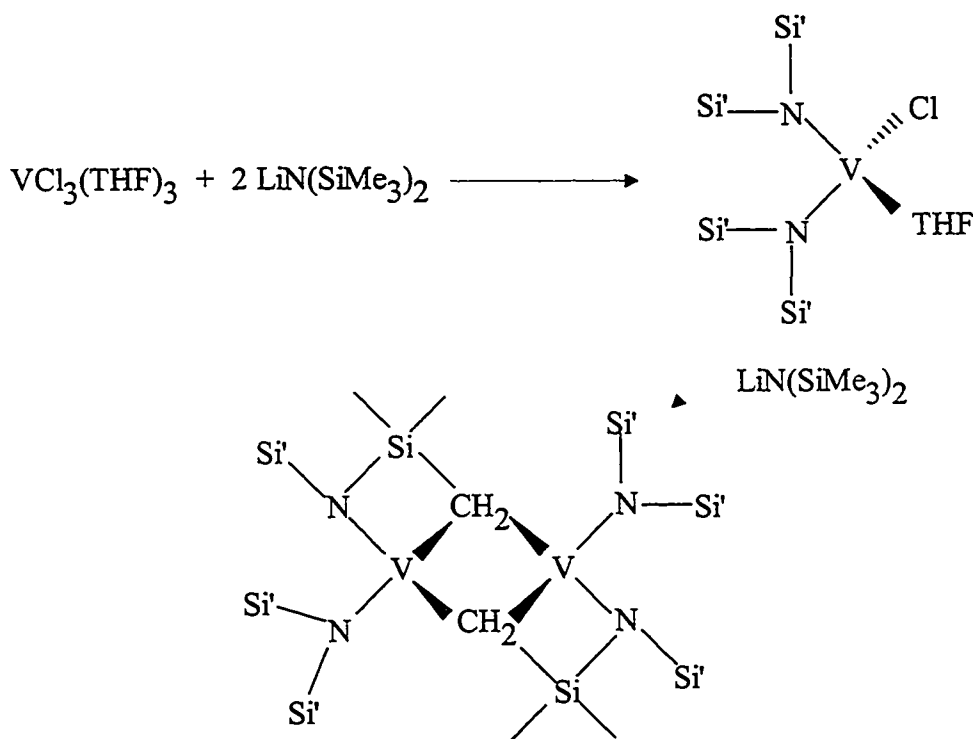


**Scheme 1.11**

An alternative possibility for the preparation of vanadium(II) amide involves the reduction of suitable vanadium(III) derivatives. With this perspective, efforts were made for the preparation of suitable complexes which may work as precursors. For example, the reaction of  $\text{VCl}_3(\text{THF})_3$  with 2 equivalents of  $\text{R}_2\text{NLi}$  [ $\text{R} = \text{Cy}, (\text{CH}_3)_3\text{Si}$ ] led to the

formation of the corresponding derivatives  $(\text{C}_2\text{N})_2\text{V}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$  and  $\{[(\text{CH}_3)_3\text{Si}]_2\text{N}\}_2\text{VCl}(\text{THF})$  respectively<sup>46</sup>. In both cases, the thermal lability of these species was ascribed to dimerization obtained *via* dissociation of THF or LiCl. However, in spite of successful characterization and transformation of these species into the corresponding alkyls and borohydrides, unambiguous results about their reduction were not obtained and it remains unclear whether or not these compounds may be used as starting materials for the preparation of divalent vanadium amides.

In striking contrast to the paucity of V(II) amide chemistry, a wealth of information is available for the corresponding V(III) derivatives. The reaction of  $\text{VCl}_3(\text{THF})_3$  with 2 equivalents of  $\text{LiN}(\text{SiMe}_3)_2$  in THF gave the monomeric  $[(\text{SiMe}_3)_2\text{N}]_2\text{VCl}(\text{THF})$ . Instead of forming the corresponding homoleptic derivative, addition of a third equivalent of  $\text{LiN}(\text{SiMe}_3)_2$  formed the dimeric  $\{[(\text{Me}_3\text{Si})_2\text{N}]\text{V}[\mu\text{-CH}_2\text{SiMe}_2\text{N}(\text{SiMe}_3)]\}_2$  (Scheme 1.12) *via* C-H bond metathesis of one methyl group<sup>44</sup>. The structure of the dimer consists of two  $[(\text{SiMe}_3)_2\text{N}]\text{V}$  moieties bridged by two  $\mu\text{-CH}_2\text{Si}(\text{Me})_2\text{N}(\text{SiMe}_3)$  units. The two bridging units form almost planar metalloazacyclobutane rings and form the overall dimeric structure by sharing the  $\text{CH}_2$  groups with the two vanadium atoms.

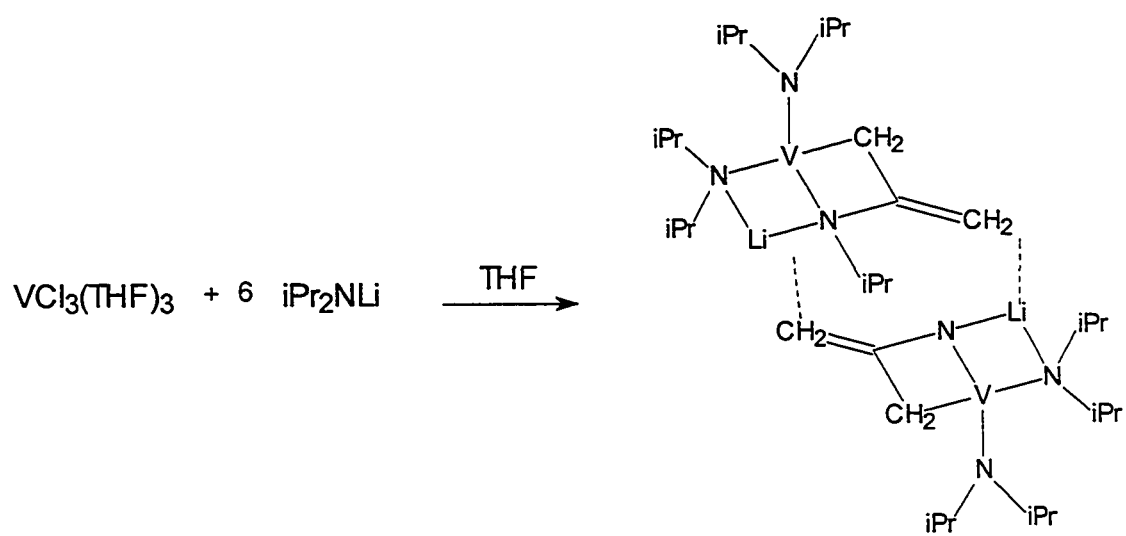


**Scheme 1.12**

The chemistry of the vanadaazacyclobutane moiety was extensively investigated with several reagents. Insertion reactions were examined with rather “classic” inserting agents such as alkynes, CO and RNC. The reaction of  $\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{V}[\mu\text{-CH}_2\text{SiMe}_2\text{N}(\text{SiMe}_3)]\}_2$  with CO (1 atm) and RNC originates a vanadium(III) dinuclear enolate and enamide complexes. The formation of both compounds arises from an anomalous insertion into the Si-CH<sub>2</sub> bond.

The result of the hydrogenolysis of the V-C bond in the presence of Me<sub>3</sub>P was described above. During other attempts to prepare divalent vanadium amide precursors to be reacted with dinitrogen, the complex [(Me<sub>3</sub>Si)<sub>2</sub>N]V[μ-CH<sub>2</sub>SiMe<sub>2</sub>N(SiMe<sub>3</sub>)](py) was also subjected to hydrogenolysis. The reaction gave the new enamido complex [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>2</sub>V(2,3-didehydropiperidinato)(py). This species arises from the uptake of two molecules of H<sub>2</sub> with cleavage of the V-CH<sub>2</sub> bond and partial hydrogenation of the pyridine ring. During the formation of this product, the hydride [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>2</sub>V(H)(py) was probably formed as an unstable intermediate. This result indicates that a surprisingly high reactivity may be expected for the V-H species which certainly are promising reagents with which to test the reactivity of dinitrogen.

The reaction of VCl<sub>3</sub>(THF)<sub>3</sub> with excess of <sup>i</sup>PrNLi gave a dinuclear complex formulated as {[<sup>i</sup>Pr<sub>2</sub>N]<sub>2</sub>V[μ-CH<sub>2</sub>C(=CH<sub>2</sub>)N(<sup>i</sup>Pr)]Li}<sub>2</sub><sup>13</sup>. Similar to the case of the silazane mentioned above, the metallocycle was formed by deprotonation of one amido group which then chelates the vanadium atom by using the nitrogen and one deprotonated methyl group, thus forming a four-membered vanadacyclobutane ring (Scheme 1.13). The second carbon atom and the methylene carbon of the same isopropyl group engaged in the formation of the metallacycle have also been dehydrogenated to form an exocyclic C=CH<sub>2</sub> double bond. This result is rather intriguing since the formal elimination of H<sub>2</sub> implies a redox process.



**Scheme 1.13**

## **Conclusions**

The scope of this thesis was to study the synthesis, characterization and reactivity of novel low- and medium-valent vanadium complexes. The main long term goal of this research was to understand the steps through which dinitrogen is reduced to ammonia and hydrazine, and to understand the factors which favor the fixation and activation of this exceedingly stable molecule. For this purpose I have used nitrogen donor-based compounds as ligand system. As part of this research, I have synthesized during this thesis work new vanadium amide-based complexes. I found that these species act as efficient catalysts for the Ziegler-Natta type polymerization of olefins. A preliminary study along this line is also reported.

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## Chapter 2

### Preparation and Characterization of a Vanadium (III) Dinitrogen Complex

#### Supported by a Tripodal Anionic Amide Ligand

#### Introduction

Since the original discovery 36 years ago of the ability of reactive transition metal complexes to form stable dinitrogen complexes,<sup>1</sup> the literature has experienced a steady growth of interest in the reactivity of coordinated dinitrogen.<sup>2</sup> The understanding of the factors which promote or disfavor the coordination of this exceedingly stable molecule and which promote its further transformation is a major challenge and the main goal in this field. In fact, clarifying this point is central to the development of suitable catalytic cycles through which a nitrogen atom from the dinitrogen molecule will be transferred to other substrates.<sup>3</sup>

Medium valent vanadium and titanium species seem to be adequate substrates for this type of study given the well known ability of these derivatives to perform a few cycles of catalytic transformation of dinitrogen into ammonia and hydrazine under mild reaction conditions.<sup>4,5</sup> For this reason, this laboratory has embarked on a long term project to develop the coordination chemistry of di- and trivalent vanadium and titanium complexes.<sup>6</sup> This work has led to the discovery of unprecedented dinitrogen complexes of these metals in a non-organometallic environment.<sup>7</sup> Of particular interest was the finding that a fairly high oxidation state such as V(III), in combination with a diisopropyl amide ligand, is capable of forming exceptionally stable dinitrogen complexes.<sup>7b</sup> The nature of

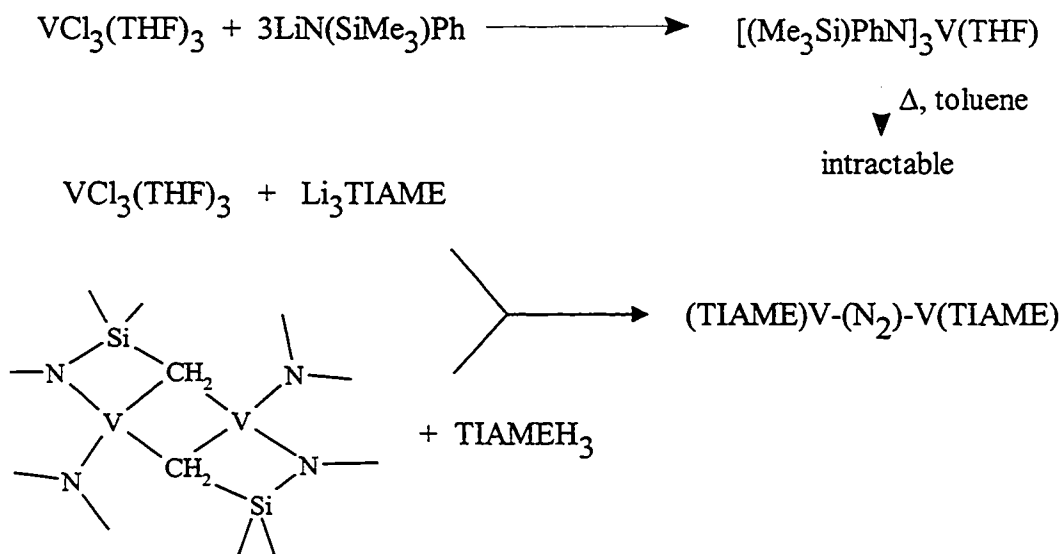
the amide organic substituent seems to play a crucial role in determining the ability of *in situ* generated homoleptic V(III) amides to interact with dinitrogen. In contrast to the R<sub>2</sub>N [R = *i*-Pr, cyclohexyl] amide derivatives which formed robust dinitrogen complexes, trimethylsilyl amide gave cyclometallation,<sup>8</sup> while aromatic amides gave coordination of Lewis bases such as THF.<sup>9</sup> These contrasting observations indicate that V(III) amides indeed may provide a suitable system to study the factors which promote or disfavor the coordination of dinitrogen. Central to reaching this goal is the preparation of a series of V(III) amide complexes where the nature of the amide organic substituents is systematically varied. Herein I report some of the preliminary observations.

## Results and Discussion

The ligands selected for this preliminary structural work were the  $\{[(\text{CH}_3)_3\text{Si}]\text{NPh}\}^-$  anion<sup>10</sup> and the tripodal, trianionic and dimeric  $[\{\text{CH}_3\text{C}[(\text{CH}_2)\text{NH}(\textit{i}\text{-Pr})]_3\}\text{Li}_3]_2$  (TLAME).<sup>11a</sup> This ligand was successfully used by Gade in the chemistry of titanium.<sup>11b,c</sup>

As summarized in Scheme 1, reaction of  $\text{VCl}_3(\text{THF})_3$  with 3 equivalents of  $[(\text{CH}_3)_3\text{Si}]\text{NPhLi}(\text{Et}_2\text{O})$ , led to the formation of the corresponding  $\{[(\text{CH}_3)_3\text{Si}]\text{NPh}\}_3\text{V}(\text{THF})$  (**1**) which was isolated in good yield as a green crystalline complex. The magnetic moment of **1**, calculated on the basis of the formula suggested by combustion analysis data, was as expected for a  $d^2$  electronic configuration. The structure was elucidated by an X-ray diffraction analysis (Figure 1). The monomeric compound consists of a distorted tetrahedral vanadium atom [N1-V1-N2 = 117.2(1)°, N1-V1-N3 = 119.2(1)°, N2-V1-N3 =

Scheme 1



Scheme 2.1

115.5(1)°, O1-V1-N1 = 93.6(1)°, O1-V1-N2 = 104.1(1)°] surrounded by three bulky amide and one molecule of THF [V1-O1 = 2.070(3)Å]. The V-N distances are rather short [V1-N1 = 1.977(3)Å, V1-N2 = 1.962(3)Å, V1-N3 = 1.944(3)Å] and together with the trigonal coordination geometry of the nitrogen atoms [Si1-N1-C4 = 117.9(3)°, Si1-N1-V1 = 124.6(2)°, C4-N1-V1 = 117.1(2)°], indicate the presence of some extent of  $\pi$ -bonding.

Different from the isostructural  $(\text{Ph}_2\text{N})_3\text{V}(\text{THF})$  complex 1 is thermally labile while in the solution of a non-coordinating solvent. The rapid color change to brown obtained upon heating its blue-green solution in toluene, possibly suggests that the coordinated molecule of THF may be lost during the heating. However, attempts to isolate new species by removing THF via azeotropic distillation of the toluene solution yielded only intractable materials.

Reaction of  $\text{VCl}_3(\text{THF})_3$  with  $\text{CH}_3\text{C}[(\text{CH}_2)\text{N}(\text{i-Pr})\text{Li}]_3$  (TIAME) under nitrogen atmosphere gave the new dinitrogen complex (TIAME)V-N<sub>2</sub>-V(TIAME) which was isolated in crystalline form from a toluene solution as intensely red diamagnetic crystals. While the NMR spectrum showed the characteristic absorptions of the ligand in the appropriate ratio, correct combustion analysis data consistent with the proposed formulation were not obtained due to the high air-sensitivity of this species. The complex was also conveniently prepared *via* transamination reaction of the dinuclear  $\{[(\text{CH}_3)_3\text{Si}]_2\text{NV-N}[\text{Si}(\text{CH}_3)_3]\text{Si}(\text{CH}_3)_2\text{CH}_2\}_2$  with the free ligand TIAMEH<sub>3</sub>.

The structure of complex **2** was elucidated by X-ray analysis. The complex is dinuclear with two identical (TIAME)V fragments linked together by a dinitrogen molecule, forming a linear V-N<sub>2</sub>-V vector [ $\text{V1-N1-N1a} = 180.0^\circ$ ] (Figure 2). The coordination geometry around each vanadium atom is tetrahedral and is defined by the three nitrogens of the tripodal amide [ $\text{N2-V1-N2a} = 105.7(1)^\circ$ ] and the nitrogen atom of the bridging dinitrogen [ $\text{N1-V1-N2} = 112.96(6)^\circ$ ]. The coordination geometry around each amide nitrogen atom is trigonal planar [ $\text{C1-N2-V1} = 103.6(1)^\circ$ ,  $\text{C4-N2-V1} = 139.4(1)^\circ$ ,  $\text{C1-N2-C4} = 115.8(2)^\circ$ ] with V-N bond distances [ $\text{V1-N2} = 1.855(2)\text{\AA}$ ] in the expected range. Similar to the case of the other V(III) dinitrogen complexes,<sup>6,7,11</sup> the V-N bond distance formed by the metal center with the coordinated dinitrogen is remarkably short [ $\text{V1-N1} = 1.707(3)\text{\AA}$ ] thus suggesting significant multiple bond character. However, the N-N distance [ $\text{N1-N1c} = 1.257(6)\text{\AA}$ ] is not particularly long and is somewhat in the range expected for a N-N double bond.

## Experimental section

### Preparation of $\text{Me}_3\text{Si(Ph)NLi(Et}_2\text{O)}$

Freshly distilled aniline (25 mL, 0.27 mol.) was dissolved in ether (100 mL) and then cooled to  $-78^\circ\text{C}$ . A solution of MeLi in ether (196 mL, 1.4 M, 0.27 mol.) was added dropwise. The reaction mixture was stirred and allowed to warm up to room temperature. The solution was then cooled again to  $-78^\circ\text{C}$ . The addition of  $(\text{CH}_3)_3\text{SiCl}$  (35 mL, 0.27 mol.) formed a precipitate of LiCl which, after warming up to room temperature, was removed by filtration. The resulting clear solution was cooled to  $-78^\circ\text{C}$  and treated with an hexane solution of n-BuLi (110 mL, 2.5 M, 0.27 mol.). After further filtration, the clear solution was concentrated and cooled to  $-30^\circ\text{C}$  overnight. Extremely air-sensitive  $\text{Me}_3\text{Si(Ph)NLi(Et}_2\text{O)}$  was formed as a colorless microcrystalline precipitate (33g, 0.13 mol, 48%). I.R. (Nujol,  $\text{cm}^{-1}$ )  $\nu$ : 1582(s), 1271(sh), 1269(vs), 1180(m), 1153(m), 1075(m), 1027(m), 991(s), 917(vs), 830(vs), 762(s), 695(s), 669(m), 623(m).  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ , 200MHz)  $\delta$ : 7.19(dd, 2H, Ph), 6.82(dd, 2H, Ph), 6.78(t, 1H, Ph), 3.06(q, 4H, ether), 0.76(t, 6H, ether), 0.32(s, 9H, silyl).  $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ , 75MHz)  $\delta$ : 159.3, 129.8, 123.0, 115.3(Ph), 64.8(ether), 14.3(ether), 2.8 (silyl). The extreme air-sensitivity prevented combustion analysis determinations.

### Preparation of $\{[(\text{CH}_3)_3\text{Si}]\text{NPh}\}_3\text{V}(\text{THF})$ (1)

A stirred suspension of  $\text{VCl}_3(\text{THF})_3$  (2.6 g, 7.0 mmol) in toluene (100 mL) was treated with freshly prepared  $\text{Me}_3\text{SiNPhLi}(\text{Et}_2\text{O})$  (5.2 g, 21.2 mmol). The color of the mixture rapidly turned blue-green and stirring was continued for additional 30 min. A small amount of colorless insoluble material was eliminated by filtration. After concentration to small volume, the resulting solution was allowed to stand overnight at  $5^\circ\text{C}$  upon which dark-green crystals of **1** separated (1.73 g, 2.8 mmol, 40%). I.R. (Nujol,  $\text{cm}^{-1}$ )  $\nu$ : 1584 (s, Ph group), 1030 and 833 (s, THF), 1253 (vs,  $\text{Me}_3\text{Si}$ ). Anal Calcd (found) for  $\text{C}_{31}\text{H}_{50}\text{N}_3\text{Si}_3\text{VO}$ : C 62.06(61.99), H 9.90(9.79), N 18.35(18.27).  $\mu_{\text{eff}} = 2.95 \mu_{\text{B}}$  at room T.

Crystal Data for **1**:  $\text{C}_{31}\text{H}_{50}\text{N}_3\text{Si}_3\text{VO}$ , *F.W.* 615.95, monoclinic  $P2_1/n$ ,  $a = 10.762(2)$  Å,  $b = 18.461(2)$  Å,  $c = 17.226(2)$  Å,  $\beta = 97.34(1)^\circ$ ,  $V = 3394(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $\text{CuK}\alpha$  ( $\lambda = 1.54178$  Å),  $D_{\text{calc}} = 1.205 \text{ g/cm}^3$ ,  $F_{000} = 1320$ ,  $\mu = 37.0 \text{ cm}^{-1}$ ,  $T = -153^\circ\text{C}$ ,  $R = 0.046$ ,  $wR^2 = 0.059$ , *G.o.F.* = 2.78 for 346 parameters and 3128 reflections out of 3635 unique. Non hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at their idealized positions. Absorption corrections (DIFABS) were applied to the data. One atom of the coordinated molecule of THF was found disordered over two positions with equal occupancy.

## Preparation of (TIAME)V-N<sub>2</sub>-V(TIAME) (2)

### Method A.

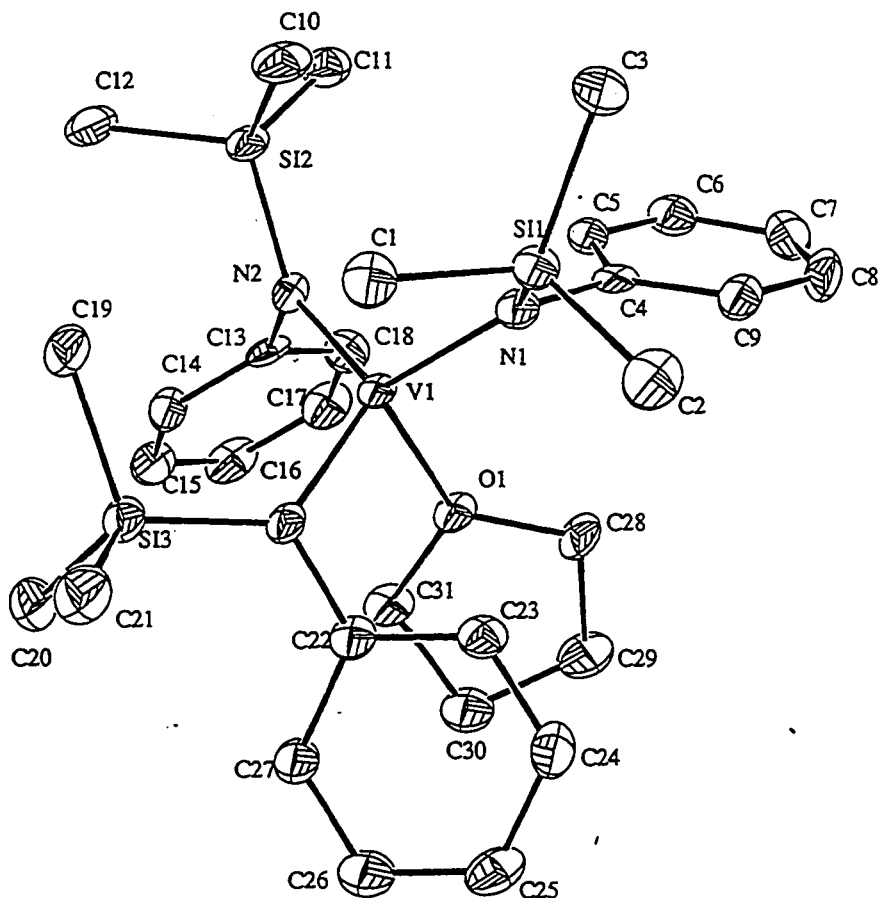
A toluene solution of the dinuclear  $\{[(\text{CH}_3)_3\text{Si}]_2\text{NVN}[\text{Si}(\text{CH}_3)_3]\text{Si}(\text{CH}_3)_2\text{CH}_2\}_2$  (2.3 g, 3.1 mmol) in toluene (150 mL) was treated with TIAME (1.52 g, 6.2 mmol). The resulting blue-purple solution slowly turned dark red. After 36 hrs of stirring, the resulting intense bright red solution was evaporated in vacuo and the residual solid redissolved in hexane. Dark red crystals of **2** separated upon allowing the resulting solution to stand at -15°C overnight (0.7 g, 1.14 mmol, 37%).

### Method B.

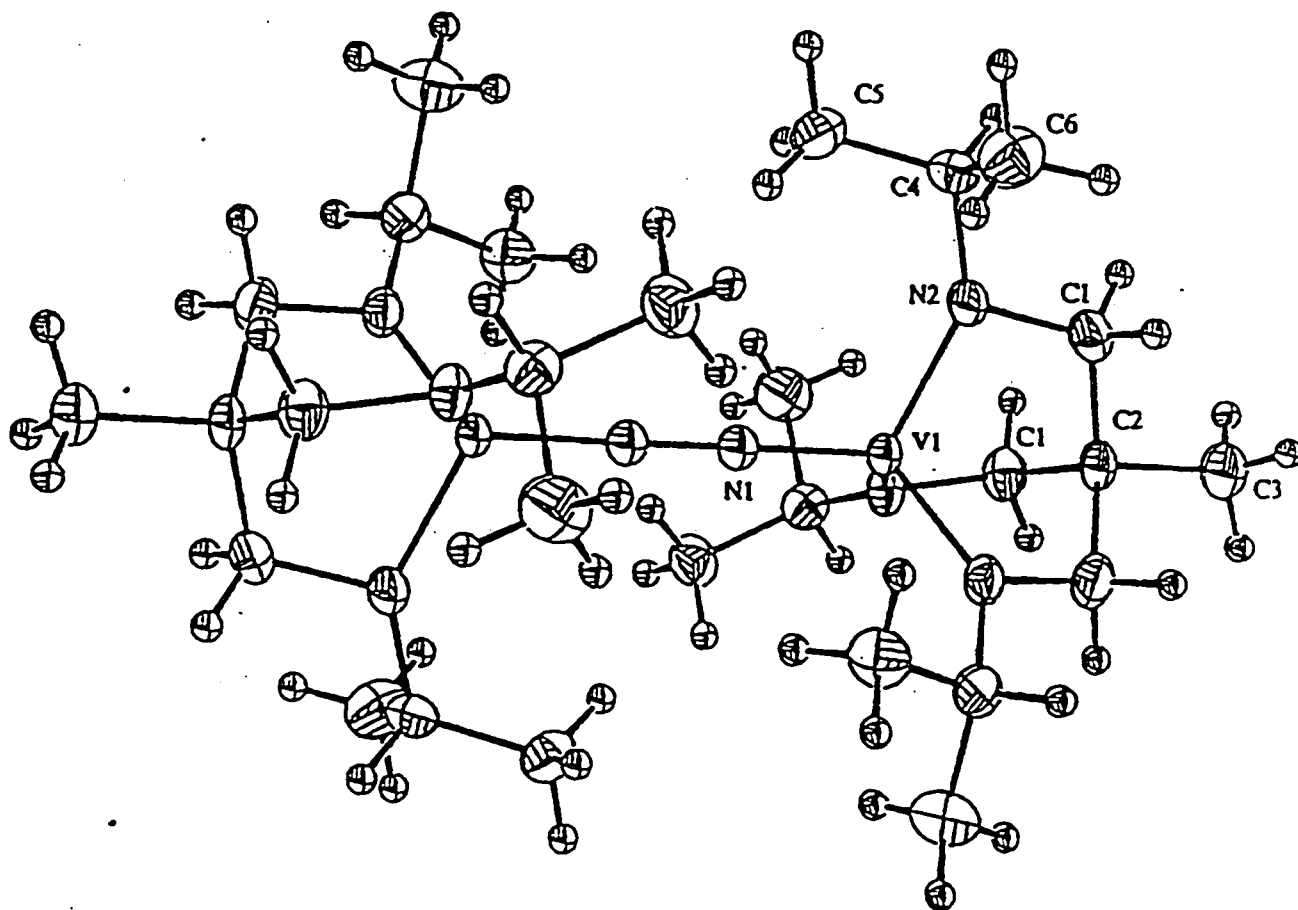
A solution of  $\text{VCl}_3(\text{THF})_3$  (2.8 g, 7.4 mmol) in THF (75 mL) was treated with freshly prepared  $\text{TiAMELi}_3$  (2.0 g, 7.5 mmol). The solution turned intense red and stirring was continued for overnight. The solvent was removed in vacuo and the residual dark residue redissolved in hexane. After filtration and concentration the solution was allowed to stand at -30°C overnight, upon which dark crystals of **2** separated (0.8g, 1.3 mmol, 35%). I.R. (Nujol,  $\text{cm}^{-1}$ )  $\nu$ : 2552(m), 1375(s), 1315(sh), 1301(m), 1276(w), 1207(sh), 1180(vs and br), 1139(m), 116(m), 1068(m), 1016(m), 971(s), 933(m), 904(s), 848(m), 500(vs), 443(vs). <sup>1</sup>H-NMR ( $\text{C}_6\text{D}_6$ , 25°C, 200MHz)  $\delta$ : 3.41(s, 6H,  $\text{CH}_2$ ), 3.35(septet, 3H,  $\text{CH}_{i\text{-Pr}}$ ), 1.53(d, 18H,

Me<sub>i-Pr</sub>), 1.07(s, 3H, Me). <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>, 25°C, 75MHz) δ: 65.0 (CH<sub>2</sub>), 61.5(CH<sub>i-Pr</sub>), 60.3(quaternary C), 28.2(Me), 26.0(Me<sub>i-Pr</sub>).

2: C<sub>28</sub>H<sub>60</sub>N<sub>8</sub>V<sub>2</sub>, *F.W.* 610.72, trigonal *R*-3, *a* = 13.372(5) Å, *c* = 16.295(7) Å, *V* = 2523(1) Å<sup>3</sup>, *Z* = 3, *D<sub>calc</sub>* = 1.206 g/cm<sup>3</sup>, *F*<sub>000</sub> = 989, μ = 57 cm<sup>-1</sup>, *T* = -150°C, *R* = 0.029, *wR*<sup>2</sup> = 0.032, *G.o.F.* = 3.72 for 98 parameters and 782 observed reflections out of 801 unique. Non hydrogen atoms were refined anisotropically. Hydrogen atom were introduced at their idealized positions. Absorption corrections (DIFABS) were applied to the data.



**Figure 1.** Thermal ellipsoid plot of  $\{[(\text{CH}_3)_3\text{Si}]\text{NPh}\}_3\text{V}(\text{THF})$ . Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances ( $\text{\AA}$ ) and angles (deg):  $\text{V1-O1} = 2.070(3)$ ,  $\text{V1-N1} = 1.977(3)$ ,  $\text{V1-N2} = 1.962(3)$ ,  $\text{V1-N3} = 1.944(3)$ ,  $\text{N1-Si1} = 1.749(3)$ ,  $\text{N1-C4} = 1.409(5)$ ,  $\text{O1-V1-N1} = 93.6(1)$ ,  $\text{O1-V1-N2} = 104.1(1)$ ,  $\text{O1-V1-N3} = 101.1(1)$ ,  $\text{N1-V1-N2} = 117.2(1)$ ,  $\text{N1-V1-N3} = 119.2(1)$ ,  $\text{N2-V1-N3} = 115.5(1)$ ,  $\text{Si1-N1-C4} = 117.9(3)$ ,  $\text{V1-N1-Si1} = 124.6(2)$ ,  $\text{V1-N1-C4} = 117.1(2)$ .



**Figure 2** Thermal ellipsoid plot of **(TIAME)V-N<sub>2</sub>-V(TIAME)**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (deg): N1-N1c = 1.257(6), V1-N1 = 1.707(3), V1-N2 = 1.855(2), N2-C1 = 1.466(3), N2-C4 = 1.455(3), V1-N1-N1c = 180.0, N1-V1-N2 = 112.96(6), N2-V1-N2a = 105.8(1), C1-N2-C4 = 115.8(2), V1-N2-C1 = 103.6(1), V1-N2-C4 = 139.4(1).

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## Chapter 3

### **Preparation and Characterization of a Homoleptic Vanadium(III) Amide Complex and its Transformation into Terminal Chalcogenide Derivatives [(3,5-Me<sub>2</sub>Ph)AdN]<sub>3</sub>V(=E) [E = S, Se; Ad = adamantyl].**

#### **Introduction**

One of the most attractive characteristics provided by anionic organic amides as ligands is the unlimited possibility to adjust the steric hindrance around the metal center *via* the appropriate selection of the organic substituents. In particular, the utilization of sterically demanding amides has allowed the preparation of coordinatively unsaturated species able to perform several important transformations. This strategy was first successfully adopted by Wolczanski for the preparation of precursors for lanthanide nitrides<sup>1</sup> and it was more recently used to perform the first example of well documented transformation of dinitrogen into nitride,<sup>2</sup> NO cleavage<sup>3</sup> and trapping of unstable and rare functionalities.<sup>4</sup>

Our interest in this field is mainly focused on low- and medium valent early transition metals where the amide ligands considerably enhance the reactivity of the metal center and allow a number of transformations spanning a broad range of reactivity (dinitrogen fixation,<sup>5</sup> dinitrogen cleavage,<sup>6</sup> formation of carbenes,<sup>7</sup> metallacycles<sup>8</sup> and nitrides,<sup>9</sup> hydrogen transfer,<sup>10</sup> deoxygenation and fragmentation of THF,<sup>11</sup> formation of unsupported M-M bonds,<sup>12</sup> reductive couplings<sup>13</sup>). In addition, the M-N bond of a vanadium amide may undergo hydrogenolysis<sup>6</sup> and hydrogen may be removed from the

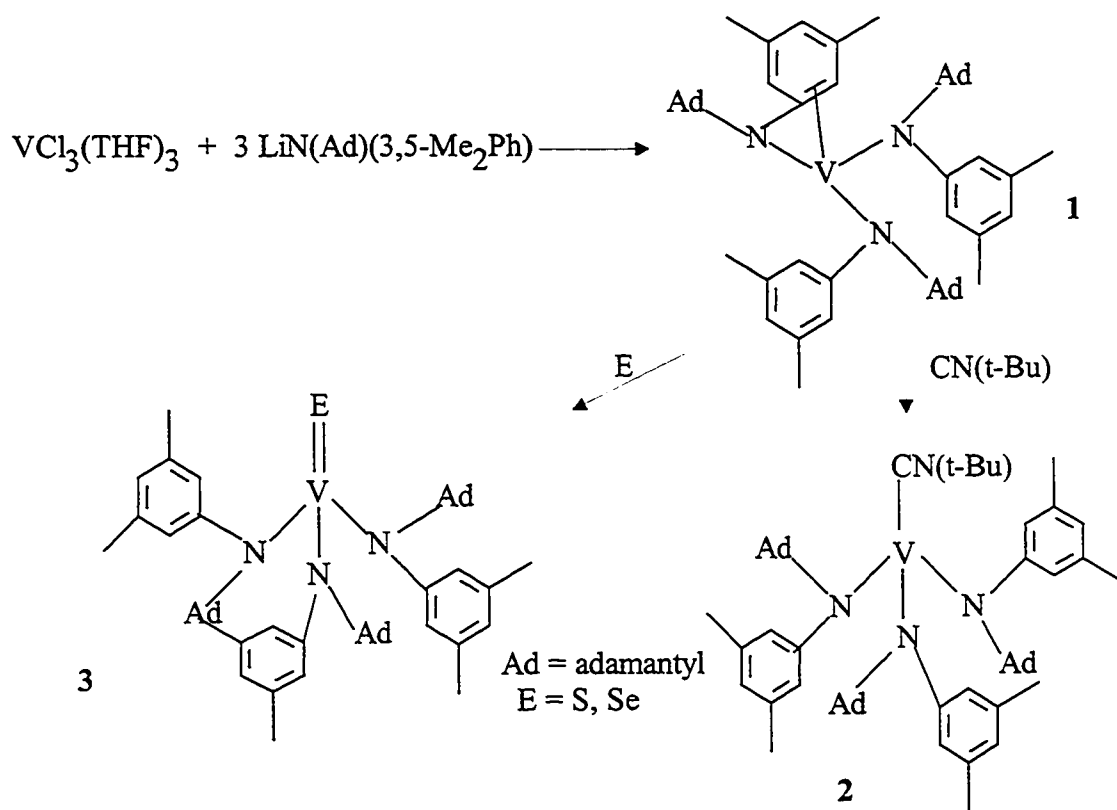
amide alkyl side chain<sup>5c,14</sup> which of course are desirable performances in view of using Transition Metals amides as active intermediates of catalytic cycles.

I have recently prepared a series of tris-vanadium amide derivatives where the fourth coordination site around vanadium was invariably occupied by either a Lewis base or a bridging nitrogen molecule. This chapter describes the preparation and preliminary studies into the chemical behavior of a rare example of a mononuclear and homoleptic V(III) amide.

## Results and Discussion

Scheme 1 outlines the reaction of  $VCl_3(THF)_3$  with three equivalents of (3,5-Me<sub>2</sub>Ph)AdNLiEt<sub>2</sub>O [Ad = adamantyl] in THF which gave several subsequent color changes from orange to red-violet, to olive green and finally to brown-green. Dark greenish-brown crystals of the paramagnetic [(3,5-Me<sub>2</sub>Ph)AdN]<sub>3</sub>V (**1**) were isolated in reasonable yield from ether solution. The formulation was initially inferred from elemental analysis results and of a magnetic moment measurement [ $\mu_{eff} = 2.72\mu_B$ ] which was in agreement with the expected d<sup>2</sup> electronic configuration of the V(III) metal center. A characteristic 8 lines EPR spectrum was obtained in solution of benzene ( $g = 1.99$ ,  $A = 50$  gauss).

The molecular connectivity of **1** was confirmed by an X-ray crystal structure determination. The molecule features a trigonal planar vanadium atom connected to three



**Scheme 3.1**

nitrogen atoms of three amide ligands (Figure 3). The coordination geometry around each of the three nitrogen is trigonal planar suggesting a considerable extent of N-V  $\pi$ -donation. In agreement, the V-N distances are noticeably short in spite of the considerable steric bulk. An aromatic ring of one of the three amide groups is significantly bent towards the vanadium atom forming a bonding contact between vanadium and two ring carbon atoms thus originating with the amido nitrogen a sort of  $\eta^3$ -allylic-like system.<sup>15</sup> Corresponding bond alterations have also been observed within the ring C-C and the  $\text{C}_{\text{ring}}\text{-N}$  distances.

Since  $(\text{R}_2\text{N})_3\text{V-N}_2\text{-V}(\text{NR}_2)_3$  complexes are remarkably robust,<sup>5b</sup> the inactivity of 1 to elemental nitrogen or THF<sup>5a,b,c,d</sup> might be ascribed to the large steric bulk of the

adamantyl group which hinders accessibility to the vanadium atom. It is possible that the pyramidalization of the vanadium center, necessary for the fixation of N<sub>2</sub> is sterically demanding and might be not triggered by the non-polar N<sub>2</sub> molecule. Conversely, reactions of **1** with t-BuNC, which is strongly polar and with a negative charge on the isocyanide carbon atom, readily gave the corresponding tetrahedral adduct [(3,5-Me<sub>2</sub>Ph)AdN]<sub>3</sub>V[CN(t-Bu)] (**2**). This observation prompted me to explore the reactivity of **1** with oxidizing agents which, by increasing the steric hindrance around the metal center, should in principle lead to major molecular reorganization or to the trapping of rare and unstable functionalities. I have selected for this preliminary study, the chalcogens (S, Se) due the large atomic dimensions and moderately strong oxidizing ability.

Addition of the elemental chalcogen E (E = S<sub>8</sub>, Se) to a toluene solution of **1** gave an immediate color change to dark reddish-violet from which the corresponding derivatives [(3,5-Me<sub>2</sub>Ph)AdN]<sub>3</sub>V(=E) [E = S(**3a**), Se(**3b**)] were isolated in crystalline form. The two complexes are diamagnetic and combustion analysis data were in agreement with the formulation [(3,5-Me<sub>2</sub>Ph)AdN]<sub>3</sub>V(=E) [E = S(**3a**), Se(**3b**)]. Both complexes reacted readily with acids to liberate the corresponding H<sub>2</sub>E. The I.R., <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were almost identical for the two complexes thus suggesting that the two compounds are isostructural. A very small shift to upfield was observed for the <sup>1</sup>H-NMR resonances of the selenide derivative. Despite repeated efforts using the widest possible range of frequencies associated with selenium, no resonance was observed in the <sup>77</sup>Se-NMR spectrum. This is probably due to a large coupling constant between the <sup>77</sup>Se and the quadrupolar <sup>51</sup>V nuclei.<sup>16</sup> Nevertheless, X-ray fluorescence experiments consistently confirmed the presence of this element in a 1:1 ratio with vanadium.

The  $^1\text{H}$ -NMR spectra of both compounds show some unusual features. The methylene proton resonances of the adamantyl groups are observed as two separate resonances each appearing as doublet of doublets while the methyne proton resonance is a slightly broad singlet. HQMC experiments correlate this resonance with a C-H line of the  $^{13}\text{C}$ -NMR spectrum. The broadness of the methyne line is probably due to a second order effect since the COSY spectrum clearly indicated that this singlet is coupled with both doublet of doublets. The methyl groups attached to phenyl rings are non-equivalent and display proton resonances with well separated chemical shifts. In a parallel fashion, the aromatic ring protons resonate as three distinct singlets at 7.21, 6.67 and 4.58, and at 7.09, 6.66 and 4.50 for **3a** and **3b** respectively. Correlation experiments clearly indicated that the three resonances correspond to the aromatic methyne in spite of the very unusual chemical shifts of one of them. Variable temperature experiments show that the resonances at 7.21 and 4.58 coalesce at 350 K forming a broad feature centered at 5.9 ppm. This indicates that the two resonances are caused by the two *ortho* protons, obviously experiencing remarkably different magnetic environments. The solid state crystal structure clearly shows that while one of these two protons points outside the molecule, the other points against the aromatic ring of another amide function. If we assume that due to the large steric bulk the solid state structure is preserved in solution, by pointing against the plane of an aromatic ring, one *ortho* proton is placed in the anisotropic magnetic field of the ring. This can cause a significant shielding which may reasonably explain the unusual chemical shift of this proton. Correspondingly, the two methyl group resonances also significantly broaden without reaching coalescence within the temperature frame used for the experiment.

In the case of **3a**, the connectivity was elucidated by X-ray analysis. Although one badly disordered molecule of ether present in the unit cell prevented satisfactory convergence, nevertheless, the structure was of sufficient accuracy to determine the molecular connectivity. The structure features a monomeric complex with the vanadium center surrounded by three bulky amide groups and one terminal sulfide atom in a distorted tetrahedral geometry (Figure 4). The V-S distance is not particularly short [V1-S1 = 2.045(3)Å] given the high oxidation state of vanadium and compares well with those of the few other terminal thiovanadyl species reported in the literature.<sup>17</sup>

The solid state structure is in agreement with the solution NMR features of the complex. In fact the non-equivalent *ortho* hydrogen may well become equivalent at high temperature due to an increased rotation of the aromatic ring along the C<sub>ring</sub>-N bond. However, the very unusual chemical shift of one of the protons is not clearly understood since the analogous proton-vanadium interatomic separations of all three adamantyl moieties are comparable and consistently too far apart for significant agostic interactions in the solid state. Investigations into trapping highly reactive functionalities utilizing **1** and in the thermal degradation chemistry of **3** are currently underway.

## Experimental Section

All operations were performed under inert atmosphere by using standard Schlenk techniques.  $VCl_3(THF)_3$  was prepared according to standard procedures. *t*-BuNC,  $S_8$ , 1-bromoadamantane (AdBr) and 3,5-Me<sub>2</sub>PhNH<sub>2</sub> (Aldrich) were used as received. Solvents were dried with the appropriate drying agents and distilled prior to use. Infrared spectra were recorded on a Mattson 9000 FTIR instrument from Nujol mulls prepared in a dry-box. Samples for magnetic susceptibility measurements were weighed inside a dry-box equipped with an analytical balance, and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature. The magnetic moment was calculated following standard methods,<sup>18</sup> and corrections for underlying diamagnetism were applied to data.<sup>19</sup> Elemental Analyses were carried out with a Perkin Elmer 2400 CHN analyzer. Ratios between heavy atoms were determined by X-ray fluorescence by using a Philips 2400 instrument.

### Preparation of 3,5-Me<sub>2</sub>PhN(Ad)H [Ad = adamantyl]

In a modification of a published procedure,<sup>20</sup> AdBr (15.5g, 72 mmol) was heated for 4 hours at 165°C in the presence of the stoichiometric amount of 3,5-Me<sub>2</sub>PhNH<sub>2</sub> (8.7 g, 72 mmol). The resulting light yellow solid was ground and washed with 3 portions of ether, yielding a white solid. The solid was treated with an aqueous solution of NaOH (10%) until basic pH. The mixture was extracted with several portions of CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was washed with water and dried over MgSO<sub>4</sub>. After filtration, the solvent was removed *in vacuo* yielding 3,5-Me<sub>2</sub>PhN(Ad)H (16.0g, 63mmol, 87%) as colorless microcrystalline solid. The purity was sufficient for the subsequent lithiation and no

further purification by recrystallization was necessary. El. Anal. Calcd (Found) for  $C_{18}H_{25}N$ : C 84.63(84.96), H 9.87(10.10), N 5.48(5.35). I.R. (nujol)  $\nu$ : 3288(m), 1598(s), 1356(m), 1302(m), 1167(m), 1118(s), 1091(s), 846(s), 830(s), 803(m), 711(w), 640(w).).  $^1H$ -NMR ( $CDCl_3$ , 20°C, 200MHz)  $\delta$ : 6.44(m, 3H,  $C-H_{aromatic}$ ), 2.9(broad, 1H, N-H), 2.22(s, 6H, Me-Ph), 2.08(br s., 3H,  $CH_{adamantyl}$ ), 1.85(br. s, 6H,  $CH_{2adamantyl}$ ), 1.66(br. s, 6H,  $CH_{2adamantyl}$ ).

### Preparation of 3,5-Me<sub>2</sub>PhN(Ad)Li.Et<sub>2</sub>O

A solution of 3,5-Me<sub>2</sub>PhN(Ad)H (12.9g, 50 mmol) in ether (250 mL) cooled at -80°C was treated with a solution of MeLi in ether (36mL, 1.4M, 50 mmol). The mixture was allowed to slowly warm up to room temperature while a white solid precipitated. After one hour stirring at room temperature, the solution was concentrated *in vacuo* and allowed to stand at room temperature. The resulting white precipitate was filtered under nitrogen (13.3 g, 39 mmol, 78%) and sealed in ampoules. The extreme air-sensitivity prevented obtaining reproducible results of combustion analysis. I.R. (nujol)  $\nu$ : 1573(s), 1350(w), 1324(s), 1297(s), 1179(s), 1091(s), 1064(s), 979(m), 899(w), 845(m), 801(s), 726(m), 706(w), 674(m).  $^1H$ -NMR ( $d^8$ -THF, 20°C, 500MHz)  $\delta$ : 5.79(s, 2H,  $C-H_{aromatic}$ ), 5.37(s, 1H,  $CH_{aromatic}$ ), 3.38(q, 4H,  $CH_2_{ether}$ ), 1.95(broad s, 6H, Me-Ph), 2.00(br s., 3H,  $CH_{adamantyl}$ ), 1.89(br. s, 6H,  $CH_{2adamantyl}$ ), 1.66(broad t, 6H,  $CH_{2adamantyl}$ ) 1.11(t, 6H,  $CH_3_{ether}$ ).  $^{13}C$ -NMR(  $d^8$ -THF, 20°C, 125MHz)  $\delta$ :160.69(quaternary, aromatic), 135.55(quaternary aromatic), 114.69(C-H aromatic), 108.12(aromatic C-H), 66.28(ether), 52.66(quaternary

adamantyl), 44.95(CH<sub>2</sub> adamantyl), 38.67(CH<sub>2</sub> adamantyl), 31.75(C-H adamantyl), 22.48(CH<sub>3</sub> aromatic), 15.65(CH<sub>3</sub> ether). <sup>7</sup>Li-NMR (d<sup>8</sup>-THF, 20°C, 194MHz) δ: 0.87

#### **Preparation of [3,5-Me<sub>2</sub>PhN(Ad)]<sub>3</sub>V (1)**

A suspension of Ad(3,5-Me<sub>2</sub>Ph)NLi.Et<sub>2</sub>O (4.3 g, 12.7 mmol) in toluene (100 mL) at 20°C was reacted with VCl<sub>3</sub>(THF)<sub>3</sub> (1.6 g, 4.3 mmol). After several color changes, the solution finally turned brownish-red. The reaction mixture was heated to about 70°C for an hour and subsequently stirred at 20°C for additional 10 hrs. The resulting dark greenish brown solution was evaporated to dryness, the residual solid redissolved in ether (120 mL) and the solution quickly filtered. The filtrate was stored at room temperature for a few hours until incipient crystallization and subsequently at -30°C to increase the yield. Dark green crystals of **1** separated (1.7 g, 2.0 mmol, 48%). El. Anal. Calcd (Found) for C<sub>54</sub>H<sub>72</sub>N<sub>3</sub>V: C 79.67(79.73), H 8.91(9.03), N 5.16(4.92). I.R. (nujol) ν: 1583(s), 1352(m), 1327(w), 1297(s), 1197(m), 1181(w), 1156(m), 1110(s), 1087(s), 1029(m), 992(s), 950(s), 924(s), 845(s), 823(s), 804(m), 689(s). μ<sub>eff</sub> = 2.72 μ<sub>B</sub>

#### **Preparation of [3,5-Me<sub>2</sub>PhN(Ad)]<sub>3</sub>V[CN(t-Bu)].Et<sub>2</sub>O (2)**

A solution of **1** (1.44g, 1.8 mmol) in toluene (65 mL) was treated with neat t-BuNC (0.15g, 1.8 mmol) at room temperature. The color slowly changed to dark brown-purple and finally to violet. After about 10 hrs stirring, the solution was evaporated *in vacuo* to dryness. The residual solid was redissolved in ether (80 mL) and the solution filtered, concentrated and allowed to stand at -30°C overnight, upon which violet microcrystals of **2** separated (1.12g, 66%). Anal Calcd (Found) for C<sub>63</sub>H<sub>91</sub>N<sub>4</sub>OV: C (77.88(77.45), H 9.46(9.32), N 5.77(6.00). I.R. (nujol) ν: 1583(s), 1350(m), 1302(m), 1288(s), 1207(w),

1184(w), 1150(m), 1106(m), 1081(s), 1025(w), 987(w), 949(m), 922(s), 846(m), 709(m), 689(s).  $\mu_{\text{eff}} = 2.78 \mu_{\text{B}}$

**Preparation of [3,5-Me<sub>2</sub>PhN(Ad)]<sub>3</sub>V(E).0.5Et<sub>2</sub>O [E = S(3a), Se(3b)]**

A greenish-brown solution of **1** (1.47g, 1.8 mmol) in toluene (80 mL) was treated with chalcogen (0.3 mmol). The color changed to the burgundy red, immediately in the case of sulfur, and more slowly in the case of selenium. After stirring overnight at room temperature the mixture was filtered and the solvent evaporated *in vacuo*. The solid residue was redissolved in ether to yield burgundy red crystals of **3** which were collected by filtration. A second crop of crystalline material was obtained upon allowing the mother liquor to stand in the freezer at -30°C.

**3a.** Yield 1.16g, 1.4 mmol, 76%. El. Anal. Calcd (Found) for C<sub>54</sub>H<sub>72</sub>N<sub>3</sub>VS.1/2Et<sub>2</sub>O: C 76.15(76.98), H 8.79(8.47), N 4.76(5.35). I.R. (nujol)  $\nu$ : 1599(m), 1585(m), 1352(w), 1342(w), 1299(s), 1185(w), 1145(m), 1103(m), 1051(s), 1025(m), 945(m), 925(s), 889(m), 850(w), 817(m), 728(m), 706(s), 691(s). <sup>1</sup>H-NMR (d<sup>8</sup>-toluene, 20°C, 500MHz)  $\delta$ : 7.21(s, 3H, CH<sub>aromatic</sub>), 6.67(s, 3H, CH<sub>aromatic</sub>), 4.58(s, 3H, CH<sub>aromatic</sub>), 3.24(q, 2H, ether), 2.56-2.25(dd, 18H, CH<sub>2</sub> adamantyl), 2.21(s, 9H, CH<sub>3</sub>) 2.20(s, 9H, CH adamantyl), 2.04(s, 9H, CH<sub>3</sub>), 1.73-1.62(dd, 18H, adamantyl), 1.12(t, 3H, ether). <sup>13</sup>C-NMR(d<sup>8</sup>-toluene, 20°C, 125.7MHz)  $\delta$ : 154.1, 136.6, 135.9(C<sub>quaternary</sub>, aromatic), 128.9, 127.7, 127.1(CH aromatic), 65.5(C<sub>quaternary</sub>, adamantyl), 46.1, 36.9(CH<sub>2</sub> adamantyl), 31.4(CH, adamantyl), 21.9, 21.3(CH<sub>3</sub>, aromatic). <sup>51</sup>V-NMR(d<sup>8</sup>-toluene, 20°C, 131.4MHz)  $\delta$ : 676.2.

**3b.** Yield 1.13 g, 1.3 mmol, 70%. El. Anal. Calcd (Found) for C<sub>54</sub>H<sub>72</sub>N<sub>3</sub>VSe.1/2Et<sub>2</sub>O: C 72.31(72.87), H 8.34(8.16), N 4.52(4.31). I.R. (nujol)  $\nu$ : 1599(m), 1584(m), 1351(w),

1341(w), 1298(s), 1285(m), 1262(w), 1184(w), 1145(w), 1102(m), 1047(s), 1025(m), 942(m), 923(s), 888(m), 850(w), 804(w), 728(m), 706(s), 690(s). <sup>1</sup>H-NMR (d<sup>8</sup>-toluene, 20°C, 500MHz) δ: 7.11(s, 3H, CH<sub>aromatic</sub>), 6.66 (s, 3H, CH<sub>aromatic</sub>), 4.50(s, 3H, CH<sub>aromatic</sub>), 3.25(q, 2H, ether), 2.58-2.25(dd, 18H, CH<sub>2</sub> adamantyl), 2.23(s, 9H, CH<sub>3</sub>) 2.16(s, 9H, CH adamantyl), 2.06(s, 9H, CH<sub>3</sub>), 1.73-1.61(dd, 18H, CH<sub>2</sub> adamantyl), 1.12(t, 3H, ether). <sup>13</sup>C-NMR(d<sup>8</sup>-toluene, 20°C, 125.7MHz) δ: 153.5, 136.5, 135.9(C<sub>quaternary</sub>, aromatic), 129.3, 128.1, 127.0(CH aromatic), 64.8(C<sub>quaternary</sub>, adamantyl), 46.5, 36.9(CH<sub>2</sub> adamantyl), 31.4(CH, adamantyl), 21.9, 21.3(CH<sub>3</sub>, aromatic). <sup>51</sup>V-NMR(d<sup>8</sup>-toluene, 20°C, 131.4MHz) δ: 1001.2.

### X-ray Crystallography

Data were collected at room temperature and at 233 and 111 K for **1** and **3a** respectively. Air-sensitive crystals were mounted on glass fibers inside a drybox and transferred under the liquid nitrogen stream of the cooling system of the X-ray diffractometer. The ω-2θ (**1**) and θ-2θ (**3a**) scan techniques were used. Cell constants and orientation matrices were obtained from the least-squares refinement of 25 and 24 centered reflections for **1** and **3a** respectively. The intensities of three standard reflections, measured after every 150 reflections, showed no statistically significant decay over the duration of the data collections. Data were corrected for Lorentz and polarization effects and for absorption (PSI scan). The structures were solved by direct methods resulting in locating all the non-hydrogen atoms. Their positions were refined anisotropically. Hydrogen atom positions were calculated but not refined. In the case of complex **3a** a disordered molecule of ether was found in the lattice. Failure to successfully model the disorder prevented the

convergence of the agreement factors to acceptable values. Nevertheless, the structure was sufficient to demonstrate the chemical connectivity. Refinements were carried out by using full-matrix least-squares techniques on  $F$  minimizing the function  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 4F_o^2/\sigma^2(F_o^2)$  and  $F_o$  and  $F_c$  are the observed and calculated structure factors. Atomic scattering factors and anomalous dispersion terms were taken from the usual sources.<sup>21</sup> Details on the data collections and structure refinement are listed in Table 3.1. The final atomic coordinates are given as Supplementary Material. Selected bond distances and angles are given in Table 3.2. List of atomic coordinates for both complexes are given as Supporting Information Available. All the calculations were performed on UNIX Silicon Graphics workstations by using the SHELXL and the NRCVAX structure solution and refinement packages.

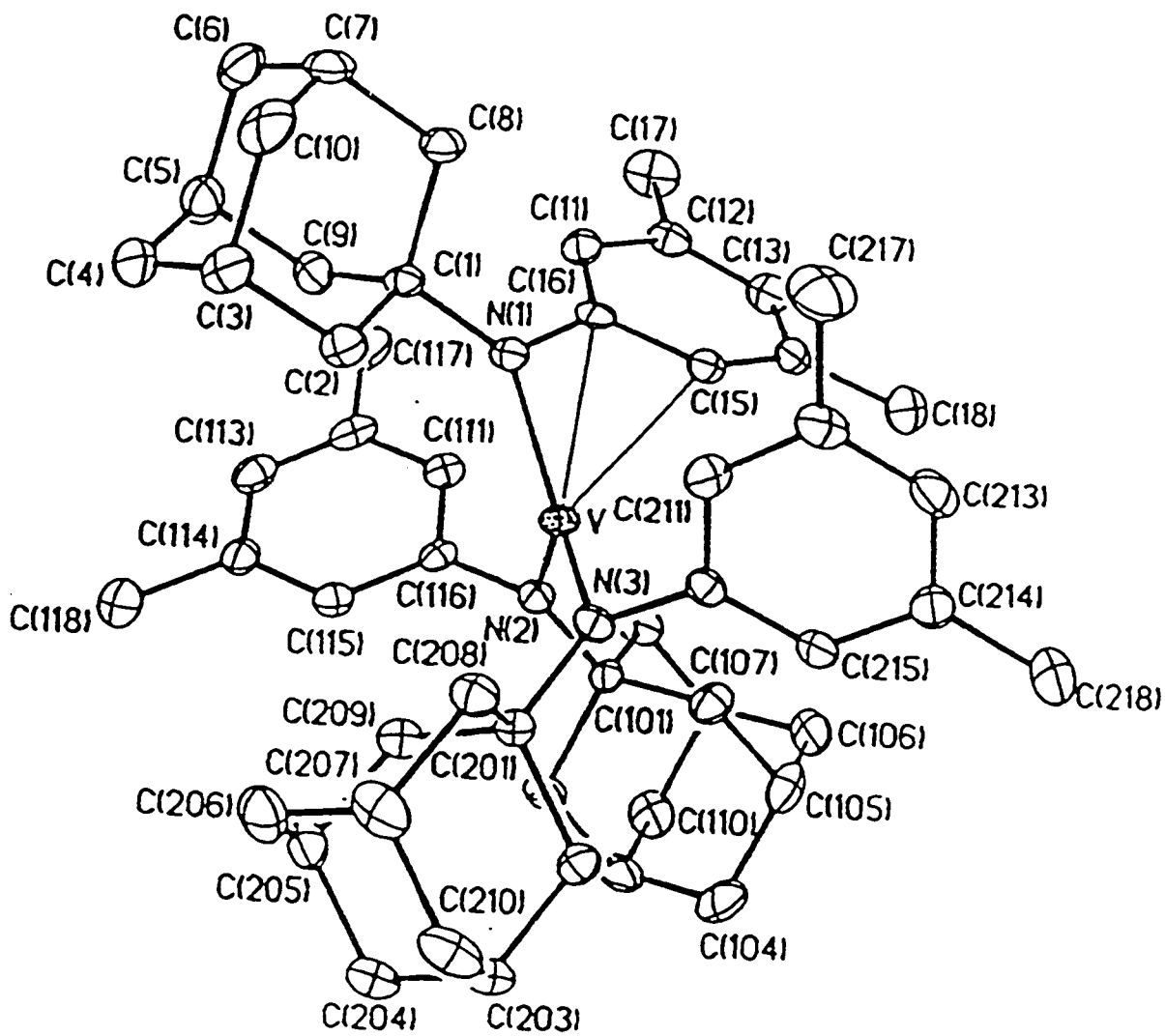


Figure 3 ORTEP plot of [3,5-Me<sub>2</sub>PhN(Ad)]<sub>3</sub>V. Thermal ellipsoids are drawn at the 50% probability level.

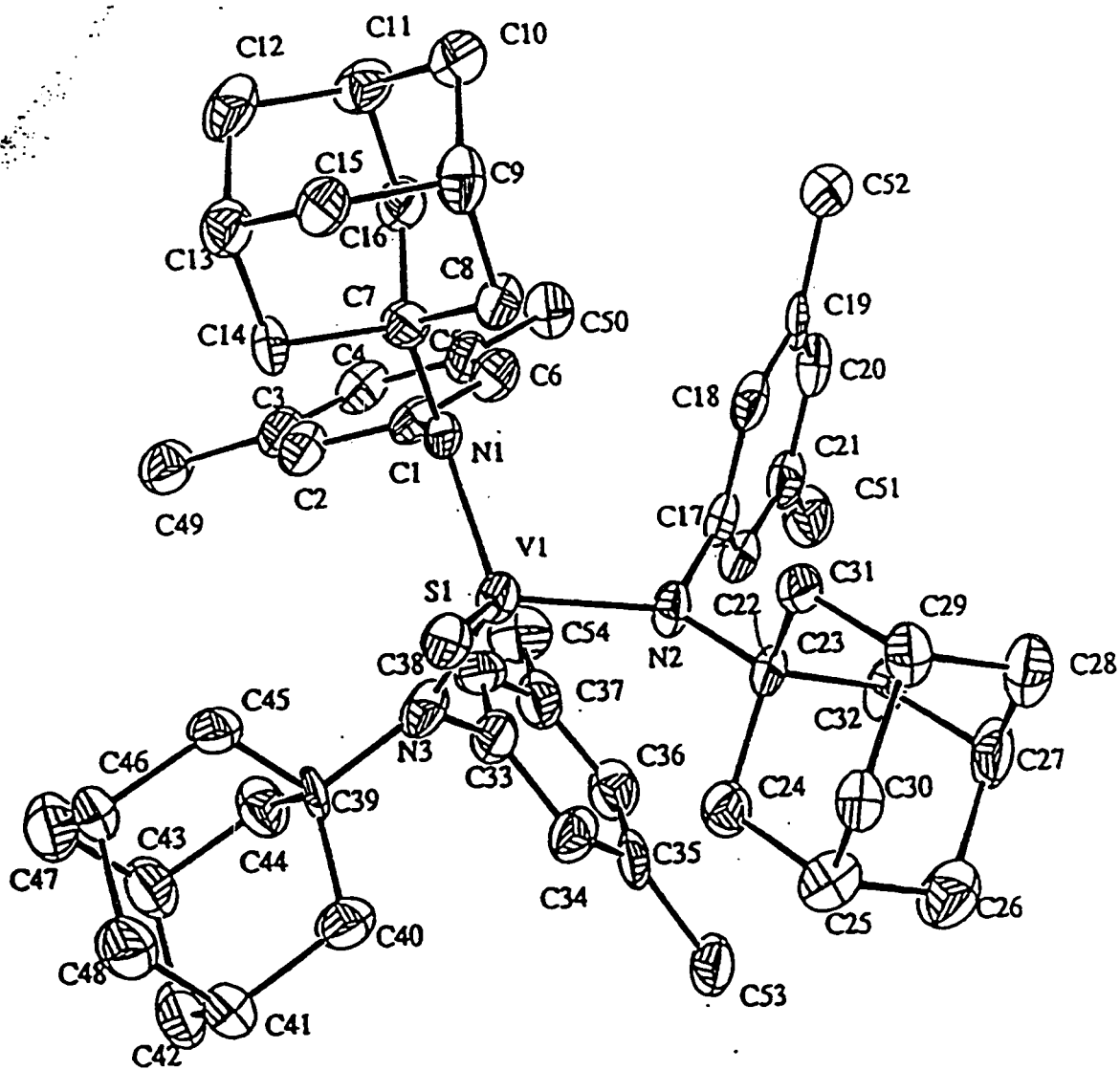


Figure 4 ORTEP plot of  $[3,5\text{-Me}_2\text{PhN(Ad)}]_3\text{V(E)}.0.5\text{Et}_2\text{O}$  [ $\text{E} = \text{S(3a)}$ ]. Thermal ellipsoids are drawn at the 50% probability level

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## Chapter 4

### Preparation and Characterization of $(R_2N)_2VCl_2$ [R = Cy, i-Pr] and its Activity as Olefin Polymerization Catalyst.

#### Introduction

The employment of group 4 metals and lanthanides plays a primary role in the vast literature of Ziegler-Natta catalysis.<sup>1</sup> This is mainly due to the distinct versatility of the metallocenic derivatives of these metals for which a wealth of synthetic methodologies were developed.<sup>2</sup> By contrast, limited information is available for the group 5 elements, in spite of the fact that a few medium and high valent vanadium complexes [ $VCl_4$ ,  $VOCl_3$  and  $V(acac)_3$ ] display, in conjunction with organoaluminum cocatalyst, a remarkable catalytic activity as Ziegler-Natta polymerization catalysts.<sup>3</sup> These species are currently used for the commercial production of ethylene-propylene-diene elastomers [EP(D)M].<sup>3s</sup> Vanadium compounds, although exhibiting lower catalytic activity than group 4 metal metallocene, display the advantage to perform well in a variety of oxidation states by producing polymers and copolymers with desirable physical properties and a high level of tacticity.<sup>4</sup> In contrast to this great potential, vanadium was largely ignored by the recent revival of interest for the new generation of Ziegler-Natta catalysts since the focus of the current polyolefin literature mainly remains on the employment of group 4 metals with a minor emphasis on lanthanides. Conversely, developing new vanadium-based Ziegler-Natta type catalysts may pose significant synthetic challenges, given that group 5 metallocene or cyclopentadienyl derivatives do not show a particularly strong inclination towards insertion reactions<sup>5</sup> (an obvious

prerequisite for Ziegler-Natta catalysis). Thus in an attempt to take advantage of the potential of vanadium as a Ziegler-Natta catalyst, this laboratory recently embarked on a project aimed to the development of new vanadium complexes containing anionic organic amides as ancillary ligands.<sup>6</sup> What is making this family of ligands particularly attractive is the possibility of fine tuning the electronic and steric features around the metal center through a virtually unlimited choice of the organic substituents attached to the nitrogen donor atom.

In this chapter the preparation of novel V(IV) amide complexes was described, as well as a preliminary study of their organometallic chemistry and utility for olefin polymerization.

## Results and Discussion

The reaction of  $\text{VCl}_3(\text{THF})_3$  with anionic organic amides forming a series of monomeric and dimeric bis-amide V(III)  $(\text{R}_2\text{N})_2\text{VCl}$  derivatives<sup>7</sup> was described recently. The fact that these complexes can be prepared in a rather straightforward manner via chlorine replacement reaction, implies that a mononuclear “(amide) $\text{VCl}_2$ ” complex is formed as a transient intermediate. In an attempt to isolate and characterize this intermediate species we have reacted  $\text{VCl}_3(\text{THF})_3$  with one equivalent of  $\text{R}_2\text{NLi}$  [ $\text{R} = i\text{-Pr}$ ,  $\text{Cy}$ ,  $\text{Bz}$ ]. The reaction proceeds forming an intense red color upon mixing. Dark orange crystals of  $(\text{R}_2\text{N})_2\text{VCl}_2$  [ $\text{R} = i\text{-Pr}$  (**1a**),  $\text{Cy}$  (**1b**)] were isolated after suitable work-up upon cooling their hexane solutions. The complexes are paramagnetic, moderately air sensitive and test positive for the presence of chlorine and negative for lithium. X-ray fluorescence

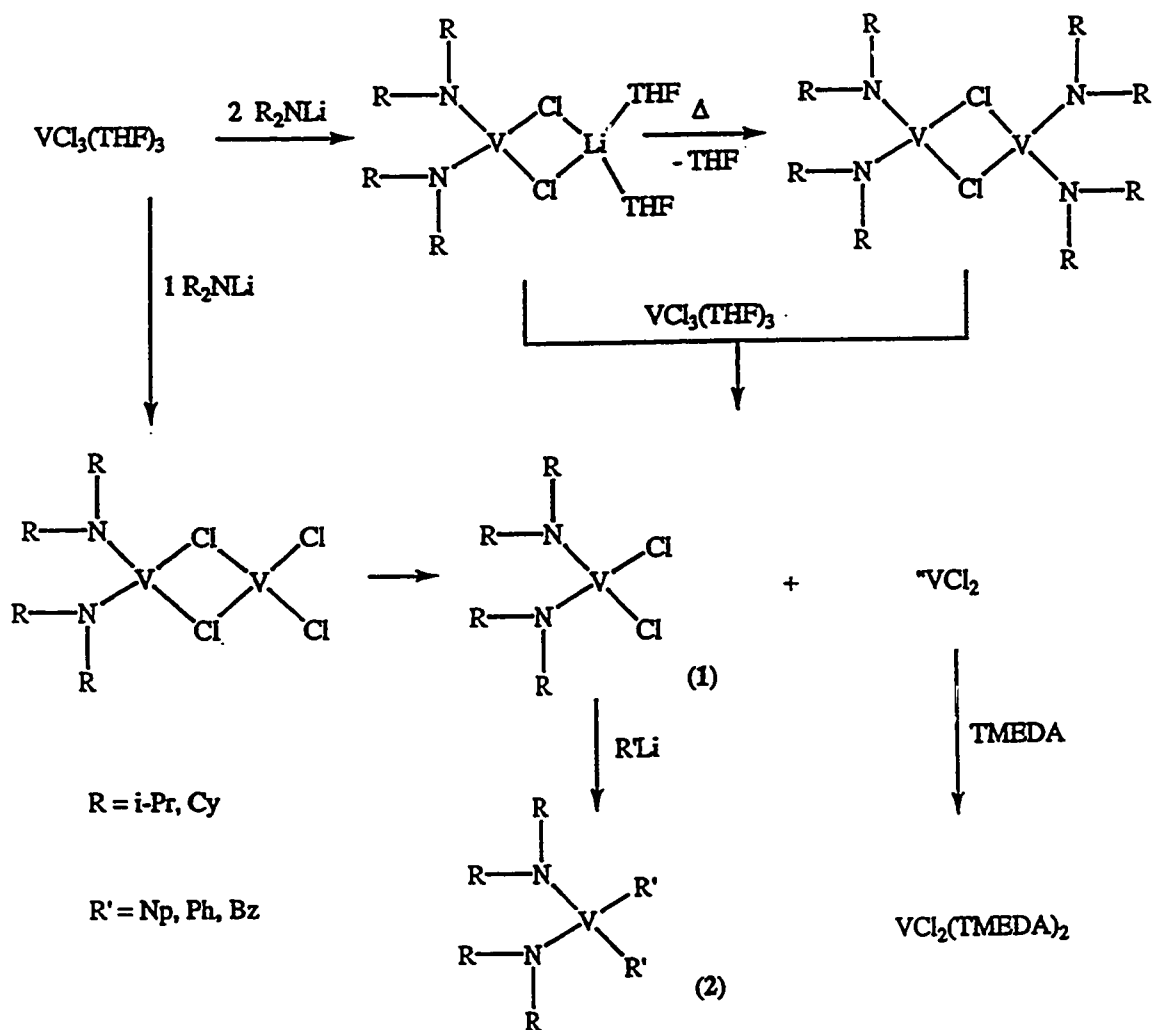
experiments yielded a 1:2 vanadium to chlorine ratio. Combustion analysis data were consistent with the proposed formulation while the magnetic moments, calculated on the basis of this formula, were always in agreement for the  $d^1$  electronic configuration of tetravalent vanadium.

The molecular connectivity and the formula were confirmed by a crystal structure obtained in the case of the cyclohexyl derivative **1b**. The complex is monomeric and is formed by a vanadium atom surrounded by two amide groups and two chlorine atoms which impose a distorted tetrahedral coordination geometry to the metal center [N1-V1-Cl1 = 105.0(2)°, N1-V1-N2 = 106.8(2)°, N1-V1-Cl2 = 113.6(2)°, N2-V1-Cl2 = 104.0(2)°, N2-V1-Cl1 = 114.2(2)°] (Figure 1). The V-Cl distances [V1-Cl1 = 2.256(2)Å, V1-Cl2 = 2.217(2)Å] and angles [Cl1-V1-Cl2 = 113.3(1)°] fall in the expected range. As usual, the coordination geometry around the amide nitrogen is trigonal planar [V1-N1-C1 = 124.8(4)°, V1-N1-C7 = 120.1(4)°] which, together with the short V-N distances [V1-N1 = 1.808(5)Å, V1-N2 = 1.834(5)Å], suggests the presence of a significant extent of V-N double bond.

The formation of a tetravalent vanadium from a trivalent starting material is rather surprising given that anionic organic amides are well known to act as reducing agents<sup>8</sup> and are able to stabilize low-valent states.<sup>9</sup> Therefore, the formation of these species by disproportionation needs explanations, perhaps similar to that observed in the case of dinuclear Zr(III) derivatives.<sup>10</sup> In this event, a V(II) species [probably  $VCl_2(THF)_x$ ] should be formed as byproduct of the reaction. To probe this possibility, I have treated the reaction mixture with TMEDA. The treatment produces a light blue crystalline solid in

low yet significant yield which was identified as  $\text{VCl}_2(\text{TMEDA})_2$  by comparison of the spectroscopic properties with those of an analytically pure sample.

The simplest way of envisioning the process and accounting for these observations is through the reaction sequence depicted in Scheme 4.1.



Scheme 4.1

The reaction may be explained by assuming the formation of an asymmetric dinuclear intermediate which undergoes slow and spontaneous cleavage to produce the two V(IV) and V(II) moieties. The stability of the two species is likely to be the thermodynamic driving force for the cleavage of the dinuclear structure. In agreement with this hypothesis, the reaction of both  $[(R_2N)_2V(\mu-Cl)]_2$  and  $(R_2N)_2V(\mu-Cl)_2Li(THF)_2$  with  $VCl_3$  also gave similar yield of  $(R_2N)_2VCl_2$ . Even in this case “ $VCl_2$ ” was isolated and identified as  $VCl_2(TMEDA)_2$  after treating the reaction mixture with TMEDA.

Attempts to replace the chlorine atoms in **1** with alkyl functions were carried out with a few alkyl lithium reagents. The reactions of **1** and RLi proceeded rapidly at  $-10^\circ C$  in ether or hexane to produce the corresponding dialkyl derivatives  $(R_2N)_2VR_2$  [R = Np (**2a**), Ph (**2b**), Bz (**2c**)]. All these compounds were isolated in crystalline form as dark brown air sensitive materials. All the compounds tested negative for chlorine, thus confirming that both the chlorine atoms were replaced and satisfactory combustion analysis data in agreement with the proposed formulation were obtained for all the compounds. The magnetic moments were in all cases in agreement with the  $d^1$  electronic configuration expected for a V(IV) species. Compounds **2** are only moderately stable at room temperature, and rapidly decompose at about  $60^\circ C$  to form new species whose structure is currently under investigation.

In the case of the neopentyl derivative, the molecular connectivity was elucidated by an X-ray crystal structure. The structure consists of a distorted tetrahedral vanadium center [N1-V1-N2 =  $117.5(1)^\circ$ , N1-V1-C25 =  $110.1(1)^\circ$ , N1-V1-C30 =  $106.0(1)^\circ$ , N2-V1-C25 =  $105.6(1)^\circ$ , N2-V1-C30 =  $111.3(1)^\circ$ , C25-V1-C30 =  $105.8(1)^\circ$ ] surrounded by

two nitrogen atoms of the two amides and two alkyl groups (Figure 2). The V-N distances are normal [V1-N1 = 1.877(2)Å, V1-N2 = 1.878(2)Å] and compare well with those of the dichloro derivative **1b**. The V-C distances are also in the expected range [V1-C25 = 2.088(3)Å, V1-C30 = 2.095(3)Å]. The coordination geometry around the nitrogen atom is trigonal planar as expected [V1-N1-C1 = 127.1(2)°, V1-N1-C7 = 115.9(2)°, C1-N1-C7 = 116.9(2)°].

Not surprisingly, complexes **2** did not display any significant olefin polymerization activity under the usual reaction conditions. Just a violent reaction was observed with butadiene leading to the formation of a viscous polymer. Even in attempt to improve reactivity by treatment with Lewis acids such as VCl<sub>3</sub> or (F<sub>5</sub>C<sub>6</sub>)<sub>3</sub>B did not modify the inertness of this system toward polymerization. Conversely, simple treatment of **2** with anhydrous AlCl<sub>3</sub> gave an active polymerization catalyst (188 Kg of polyethylene per mole of catalyst per hour at a maximum pressure of 1 bar). These results clearly show that the concomitant presence of both vanadium and aluminium is indeed necessary to produce catalytic activity. Accordingly, complexes **1** act as ethylene polymerization catalysts at room temperature and under one atmosphere of ethylene while in conjunction with a wide variety of aluminum alkyl cocatalysts (Me<sub>3</sub>Al, Et<sub>3</sub>Al, EtAlCl<sub>2</sub>, Et<sub>1.5</sub>AlCl<sub>1.5</sub>, *i*-BuAlCl<sub>2</sub>). I have observed that upon mixing the catalyst with the cocatalyst, an immediate color change occurred in the hexane solution, suggesting that the coordination sphere of the vanadium atom was modified by the interaction with the aluminium cocatalyst. Unfortunately, attempts to isolate and characterize the catalytically active species led to highly pyrophoric microcrystalline catalysts in good yield, whereas efforts

to grow crystals of suitable size for crystal structure determination were so far unsuccessful.

By using the most effective catalyst/cocatalyst system, the production of PE reached the amount of about 265 Kg of polymer per mole of catalyst per hour at 1 bar. After the initial production of ethylene during the first 15-30 minutes, the reaction proceeded at a low steady rate for about 20 hours, when no further production of PE was observed. This indicates that the catalyst was probably deactivated. Addition of chlorinated hydrocarbon (BzCl, ClCH<sub>2</sub>CH<sub>2</sub>Cl or CHCl<sub>3</sub>) to the reaction mixture, followed by addition of the cocatalyst, restarted the polymerization. The deactivation of vanadium Ziegler Natta catalysts is commonly ascribed to the reduction of the metal center (probably through  $\beta$ -H elimination) towards formation of divalent species.<sup>3</sup> However, homopolymerization of ethylene with trivalent  $(R_2N)_2V(\mu-Cl)_2Li(THF)_2$  or  $[(R_2N)_2V(\mu-Cl)]_2$ <sup>7</sup> did not give any appreciable polymerization reaction, while treatment of these complexes with halogenated hydrocarbons formed the tetravalent  $(R_2N)_2VCl_2$  catalyst. On the basis of these observations, I tentatively suggest that the catalyst deactivation in my system is probably caused by the reduction of  $(R_2N)_2VCl_2$  to the corresponding trivalent species.

Complexes 1 were tested for ethylene-propylene copolymerization activity with a series of  $AlR_xCl_{(3-x)}$  under 2 bar pressure. The results are shown in Table 1. Under the conditions employed, activity was negligible with Et<sub>3</sub>Al but increased with increasing chlorine content. The activity reached a maximum with Et<sub>2</sub>AlCl<sub>3</sub>, which makes this species a promising catalyst for the production of elastomers. The FTIR spectrum (Figure

3) is typical of a random copolymer as evidenced by the fingerprint region from 700 to 1200  $\text{cm}^{-1}$ . The ethylene content, evaluated via IR spectroscopy by using the ratio of peak heights of the two resonances at 1155 and 720  $\text{cm}^{-1}$  after calibration with known standards according to ASTM procedure D-3900, was typically in the range 71-73%. In a typical experiment carried out on  $(i\text{-Pr}_2\text{N})_2\text{VCl}_2$  and aluminum sesquichloride as a cocatalyst, the molecular weight was significantly high ( $M_w = 2,293,000$ ,  $M_w/M_n = 3.0$ ).

### **Experimental Section**

All operations were performed under inert atmosphere by using standard Schlenk techniques.  $\text{Cy}_2\text{NLi}^{11}$  and  $(i\text{-Pr})_2\text{NLi}^{12}$  were prepared according to published procedures. Alkyl lithium derivatives were prepared according to standard procedures. Ethylene, propylene (Matheson) were dried over a column of molecular sieves. Aluminum alkyl solutions in hexane (Aldrich) were used as received. Infrared spectra were recorded on a Mattson 9000 FTIR instrument from Nujol mulls prepared in a dry-box. Samples for magnetic susceptibility measurements were weighed inside a dry-box equipped with an analytical balance, and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature. The magnetic moments were calculated following standard methods,<sup>13</sup> and corrections for underlying diamagnetism were applied to data.<sup>14</sup> Elemental Analyses were carried out with a Perkin Elmer 2400 CHN analyzer. Ratios between heavy atoms were determined by X-ray fluorescence by using a Philips 2400 instrument.

Evaluation of the catalysts was carried out using ethylene-propylene copolymerization in hexane solution at 2 bar total pressure and 22°C. Polymerization were carried out in

200 mL of hexane in magnetically agitated glass reactors at 2 bar pressure using a continuous flow of 1000 sccm ethylene and 1000 sccm propylene. After equilibration of the hexane with the EP feed at 22°C, 0.2 mmole of cocatalyst were added followed by the addition of 5µmole vanadium catalyst. These conditions gave a final concentration of 25µM [catalyst] and 40/1 Al/V. Polymerization was carried out for 15 minutes followed by addition of 2 mL ethanol and depressurization. The EP rubber was recovered by solvent evaporation.

### Synthesis of (i-Pr<sub>2</sub>N)<sub>2</sub>VCl<sub>2</sub> (1a)

A suspension of VCl<sub>3</sub>(THF)<sub>3</sub> (1.07 g, 2.8 mmol) in THF (75 mL) was treated at room temperature with freshly prepared i-Pr<sub>2</sub>NLi (0.33 g, 3.0 mmol). The color immediately turned dark red. After stirring overnight at room temperature, the solvent was evaporated in vacuo. The residual oil was redissolved in hexane (100 mL) and the resulting suspension filtered, concentrated to small volume and allowed to stand at -78°C. Dark red crystals of (i-Pr<sub>2</sub>N)<sub>2</sub>VCl<sub>2</sub> (0.33 g, 1.0 mmol, 71 % based on Liamide) separated. IR (Nujol mull, cm<sup>-1</sup>) ν: 2897(br), 2687(br), 1457(s), 1372(s), 1338(m), 1261(w), 1185(w), 1145(m), 1124(m), 1101(s), 970(w), 924(w), 859(w), 814(w), 780(w), 723(w). El. Anal. Calcd (found) for C<sub>12</sub>H<sub>28</sub>N<sub>2</sub>Cl<sub>2</sub>V : C 44.73(44.70), H 8.76(8.72), N 8.69(9.10).  $\mu_{\text{eff}} = 1.89 \mu_{\text{B}}$ .

### Synthesis of (Cy<sub>2</sub>N)<sub>2</sub>VCl<sub>2</sub> (1b)

Method A. Freshly prepared Cy<sub>2</sub>NLi (0.47 g, 2.83 mmol) was added to a red suspension of VCl<sub>3</sub>(THF)<sub>3</sub> (1.05 g, 2.81 mmol) in THF (75 mL) at room temperature. The color immediately turned dark red and the resulting solution was stirred overnight at room

temperature. After evaporation of the solvent to dryness, hexane (100 mL) was added to the oily residue. The resulting suspension was filtered and the solution was concentrated to small volume. Dark red crystals of  $(\text{Cy}_2\text{N})_2\text{VCl}_2$  (0.57 g, 1.2 mmol, 42%) were separated after allowing the red solution to stand at  $-30^\circ\text{C}$  for two days. IR (Nujol mull,  $\text{cm}^{-1}$ )  $\nu$ : 2907(br), 2690(w), 1455(s), 1376(s), 1342(m), 1258(w), 1145(vw), 1136(m), 1077(m), 1026(m), 954(m), 889(m), 842(m), 804(m), 784(w), 723(w). El. Anal. Calcd (found) for  $\text{C}_{24}\text{H}_{44}\text{N}_2\text{Cl}_2\text{V}$  : C 59.75(60.41), H 9.19(9.50), N 5.81(6.02)  $\mu_{\text{eff}} = 2.00 \mu_{\text{B}}$ .

Method B. Brown solid  $[(\text{Cy}_2\text{N})_2\text{VCl}]_2$  (1.7 g, 1.9 mmol) was added to a red suspension of  $\text{VCl}_3(\text{THF})_3$  (1.46 g, 3.9 mmol) in THF (100 mL) at room temperature. The color turned instantaneously dark red. After evaporation of the solvent in vacuo, the dark red oil was dissolved in hexane (75 mL). Dark red crystals of **1b** [1.7 g, 3.6 mmol, 90 % based on  $\text{VCl}_3(\text{THF})_3$ ] were obtained after allowing the red solution to stand at  $-30^\circ\text{C}$  overnight.

Method C. Solid  $\text{Cy}_2\text{NLi}$  (4.45 g, 23.7 mmol) was added to a suspension of  $\text{VCl}_4(\text{dme})$  (3.3 g, 11.8 mmol) in THF (100 mL) at  $-78^\circ\text{C}$ . The color gradually changed to the purple brown and after 8 hrs stirring at room temperature, the solvent was removed in vacuo. The residue was extracted with hexane and filtered to remove LiCl. The filtrate was allowed to stand at  $-30^\circ\text{C}$  overnight yielding dark brown crystals of **1b** (3.1 g, 6.4 mmol, 55%). The compound was identified by comparison of the analytical and spectroscopic data of an analytically pure sample.

### **Isolation of $\text{VCl}_2(\text{TMEDA})_2$**

Method A. Solid  $\text{Cy}_2\text{NLi}$  (0.95 g, 5.7 mmol) was added to a red suspension of  $\text{VCl}_3(\text{THF})_3$  (1.78 g, 4.76 mmol) in THF (75 mL) at room temperature. The color turned dark red. After stirring for 30 minutes, the addition of TMEDA (1.45 mL, 9.61 mmol) to the dark red solution did not cause any significant color change. After evaporation of the solvent to dryness, hexane (75mL) was added to the dark residue. The addition of hexane caused the precipitation of a light blue solid mixed with a light brown solid. After filtration the mixed solid was recrystallized from THF affording analytically pure light blue crystals of  $\text{VCl}_2(\text{TMEDA})_2$  (35%) which were identified by comparison of the spectroscopic data with those of an analytically pure sample.

Method B. Freshly distilled TMEDA (0.82 mL, 5.3 mmol) was added to a red suspension of  $\text{VCl}_3(\text{THF})_3$  (1.00 g, 2.7 mmol) in THF (75 mL) at room temperature. Addition of solid  $\text{Cy}_2\text{NLi}$  (0.51 g, 3.0 mmol) to the resulting violet solution turned the color light brown. After evaporation of the solvent *in vacuo*, the addition of diethyl ether (75 mL) caused the precipitation of a light blue microcrystalline  $\text{VCl}_2(\text{TMEDA})_2$  (0.71g, 2.0 mmol, 74%) which was identified by comparison of the spectroscopic data with those of an analytically pure sample.

### **Synthesis of $(\text{Cy}_2\text{N})_2\text{VNp}_2 \cdot 1/4\text{hexane}$ (2a)**

Solid  $\text{NpLi}$  (0.33 g, 4.22 mmol) was added to a dark red solution of  $(\text{Cy}_2\text{N})_2\text{VCl}_2$  (0.98 g; 2.0 mmol) in hexane (75 mL) at room temperature. The color slightly turned dark orange and the resulting solution was stirred overnight at room temperature. After

filtration of LiCl, the solution was concentrated to 20-30 mL and allowed to cool down to -30°C overnight. Dark crystals of  $(\text{Cy}_2\text{N})_2\text{VNp}_2$  (0.23 g, 0.46 mmol, 23%) were separated. IR (Nujol mull,  $\text{cm}^{-1}$ ): 2905(s), 2689(w), 1456(s), 1375(sh), 1230(w), 1093(m), 1026(m), 956(sh), 891(w), 843(m), 802(m), 722(sh). El. Anal. Calcd (found) for  $\text{C}_{34}\text{H}_{66}\text{N}_2\text{V}\cdot 1/4\text{hexane}$  : C 73.90(73.56), H 12.23(12.01), N 4.92(4.66)  $\mu_{\text{eff}} = 1.85 \mu_{\text{B}}$ .

### Synthesis of $(\text{Cy}_2\text{N})_2\text{VPh}_2$ (2b)

Solid PhLi (0.29 g, 3.45 mmol) was added to a dark red solution of  $(\text{Cy}_2\text{N})_2\text{VCl}_2$  (0.66 g; 1.37 mmol) in hexane (75 mL) at room temperature. The color slightly turned dark orange and the resulting solution was stirred overnight at room temperature. After filtration of LiCl, the solution was concentrated to about 25 mL and allowed to stand at -30°C overnight. Dark microcrystalline solid of  $(\text{Cy}_2\text{N})_2\text{VPh}_2$  (0.58 g, 1.0 mmol, 73%) were separated. IR (Nujol mull,  $\text{cm}^{-1}$ ): 2907(br), 2692(w), 1457(s), 1447(vw), 1376(sh), 1366 (vw), 1260(m), 1100(vw), 1090(vw), 1080(vw), 1070(m), 1059(vw), 1038(m), 960(shw), 891(w), 813(vw), 803(m), 722(sh), 698(sh). El. Anal. Calcd (found) for  $\text{C}_{36}\text{H}_{54}\text{N}_2\text{V}$ : C 76.42(76.11), H 9.62(9.38), N 4.95(4.88).  $\mu_{\text{eff}} = 1.80 \mu_{\text{B}}$ .

### Synthesis of $(\text{Cy}_2\text{N})_2\text{VBz}_2$ (2c)

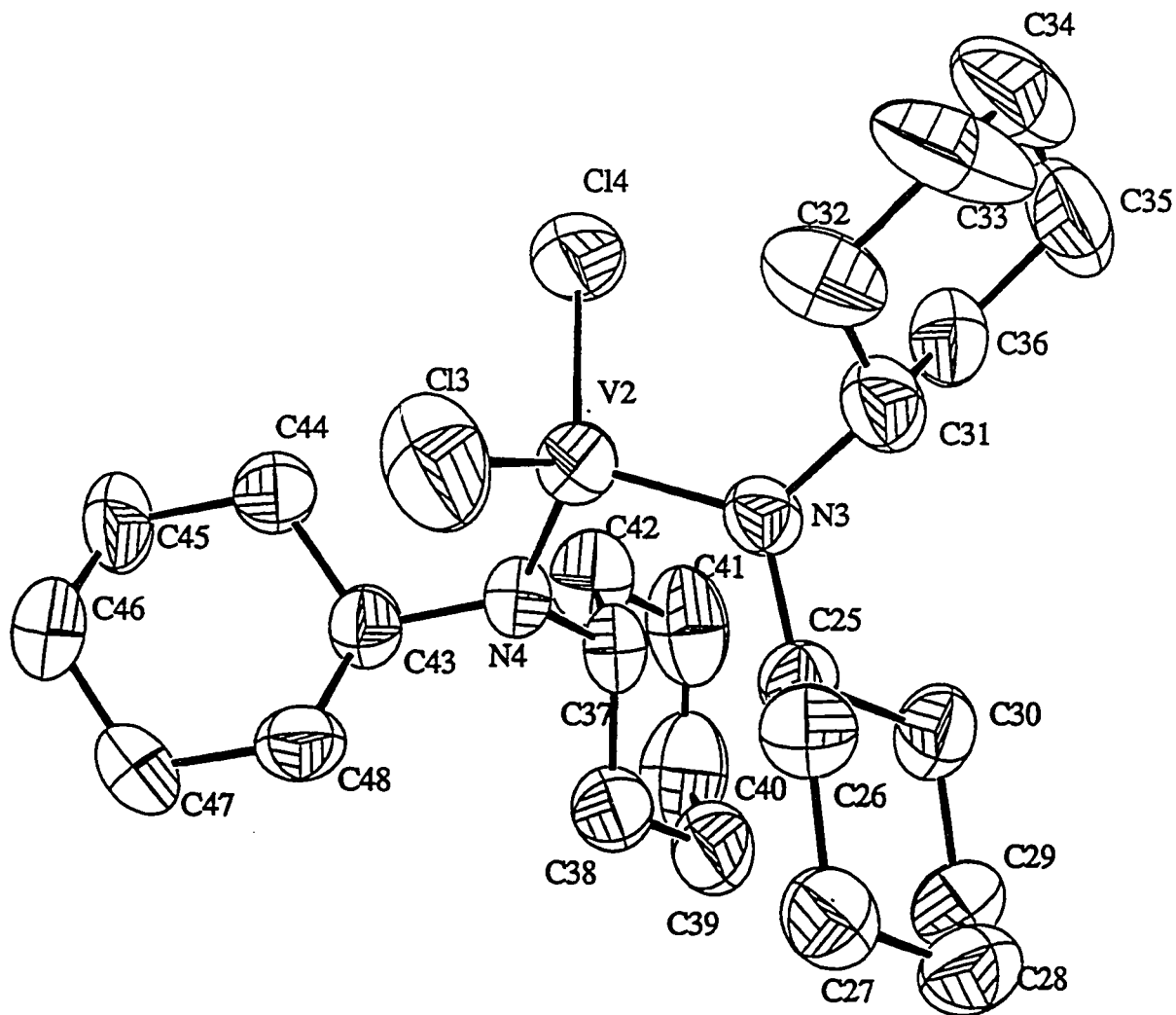
A solution of BzMgCl (5.8 mL, 5.8 mmol, 1M in ether) was added to a dark red solution of  $(\text{Cy}_2\text{N})_2\text{VCl}_2$  (1.4 g; 2.9 mmol) in hexane (75 mL) at room temperature. The color

turned brownish orange and the resulting solution was stirred overnight at room temperature. After filtration of LiCl, the solution was concentrated to 20-30 mL and allowed to stand at -30°C overnight. Dark microcrystalline solid of  $(\text{Cy}_2\text{N})_2\text{VBz}_2$  (0.9 g, 1.5 mmol, 52 %) were separated. IR (Nujol mull,  $\text{cm}^{-1}$ ): El. Anal. Calcd (found) for  $\text{C}_{38}\text{H}_{58}\text{N}_2\text{V}$  : C 76.86(76.66), H 9.85(9.69), N 4.72(4.61).  $\mu_{\text{eff}} = 1.77 \mu_{\text{B}}$ .

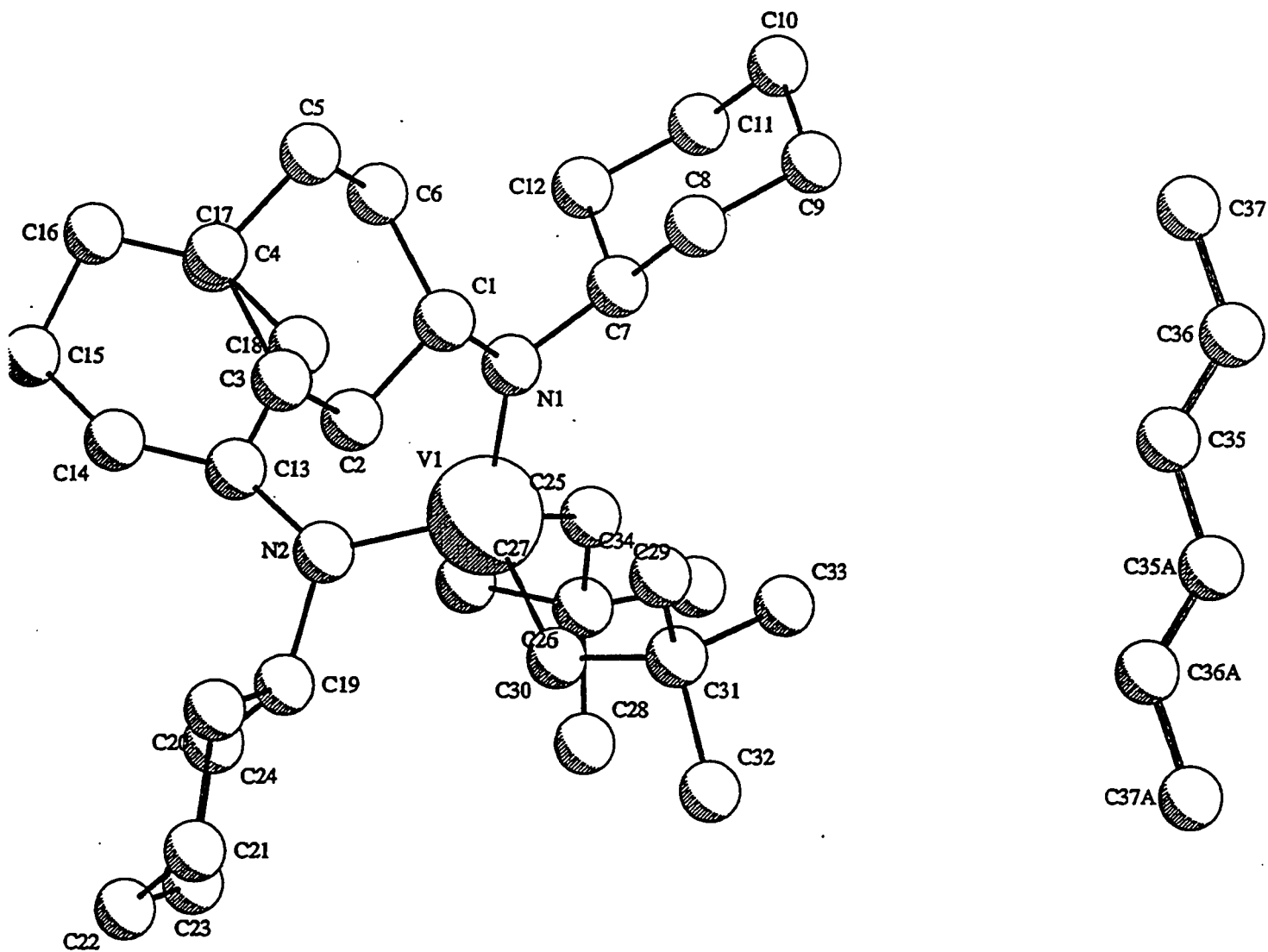
### X-ray crystallography

Data were collected at -153°C for a suitable air-sensitive crystals mounted on a glass fiber inside a drybox and transferred under the liquid nitrogen stream of the cooling system of either Nonius CAD-4 or Siemens CCD X-ray diffractometers. The  $\omega$ -2 $\theta$  scan technique was used. Data were collected until 100 deg of 2 $\theta$  for **1b** (Cu radiation) and to 57.0 deg. for **2a** (Mo radiation). Cell constants and orientation matrices were obtained from the least-squares refinement of 25 centered reflections. The intensities of three standard reflections, measured after every 150 reflections, showed no statistically significant decay over the duration of the data collections. Data were corrected for Lorentz and polarization effects and for absorption (PSI scan). The structures were solved by direct methods resulting in locating all the non-hydrogen atoms. Their positions were refined anisotropically. Hydrogen atom positions were calculated but not refined. Complex **1b** contains two crystallographically independent and nearly identical molecules in the lattice while complex **2a** has one disordered molecule of hexane per unit

cell. Attempts to model the disorder did not improve the thermal parameters and the quality of the refinement. The data were processed using the NRCVAX software packages on a Silicon Graphics workstation. Refinements were carried out by using full-matrix least-squares techniques on  $F$  minimizing the function  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 4F_o^2/\sigma^2(F_o^2)$  and  $F_o$  and  $F_c$  are the observed and calculated structure factors. Atomic scattering factors and anomalous dispersion terms were taken from the usual sources (Cromer & Waber).<sup>15</sup> Details on the data collections and structure refinement are listed in Table 4.2. The final atomic coordinates are given as Supplementary Material. Selected bond distances and angles are given in Table 4.3.



**Figure 5.** Thermal ellipsoid plot of  $(C_{12}H_{16}N_2)VCl_2$  1b. Thermal ellipsoids are drawn at the 50% probability level.



**Figure 6.** Thermal ellipsoid plot of  $(\text{C}_7\text{H}_{15}\text{N})_2\text{VNp}_2$  2a. Thermal ellipsoids are drawn at the 50% probability level.

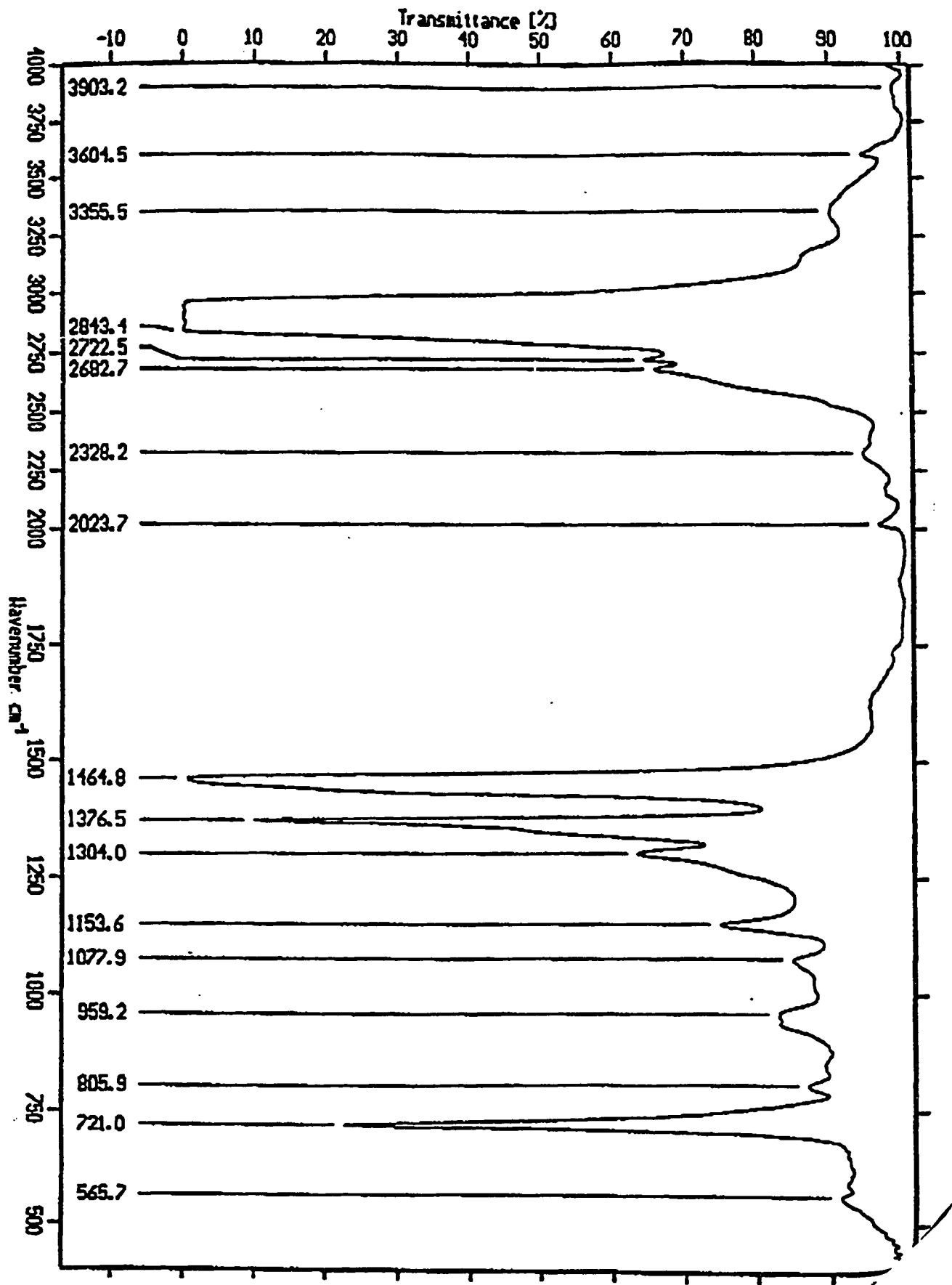


Figure 7. FTIR of the EP copolymer.

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### **Aim For Further Research**

Since the polymerization of ethylene has been achieved by titanium systems, several other transition metals have been used for the same goal. Among the transition metals employed in olefin catalysis, vanadium occupies an important place. The soluble Ziegler-Natta catalyst  $V(acac)_3$  [ $acac = acetylacetonato$ ] and  $Al(CH_2CH_3)_2Cl$  is widely used in industry for the production of rubber. Vanadium complexes containing chelating acetylacetonato ligand or amide ligands provide interesting examples for further investigations of their catalytic behavior by combining the properties of the chelating  $acac$  and those of amide ligands.

The question remaining is, what is the active species involved in the catalysis. To be able to answer that question, more studies are needed to understand and isolate the active species. For that particular goal, the emphasis should be put on the chemistry of vanadium alkyls since they are assumed to be intermediates during the catalytic process.

APPENDIX

**Table 3.1 Crystal Data and Structure Analysis Results**

	[3,5-Me <sub>2</sub> PhN(Ad)] <sub>3</sub> V	[3,5-Me <sub>2</sub> PhN(Ad)] <sub>3</sub> V=S
formula	C <sub>54</sub> H <sub>72</sub> N <sub>3</sub> V	C <sub>54</sub> H <sub>72</sub> N <sub>3</sub> VS.1/2 Et <sub>2</sub> O
formula weight	814.09	883.25
space group	triclinic, P-1	monoclinic C2/c,
a (Å)	10.441(1)	43.400(9)
b (Å)	11.648(4)	11.744(3)
c (Å)	19.321(2)	20.705(4)
α (deg)	83.69(2)	
β (deg)	83.89(1)	113.05(1)°,
γ (deg)	82.42(2)	
V (Å <sup>3</sup> )	2306.15(7)	9733(4)
Z	2	8
Radiation (Kα Å)	0.71073	1.54056
T (°K)	233	111
D <sub>calcd</sub> (g cm <sup>-3</sup> )	1.173g	1.208
μ <sub>calcd</sub> (cm <sup>-1</sup> )	2.54	24.1
F <sub>000</sub>	880	3815
R, R <sub>w</sub> <sup>2</sup> , G.o.F	0.0468, 0.0998, 0.96	0.082, 0.103(R <sub>w</sub> ), 2.35

$$R = \frac{\sum |F_o| - \sum |F_c|}{\sum |F_o|} \quad R_w = \left[ \frac{\sum (|F_o| - |F_c|)^2}{\sum w F_o^2} \right]^{1/2}$$

**Table 3.2** Selected Bond Distances (Å) and Angles (deg) for [3,5-Me<sub>2</sub>PhN(Ad)]<sub>3</sub>V (1) and [3,5-Me<sub>2</sub>PhN(Ad)]<sub>3</sub>V=S (3a).

1	3a
V-N1 = 1.945(3),	V1-S1 = 2.045(3)
V-N2 = 1.905(3),	V1-N1 = 1.897(6)
V-N3 = 1.900(3),	V1-N2 = 1.893(6)
V-C16 = 2.399(4),	V1-N3 = 1.885(7)
V-C15 = 2.425(4),	S1-V1-N1 = 108.7(2)
N1-V-N2 = 122.0(1),	S1-V1-N2 = 107.0(2)
N1-V-N3 = 118.1(1),	S1-V1-N3 = 109.3(2),
N2-V-N3 = 117.6(1),	N1-V1-N2 = 111.7(3),
V-N1-C16 = 90.6(2),	N1-V1-N3 = 108.7(3),
N1-C16-C15 = 114.4(3),	N2-V1-N3 = 111.3(3),
V-N2-C116 = 110.7(2),	C1-N1-C7 = 113.5(6),
N2-C116-C111 = 121.2(4),	V1-N1-C1 = 115.6(5),
V-N3-C216 = 114.0(2),	V1-N1-C7 = 130.0(5)
N3-C216-C211 = 119.8(3),	
V-N1-C1 = 141.0(2),	
V-N2-C101 = 130.9(3),	
V-N3-C201 = 129.1(2),	
C1-N1-C16 = 125.2(3),	

C101-N2-C116 = 118.2(3),

C201-N3-C216 = 116.1(3).

**Table 4.1 Ethylene-Propylene Copolymerization Activity of  $(R_2N)_2VCl_2$**

Catalyst $(R_2N)_2VCl_2$	Co-catalyst	Activity kg EP/mole V/hr	Composition wt% Ethylene
R = i-Pr	$Et_3Al$	24	
	$Et_2AlCl$	80	-
	$Et_{1.5}AlCl_{1.5}$	860	73
	$EtAlCl_2$	330	71
R = Cy	$Et_3Al$	40	
	$Et_2AlCl$	135	73
	$Et_{1.5}AlCl_{1.5}$	330	73
	$EtAlCl_2$	140	

**Table 4.2** Crystal Data and Structure Analysis Results for (Cy<sub>2</sub>N)<sub>2</sub>VCl<sub>2</sub> (**1b**) and (Cy<sub>2</sub>N)<sub>2</sub>VNp<sub>2</sub> (**2a**)

	<b>1b</b>	<b>2a</b>
formula	C <sub>24</sub> H <sub>44</sub> N <sub>2</sub> VCl <sub>2</sub>	C <sub>34</sub> H <sub>66</sub> N <sub>2</sub> V.1/4C <sub>6</sub> H <sub>14</sub>
formula weight	482.48	575.39
space group	<i>Pbna</i>	<i>P21/a</i>
a (Å)	15.669(4) <sup>④</sup>	17.7491(2)
b (Å)	36.004(1) <sup>④</sup>	10.6826(2)
c (Å)	18.871(4) <sup>④</sup>	20.8487(3)
β (deg)		109.479(1) <sup>④</sup>
V (Å <sup>3</sup> )	10646(4) <sup>④</sup> <sup>3</sup>	3726.8(1)
Z	8	4
Radiation (Kα Å)	1.54056	0.70930
T (°C)	-153	-153
D <sub>calcd</sub> (g cm <sup>-3</sup> )	1.205	1.026
μ <sub>calcd</sub> (cm <sup>-1</sup> )	50.4	2.9
R, R <sub>w</sub> , GoF	0.048, 0.051, 2.02	0.053, 0.77, 1.91
$R = \frac{\sum  F_o  - \sum  F_c }{\sum  F_o } \quad R_w = \left[ \frac{\sum ( F_o  -  F_c )^2}{\sum w F_o^2} \right]^{1/2}$		

**Table 4.3** Selected Bond Distances (Å) and Angles (deg) of for (Cy<sub>2</sub>N)<sub>2</sub>VCl<sub>2</sub> (**1b**) and (Cy<sub>2</sub>N)<sub>2</sub>VNp<sub>2</sub> (**2a**)

<b>1b</b>	<b>2a</b>
V1-Cl1 = 2.226(2)	V1-N1 = 1.877(2)
V1-Cl2 = 2.217(2)	V1-N2 = 1.878(2)
V1-N1 = 1.808(5)	V1-C25 = 2.088(3)
V1-N2 = 1.834(5)	V1-C30 = 2.095(3)
Cl1-V1-Cl2 = 113.3(1)	C25-V1-C30 = 105.8(1)
Cl1-V1-N1 = 105.0(2)	N1-V1-N2 = 117.5(1)
Cl1-V1-N2 = 114.2(2)	N1-V1-C25 = 110.0(1)
Cl2-V1-N1 = 113.6(2)	N1-V1-C30 = 106.0(1)
Cl2-V1-N2 = 104.0(2)	N2-V1-C25 = 105.5(1)
V1-N1-C1 = 124.8(4)	N2-V1-C30 = 111.3(1)
V1-N1-C7 = 120.1(4)	C1-N1-C7 = 116.9(2)
	V1-N1-C1 = 127.1(2)
	V1-N1-C7 = 115.8(2)