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Dedicated to my parents

Abstract

A series of V(III) catalysts with different substituted 1,3-dionates ($V(acac)_3$ **2.1**, $V(Cy-acac)_3$ **2.2**, $V(t-Bu-acac)_3$ **2.3** and $V(F-acac)_3$ **2.4**) were prepared and characterized and their activities towards olefin polymerization were systematically compared. $V(Cy-acac)_3$ **2.2** shows a slightly higher activity than the traditional catalyst $V(acac)_3$ **2.1**. The catalytically active species is relatively insensitive to modification of both the electronic and steric features of the acac ligand.

The preparation of V(II) and V(IV) 1,3-dionate complexes was designed to study the role of the oxidation state of vanadium in terms of polymerization activity. $V(acac)_2(TMEDA)$ **2.7** proved to be unreactive towards polymerization with respect to $V(acac)_3$ **2.1** under the usual reaction conditions carried out in the absence of reactivating substances, whereas products of reaction of $V(acac)_2(TMEDA)$ **2.7** and reactivator proved to be reactive towards polymerization in the presence of cocatalyst. $V(t-Bu-acac)_2Cl_2$ **2.9** was found to be more highly reactive towards polymerization with respect to $V(t-Bu-acac)_3$ **2.3** in the presence of cocatalyst. Two unprecedented V(II) complexes $(R-acac)_2V(TMEDA)$ [$R = H$ (**2.7**), $t-Bu$ (**2.7c**)] have been prepared and reacted with halocarbons to model the reactivation process. The isolation of $(t-Bu-acac)_2V(TMEDA)[X]$ [$X = ZnCl_4^-$ **2.8**, $CuCl_2^-$ **2.9**] indicates that the primary role of reactivating substances, commonly employed in the industrial processes, is to reoxidize V(II) to the trivalent state.

Reaction of $VCl_3(THF)_3$ with two equivalent of $R^1(R^2)NLi\cdot Et_2O$ ($R^1 = Ph, Bz$; $R^2 = Bz$) gave the paramagnetic and monomeric $[R^1(R^2)N]_4V$ (**3.1**) and (**3.2**). Reactions of $VCl_3(THF)_3$

with one equivalent of $R^1(R^2)NLi$ ($R^1 = Bz$; $R^2 = Ph$) and R_2NLi ($R = Bz$) formed the paramagnetic, monomeric $[R^1(R^2)N]_3VCl$ (**3.3**) and $[R_2N]_3VCl$ (**3.4**). These novel V(IV) amide compounds did not show any significantly useful activity for the polymerization of ethylene under Ziegler-Natta conditions.

Reaction of $VCl_3(THF)_3$ with an excess of $NaBH_4$ gave the paramagnetic and monomeric $V(BH_4)_2(THF)_3$ (**4.1**), $V(BH_4)_2(TMEDA)_2$ (**4.2**), and $V(BH_4)_2(py)_4$ (**4.3**), indicating that coordination of BH_4^- to the vanadium occurs through bridging hydride interactions with the metal center by adopting a bidentate or monodentate bonding mode depending on the nature of the supporting ligands.

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PUBLICATIONS

- (1) Synthesis, Reactivity, and Stability of Di- and Trivalent Samarium Amides, Ravinder K. Minhas, Yinlin Ma, Jae-Inh Song, Sandro Gambarotta, *Inorganic Chemistry*, 1996, **35**, 1866
- (2) The Question of the Metal Oxidation State in Ziegler-Natta EPDM Copolymerization Catalyzed by (Acetylacetonate)₃V, Yinlin Ma, Sandro Gambarotta, submitted

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LIST OF ABBREVIATIONS

acac	Acetylacetonate
Å	Angstroms
δ	Chemical shift
ν	Frequency
η	Hapto
μ_{eff}	Effective magnetic moment in Bohr magnetons
t-Bu-acac	2,2,6,6-Tetramethyl-3,5-Heptanedionate
Bz	Benzyl
cm^{-1}	Wave number
Cp	Cyclopentadienyl anion
Cp ⁺	Pentamethylcyclopentadienyl anion
Cy	Cyclohexyl
Cy-cac	2-Acetylcyclohexone
DIFABS	Absorption corrections
DME	Ethylene glycol dimethyl ether
EPR	Electron Paramagnetic Resonance Spectroscopy
F-acac	1,1,1,5,5,5-Hexafluoro-2,4-Pentanedionate
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
ORTEP	Oak Ridge Thermal Ellipsoid Program
Ph	Phenyl
ppm	Parts per million
py	pyridine
R	Alkyls
TMEDA	N,N,N',N'-tetramethylethylenediamine
THF	Tetrahydrofuran

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Chapter 1

Introduction

After its slow development over more than one hundred years, interest in vanadium chemistry has been steadily increasing¹. With reports of several remarkable chemical transformations and applications such as insertion reactions², coupling reactions³, Ziegler-Natta polymerization⁴ and in light of the role played by this metal in biological systems⁵, the chemistry of vanadium has become one of the current research topics for modern inorganic chemists.

A unique characteristic of this metal is the variety of its oxidation states (from -3 to +5) which provide a tremendous diversity of chemical reactivity. Potential diagram for vanadium in acidic solution is given in Fig 1.1. A dominating feature of the chemistry of vanadium lies in the fact that the most significant part of its chemistry has been developed almost exclusively with cyclopentadienyl-based systems as supporting ligands. While this has allowed great development in the chemistry of this metal, it has also been a limiting factor. Perhaps this is the reason why the most recent literature is characterized by efforts to develop the chemistry of this metal with an alternative ligand system.

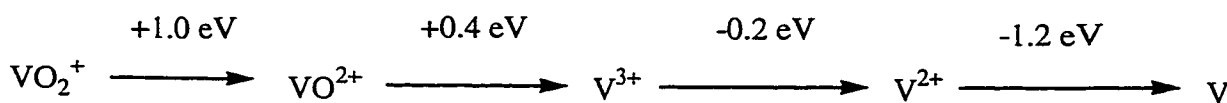


Fig 1.1. Potential Diagram for Vanadium at $[\text{H}^+] = 1$.

My research in this field was prompted by the observation that some vanadium complexes display catalytic activity toward olefin polymerization. However, there are some important questions about these catalysts which need to be addressed. On the basis of the information available to date, it is unknown which factors determine the catalytic activity. Therefore, in an attempt to gain some insight into the role played by the oxidation state of the metal center, I undertook a mechanistic and synthetic work to develop the chemistry of low- and medium-valent vanadium with 1,3-dionates and to attempt isolation of active intermediates. Through polymerization testing, I hoped to obtain insights into the factors which determine the catalytical activity of these systems. One of the preliminary conclusions from this part is that V(III) complexes are in general active as polymerization catalysts. In order to assess the role of both the supporting ligand and the reactive function in determining this type of reactivity, I carried out a synthetic work to prepare and characterize vanadium complexes with amide and hydride. Due to the tendency of V(III) to disproportionate, a series of new tetravalent vanadium compounds was isolated and preliminarily tested as a potential family of catalysts. By using borohydride as a reagent for preparing transition metal hydride species, a series of new vanadium(II) bis-tetrahydroborates complexes was isolated and characterized. Their employment for olefin polymerization has been preliminarily tested.

The well-known ability of vanadium to coordinate dinitrogen was another strong point of interest. Since low- and medium-valent vanadium display the ability to both coordinate and reduce dinitrogen depending on the metal electronic configuration, we have attempted the synthesis of new medium-valent vanadium complexes in the long-term perspective of understanding the factors which promote or inhibit this attractive preference.

The aim of this chapter is mainly to review the most relevant literature.

Ziegler-Natta polymerization based on vanadium complexes

Organometallic complexes have found wide practical application in C-C bonding-forming reactions of olefins and dienes. The polymerizations and copolymerizations of ethylene, propylene, butadiene, and isoprene are currently prepared by using Ziegler-Natta catalysts of group 4 metal. Some of the group 5 metal complexes can polymerize and copolymerize ethylene, propylene, butadiene, and isoprene while in combination with cocatalyst AlRCl_2 . Most of the ethylene-propylene copolymers and terpolymers are prepared with Ziegler-Natta catalysts based on soluble vanadium compounds. Hydrocarbon-soluble vanadium compounds were found to give many suitable catalytic systems either in the presence of trialkylaluminum compounds or alkylaluminum halides⁶⁻¹³.

At the ratios of Al and V used commercially, the vanadium-aluminum alkyl halide combination produces complexes soluble in non-polar hydrocarbon solvents proposed whose structure is shown in Fig. 1.2¹⁰ ($\square$ represents a vacant d orbital capable of complexing olefin: $\text{VCl}_4 + \text{AlR}_2\text{Cl}$). It is necessary that aluminum alkyls contain at least one halogen to be effective. Chloride bridges between aluminum centers and vanadium are believed to occupy four coordinate sites. Olefin and alkyl ligands are situated in adjacent positions, facilitating the repetitive process in which the chain of polymer is growing. There are a number of such structures that can be drawn, and in many cases more than one structure appears to exist.

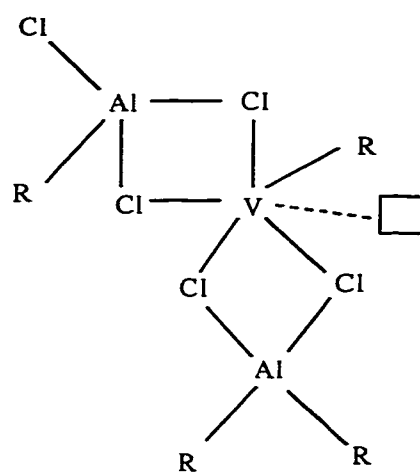
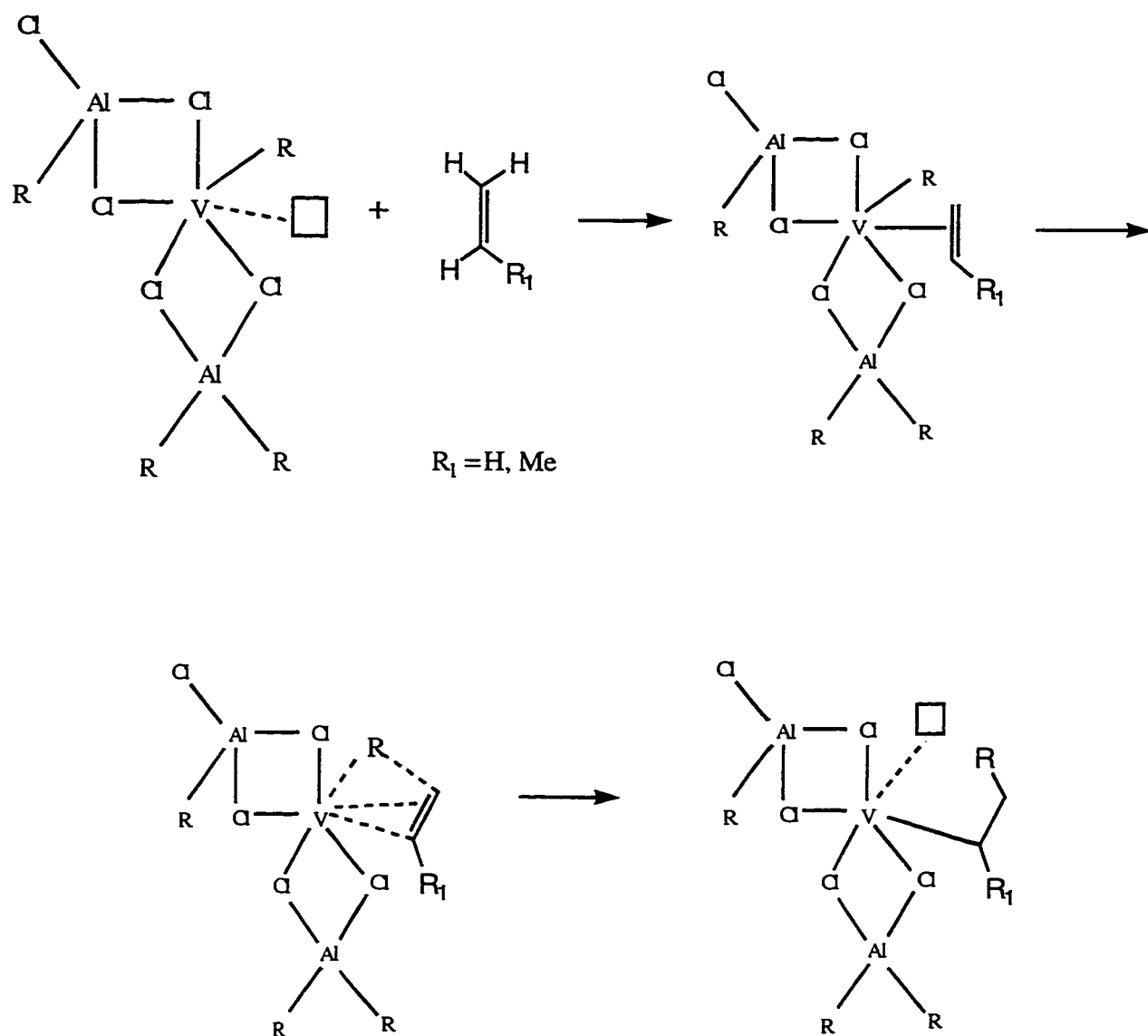


Fig. 1.2 Proposed catalyst structure

The copolymerization reaction was assumed to proceed as follows (Scheme 1.1):



Scheme 1.1

With added monomer, the active center retains a vanadium-alkyl bond and a coordinative unsaturation. The process may repeat itself by insertion of the next monomer into the new vacant d orbital.

The catalyst components may or may not be combined with the aluminum alkyl halide before introducing the monomer in the reaction. Premixing of catalyst and cocatalyst can decrease the activity of catalyst even for short premixing times and at very low temperatures. The catalyst failure observed after the first few minutes of high activity is attributed to β -H elimination process with formation of a divalent vanadium species. Divalent vanadium complexes are regarded as inert towards polymerization reaction, even though information is scarcely available due to the variety of V(II) compounds. In agreement with the common belief that reduction to V(II) is responsible for catalyst deactivation, catalyst efficiency can be increased by the addition of perchlorinated substances such as hexachlorocyclopentadiene or butylperchlorocrotonate^{14,15}.

In spite of the fact that vanadium catalysts are widely used in industry for the commercial production of elastomers, information about these species is mainly confined to patent literature. The understanding of the mechanism is very poor as well as the role played by the metal oxidation state.

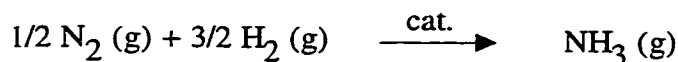
One of the goals of this research was to improve our understanding of the vanadium promote olefin homo- and copolymerization and to develop new families of catalysts.

Dinitrogen complexes of vanadium

Dinitrogen's main characteristic is its remarkable chemical inertness, which accounts for great difficulties in bring about chemical transformations such as oxidation and reduction under usual reaction conditions.

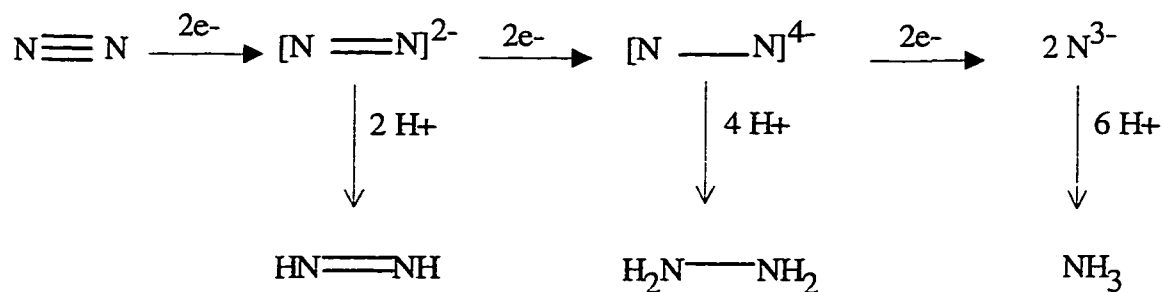
The Haber-Bosch process is the method presently employed to reduce dinitrogen on industrial scale (23 million tons per year in the US) (Scheme 1.2). This reduction process requires severe conditions such as high temperatures (400-500 °C) and high pressures (200

atm). In a convenient variation, the utilization of a ruthenium-based catalyst (Kellogg process), allows the use of substantially milder reaction conditions ($T = 250\text{ }^{\circ}\text{C}$, $P = 50\text{ atm}$).



Scheme 1.2

The reduction of dinitrogen occurs in three steps and requires a total of six electrons to completely cleave the N-N triple bond (Scheme 1.3). Diazene is formed during the first step, followed by the formation of hydrazine and nitride, respectively.

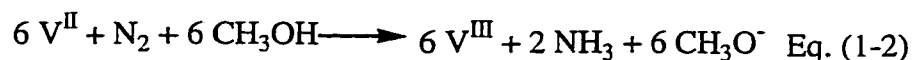
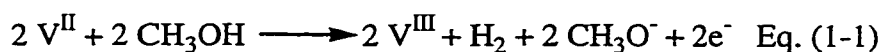


Scheme 1.3

Contrary to the severe conditions required by the Haber-Bosch process, naturally occurring systems (such as nitrogenase) perform catalytic reduction of N_2 at ambient conditions (1 atm, aqueous medium, neutral pH, room temperature)¹⁶.

In situ generated divalent vanadium with oxygen-containing ligands is known to catalytically convert dinitrogen to ammonia and hydrazine¹⁷ in protic media. In an attempt to model these transformations¹⁸, the mixed-valence tetranuclear $\text{V}^{\text{II}}/\text{V}^{\text{III}}$ complex

$[\text{Na}_2\text{V}_4(\text{OMe})_2\{\text{O}_2\text{C}_6\text{H}_2(\text{tBu})_2\}_4\{\text{OC}_6\text{H}_2(\text{OH})(\text{tBu})_2\}_2(\text{MeOH})_2]$ was isolated from a methanol solution containing VCl_2 , 3,5-di-tert-butylcatechol (dbcat) and NaOCH_3 , and proved to be a powerful reducing agent. This species evolves H_2 from the protic solvent (MeOH) in approximately 3-4 hours [Eq.(1-1)] and reduces dinitrogen [Eq.(1-2)]. Unfortunately, the reduction of N_2 is competitive with that of methanol, thus preventing practical application.

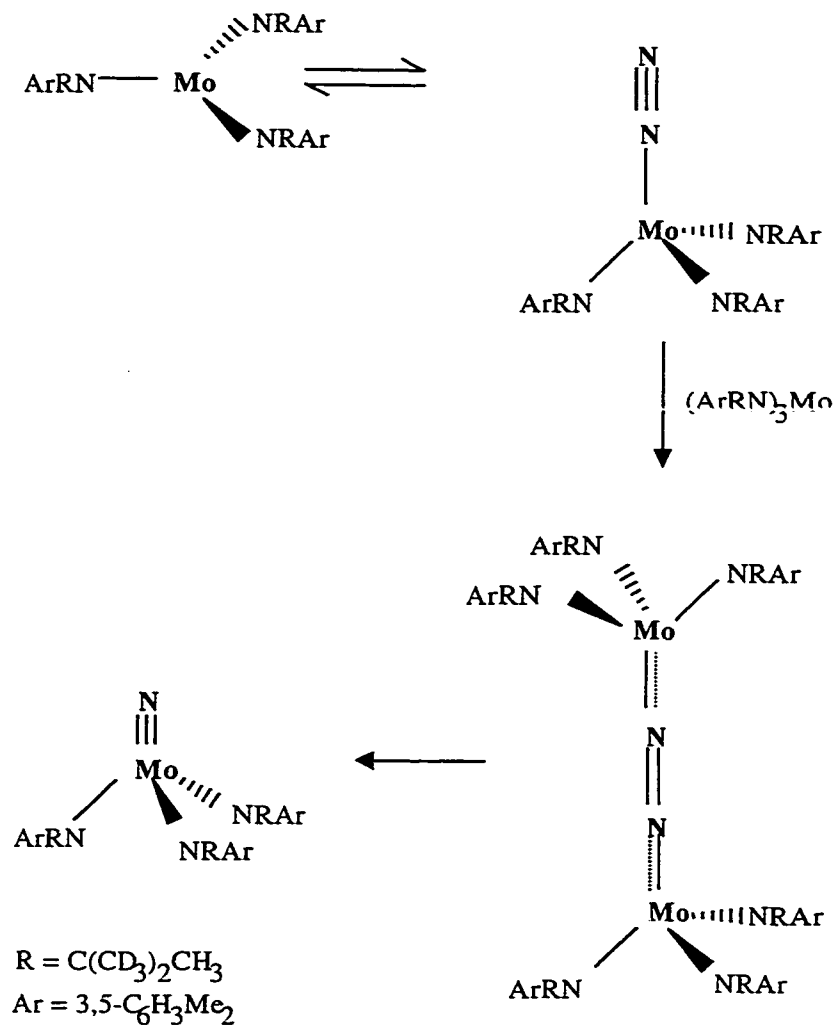


The existence of vanadium nitrogenase, a natural nitrogen fixation system, was demonstrated in 1986¹⁹. In this system, a vanadoprotein replaces the conventional molybdoprotein and functions under conditions of absence or deficiency of Mo. There is the oxidation state of vanadium in vanadium nitrogenase. Conversely, the synthetic systems able to activate N_2 always contain the metal in low oxidation state. This suggests that incorporation of dinitrogen is possible within a wide range of oxidation states.

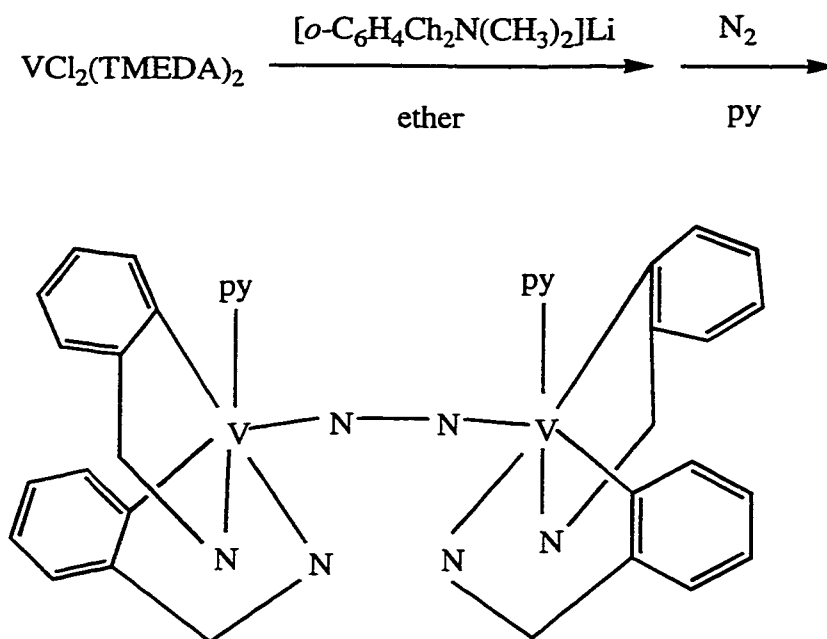
The high reactivity of low- and medium-valent vanadium, and its strong reducing power are the key to understand the ability of these species to react with an exceptionally stable molecule such as N_2 . Moreover, the d^3 electronic configuration of vanadium(II), has the highest reduction potential (Fig. 1.1). Thus working these species is very promising for activation and fixation of N_2 . A simple dinuclear vanadium(II) system might be able to provide the six electrons necessary to cleave the triple N-N bond of N_2 (Scheme 1.3).

This idea is further corroborated by the recent finding that a d^3 molybdenum(III) cleaves the triple N-N bond of N_2 . The reaction of $\text{Mo}(\text{NRAr})_3$ [$\text{Ar} = 3,5\text{-Me}_2\text{C}_6\text{H}_3$, $\text{R} =$

$\text{C}(\text{CD}_3)_2\text{CH}_3]$ with N_2 gave an end-on dinitrogen complex which further evolved into a terminal Mo-N species (Scheme 1.4)²⁰.



Scheme 1.4

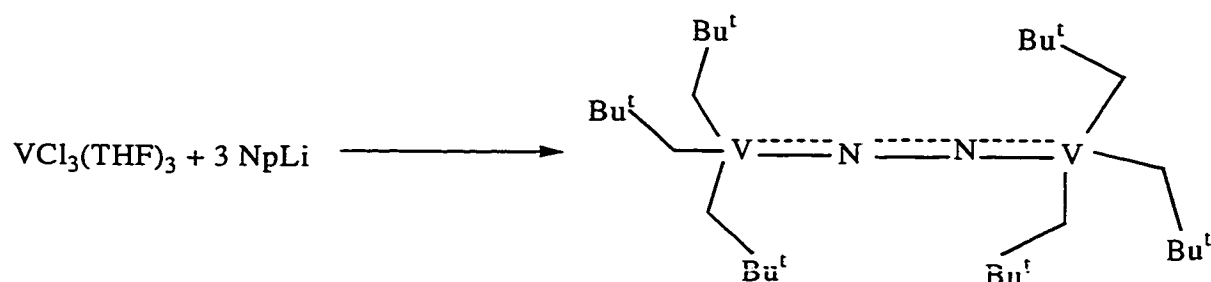


Scheme 1.5

The first complex of dinitrogen fixation promoted by V(II) complex was reported in 1989²¹. The reaction of $\text{VCl}_2(\text{TMEDA})_2$ with two equivalents of $[\text{o-C}_6\text{H}_4\text{CH}_2\text{N}(\text{CH}_3)_2]\text{Li}$ and one equivalent of py under N_2 produced a dinitrogen complex $(\mu\text{-N}_2)\{[\text{o-Me}_2\text{NCH}_2\text{C}_6\text{H}_4]_2\text{V}(\text{py})\}_2(\text{THF})_2$ (Scheme 1.5). The magnetic moment ($\mu_{\text{eff}} = 3.47 \mu_{\text{B}}$) was slightly lower than expected for a d^3 electronic configuration, indicating that partial reduction of dinitrogen occurred. The N_2 moiety was displaced by stronger Lewis base, such as py, resulting in isolation of monomeric vanadium(II) complex $[(\text{o-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_2\text{V}(\text{py})_2]$.

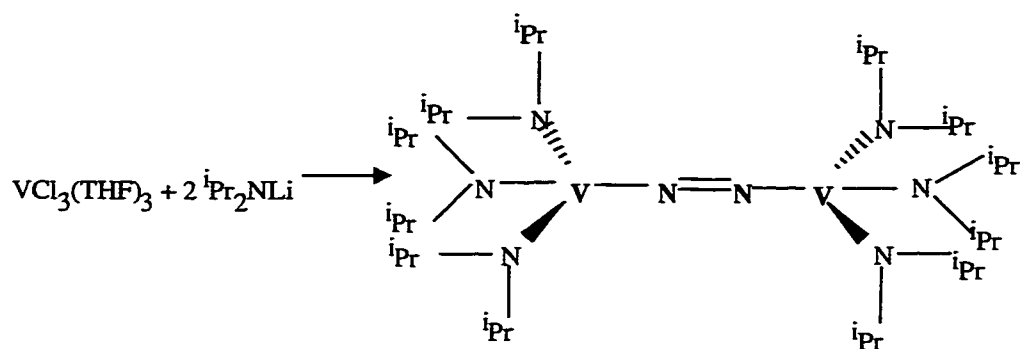
Although the d^2 electronic configuration of vanadium(III) has reduction potential ($E_{\text{red}} = -0.25 \text{ V}$) which is considerably lower than that of V(II), it is still sufficient for interacting with dinitrogen. A trivalent vanadium dinitrogen bridged complex $[(\text{Me}_3\text{CCH}_2)_3\text{V}]_2(\mu\text{-N}_2)$ was obtained when $\text{VCl}_3(\text{THF})_3$ was treated with three equivalents of $\text{Me}_3\text{CCH}_2\text{Li}$ at low temperature under nitrogen (Scheme 1.6)²². The diamagnetic dinitrogen 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 μ -N₂ moiety. In contrast to the diamagnetism, which suggests a large extent of dinitrogen reduction, the N-N distance of 1.250(3) Å is not particularly long. The μ -N₂ moiety is easily lost upon treatment of a stronger Lewis base such as pyridine indicating that N₂ is only weakly coordinated to the two Np₃V moieties.



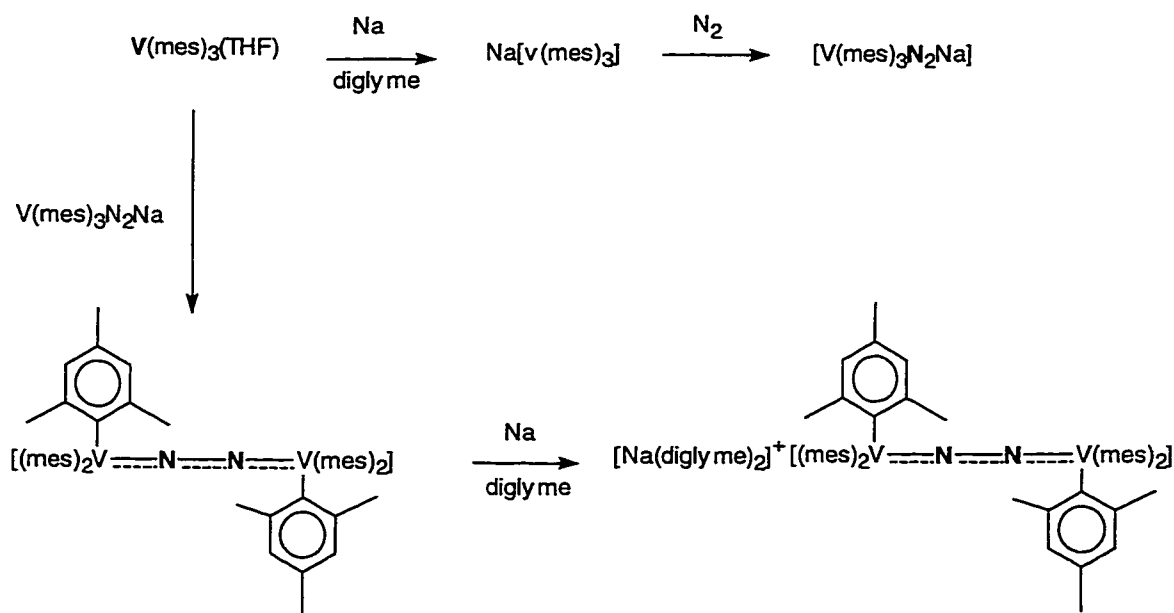
Scheme 1.6

It is thus remarkable that by using amide as a supporting ligand, V(III) complexes are still able to coordinate dinitrogen in a rather robust manner. The reaction of $\text{VCl}_3(\text{THF})_3$ with three equivalents of ${}^i\text{Pr}_2\text{NLi}$ under N₂ gave a dinuclear dinitrogen complex $(\mu\text{-N}_2)[({}^i\text{Pr}_2\text{N})_3\text{V}]_2$, where the two tetrahedral vanadium atoms are linked by one linear bridging molecule of dinitrogen (Scheme 1.7)²³. The N₂ moiety can not be removed upon treatment with a stronger Lewis base such as pyridine, nitriles or even upon treatment with oxidizing reagents such as azides, diazo, etc. In contrast to the majority of end-on bridged dinitrogen complexes of early transition metals from which N₂ can be easily removed by ligand exchange reaction (or in some cases simply by applying *vacuo*) the V-N₂-V frame was remarkably robust in this case.



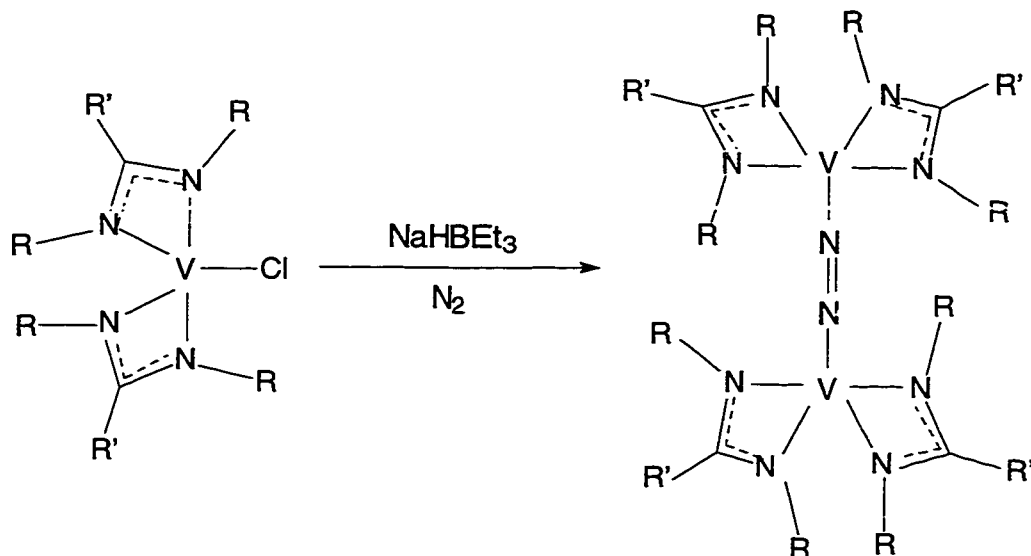
Scheme 1.7

The reduction of V(III) species with appropriate reducing agents may be a viable strategy to obtain dinitrogen vanadium complexes. The reaction of $\text{V}(\text{mes})_3(\text{THF})$ [$\text{mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$] by metallic sodium in the presence of nitrogen in diglyme, gave 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 1.8)²⁴. The magnetic moment of $1.69 \mu_{\text{B}}$ per metal center is significantly lower than expected for a $d^3\text{-}d^3$ system. Usually, coordination of N_2 does not change the magnetic properties of the original metal ion²⁵.



Scheme 1.8

A dinuclear paramagnetic ($\mu_{\text{eff}} = 0.91 \mu_{\text{B}}$ per dimer) dinitrogen complex $\{[\text{Me}_3\text{Si}]\text{NC}(\text{Ph})\text{N}(\text{SiMe}_3)]_2\text{V}\}_2(\mu\text{-N}_2)$ (Scheme 1.9)²⁶ 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 NaHBET_3 in non-coordinating solvent such as toluene. There is a weak ligation between vanadium and N_2 moiety, as indicated by a Toepler pump experiment, in which 87% of N_2 was recovered upon treatment of the complex with THF. A N-N bond distance $[1.235(6) \text{ \AA}]$ and the liability of dinitrogen coordination indicated a minimal degree of dinitrogen reduction.



Scheme 1.9

Given this scenario, I became interested in studying the chemistry of vanadium amide in the largest possible variety of oxidation states. Exciting results and a deeper understanding of the factors which enhance the ability of vanadium to interact with N_2 were anticipated as a result of this study.

Conclusions

The scopes of the thesis are summarized as follows:

- (1) carrying out mechanistic and synthetic study in vanadium-promoted homo- and copolymerization of α -olefin. For this purpose, (a) a series of catalysts of V(III)/V(IV) with substituted 1,3-dionates were prepared to study the mechanism of polymerization and to attempt the isolation of active species; (b) complexes of V(II) and V(IV) with substituted 1,3-dionates were also prepared to study the role of the oxidation state of vanadium.
- (2) synthesizing, characterizing and studying the reactivity of novel medium-valent vanadium complexes based on amide ligand system: Their potential as a family of catalysts for polymerization of olefin was explored. At the same time, we were interested in studying the ability of these species to perform coordination of N_2 .
- (3) synthesizing, characterizing and studying the reactivity of novel vanadium tetraborohydride complexes: we focused on the use these species as surrogates of inaccessible hydrides. These species were expected to provide a very strong reducing ability as well as tendency to perform insertion reaction in a variety of unsaturated systems including olefins.

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Chapter 2

Vanadium Catalyzed Ethylene-Propylene Copolymerization: the Question of the Metal Oxidation State in Ziegler-Natta Polymerization Promoted by (β -diketonate)₃V

Introduction

The Ziegler-Natta olefin polymerization process is certainly among the most famous catalytic processes discovered in this century. It is widely used internationally for the large scale production of polymers important to modern society. The process is very efficient and a remarkable wealth of technology has been developed to improve even further its efficiency and stereoselectivity.¹ However, in spite of the enormous commercial interest involved in this science, insight into its underlying of the mechanism remains limited. Major breakthroughs in this direction were obtained with the discovery of the cationic Ziegler Natta catalysts² and, more recently, with the discovery that a cationic aluminum alkyl derivative may catalyze olefin polymerization in the absence of transition metals.³ Today it is well established that an enhanced Lewis acidity and the employment of a large excess of Al-based cocatalyst are the recipe of a successful and efficient catalytic system. However, the recent discovery that some electron-rich late transition metal complexes may also act as powerful Ziegler-Natta catalysts⁴ has rejuvenated the academic and industrial interest for a better understanding of these remarkable systems.

The main stream of research in this field has relatively ignored group V metals aside from available patent literature⁵ until very recently when the appearance of a few reports⁶

indicated that a revival of interest in vanadium based Ziegler-Natta catalysis was in process.⁷ In fact, the current paucity of this literature is in striking contrast with the fact that vanadium catalysts are widely used for the industrial production of ethylene-propylene-diene elastomers (EPDM).⁸ The most peculiar aspect of this vanadium-based catalytic system consists of the employment of a coordinatively saturated $V(\beta\text{-diketonate})_3$ complex containing vanadium in the trivalent oxidation state. Given its d^2 electronic configuration and the medium oxidation state, this species certainly cannot be considered as an “acidic” complex and somewhat deviates from the usual Ziegler-Natta paradigm. Therefore, the excellent activity of this particular catalytic system poses some fascinating mechanistic questions. The fact that the catalyst is coordinatively saturated implies that one of the functions of the Al cocatalyst is to trigger a major molecular reorganization around the transition metal. It is reasonable to assume that at least one of the *acac* ligands is abstracted by the Al cocatalyst to form a coordinatively unsaturated vanadium alkyl. On the other hand, it is well established that the chlorine content of the cocatalyst is a determining factor for the activity of the catalyst.⁸ Thus, other questions arise about the structure of the catalyst and the role of the halogen. Is the active complex ionic and bears a positive charge on the transition metal or is it instead a species containing both vanadium and aluminum in the same molecular aggregate?⁹

The second point of interest concerns the oxidation state of the vanadium center during the catalytic cycle. The oxidation state +3 of vanadium is a fairly stable one and thus a few examples of stable homoleptic alkyl $V(III)$ derivatives have been reported in the literature.¹⁰ On the other hand, the aluminum alkyl cocatalyst certainly has sufficient reducing strength to lower the oxidation state of vanadium to the +2 state.^{11a} In agreement with this idea, a recent report has suggested the possibility that an in situ generated $V(II)$ alkyl complex might be the catalytically active species.^{11b} In addition, some $V(II)$ salts have been claimed to act as a

catalysts for ethylene polymerization.^{11c} However, the general consensus is that the oxidation state +2 might be inert towards polymerization especially when considering that vanadium catalysts typically die over the course of few minutes after displaying initially high polymerization rates.¹² Thus, the possible reduction of the $V(\beta\text{-diketonate})_3$ catalyst is commonly regarded as a deactivating process. This idea is further supported by the fact that the employment of mild oxidizing agents (halocarbons) as catalyst reactivators is critical for the optimization of the catalytic cycle. The role of these substances is debated since in addition to reoxidizing the metal center to the oxidation state +3 thus restarting the cycle, they may also react in a destructive manner with the cocatalyst. Since the catalyst oxidation state and the role of the reactivators remain speculative, we have carried out the present study with the aim of gaining some insight into both the catalyst structure and the metal oxidation state of the catalytically active species.

Herein we describe our findings.

Experimental Section

All operations were performed under an inert atmosphere with the use of standard Schlenk techniques or in a nitrogen-filled drybox. $VCl_2(TMEDA)_2$,¹³ $VCl_3(THF)_3$,¹⁴ and $V(acac)_3$,¹⁵ $[V_2Cl_3(THF)_6][AlCl_4]$ ¹⁶ were prepared according to published procedures. Solvents were dried by following standard procedures. NMR spectra were recorded on a Bruker AMX-500 spectrometer by using vacuum-sealed samples prepared in a dry box. 2,4-pentanedione (*acac*), 2-acetylcyclohexanone (*Cy-acac*), 2,2,6,6-tetramethyl-3,5-heptanedione (*t-Bu-acac*) and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (*F-acac*) were purchased from Aldrich and dried using activated molecular sieves. Infrared spectra were recorded on Mattson

3000 FTIR spectrometer. Nujol mulls were prepared in the drybox. $\text{Et}_3\text{Al}_2\text{Cl}_3$, Et_2AlCl (DEAC), MeLi and *i*-BuLi (Aldrich) were used as received. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature. Magnetic moments were calculated using standard methods¹⁷ and corrections for underlying diamagnetism were applied to the data.¹⁸

Synthesis of $\text{V}(\text{Cy-acac})_3$ (2.2)

According to a modification of a previously reported preparation,^{12e} an ether solution of MeLi (7.8 mL, 1.4M) was added dropwise and under vigorous stirring at -78°C to a solution of 2-acetylcyclohexanone (1.54 g, 11.0 mmol) in THF (100 mL). Stirring was continued for 1 h. After warming the reaction mixture to room temperature, the addition of $\text{VCl}_3(\text{THF})_3$ (1.37 g, 3.7 mmol) resulted in a color changed to a dark brown. The reaction mixture was stirred overnight. The solvent was evaporated *in vacuo*, and the residual brown solid was re-suspended in hexane (350 mL). After filtration of LiCl and partial removal of the solvent, the resulting solution was allowed to stand at -30°C for 2 days, upon which brown microcrystals of **2** (1.0 g, 2.2 mmol, 59%) separated. Anal. Calcd (Found) for $\text{VC}_{24}\text{H}_{33}\text{O}_6$: C 61.53 (61.12), H 7.10 (7.33); I.R. (Nujol mull, cm^{-1}): 1568(br, s), 1460(br, s), 1375(sh), 1261(m), 1166(m), 994(m), 962(m), 825(w), 711(w). $\mu_{\text{eff}} = 2.89 \mu_{\text{BM}}$.

Synthesis of $\text{V}(t\text{-Bu-acac})_3$ (2.3)

Identical procedure as per 2.2 was followed by using *t*-Bu-acacH (1.3 ml, 6.2 mmol) in THF (150 mL) and MeLi (4.5 mL 1.4 M). Yield: 0.70 g, 1.2 mmol, 57%. Anal. Calcd (Found) for $\text{VC}_{33}\text{H}_{57}\text{O}_6$: C 65.98 (64.23), H 9.56 (9.09); I.R. (Nujol mull, cm^{-1}): 1539(s), 1501(s),

1462(s), 1382(s), 1357(s), 1224(m), 1175(m), 1144(m), 1021(m), 873(m), 795 (m), 761(w), 740(w), 628(m). $\mu_{\text{eff}} = 2.86 \mu_{\text{BM}}$

Synthesis of V(*F-acac*)₃ (2.4)

Identical procedure as for 2.2 was followed by using *F-acacH* (0.9 ml, 6 mmol) in THF (150 mL) and MeLi (4.3 mL, 1.4 M) at -78°C . Yield: 0.55 g, 0.82 mmol, 41%. Anal. Calcd (Found) for $\text{VC}_{15}\text{H}_3\text{F}_{21}\text{O}_6$: C 24.71 (25.08), H 0.41 (0.42); I.R. (Nujol mull, cm^{-1}): 1596(s), 1524(s), 1456(s), 1419(s), 1381(s), 1358(s), 1275(m), 1190(w), 1163(m), 1020(m), 962(m), 825 (m), 711(m), 667(s). $\mu_{\text{eff}} = 2.90 \mu_{\text{BM}}$

Reaction of (*acac*)₃V with AlCl₃. Preparation of [Al(*acac*)₂(THF)₂][AlCl₄] (2.5)

Solid V(*acac*)₃ (0.97 g, 2.8 mmol) was dissolved in THF (150 mL) and treated with AlCl₃ (0.75 g, 5.6 mmol). The resulting solution slowly changed color from reddish brown to light yellow. After concentration to small volume, the resulting solution was allowed to stand at -78°C for 2 days, upon which colorless crystals of [Al(*acac*)₂(THF)₂][AlCl₄] separated (0.40 g, 0.74 mmol, yield 28%). Anal. Calcd (Found) for $\text{Al}_2\text{C}_{18}\text{H}_{30}\text{O}_6\text{Cl}_4$: C 40.17 (39.66), H 5.62 (5.67); I.R. (Nujol mull, cm^{-1}): 1574(s), 1538(s), 1459(s), 1399(s), 1377(s), 1345(m), 1295(m), 1198(w), 1021(s), 953(m), 872(s), 808(s), 702(m), 660(m), 620(m). ¹H-NMR (THF-d₈, 500 MHz, ppm) δ : 5.78 (2H, CH *acac*), 3.58 (CH₂ THF), 2.03 (12H, CH₃ *acac*), 1.74 (CH₂, THF); ¹³C-NMR (THF-d₈, 125.7 MHz, ppm) δ : 195.22 (C=O, *acac*), 103.92 (CH, *acac*), 68.598 (CH₂, THF), 26.855 (CH₃, *acac*), 26.351 (CH₂, THF), ²⁷Al-NMR (THF-d₈, 130.3 MHz, ppm) δ : 102.57 (sharp s, [Al(*acac*)₂(THF)₂]⁺), 3.01 (very broad, [AlCl₄]).

Reaction of V(*acac*)₃ with EtAlCl₂

The addition of a hexane solution of EtAlCl_2 (18 mL 1.0 M) to a solution of $\text{V}(\text{acac})_3$ (2.1 g, 6.0 mmol) in toluene (150 mL) at room temperature changed the color instantaneously from reddish-brown to brown. An insoluble light brown precipitate appeared almost immediately (1.2 g) which was filtered after the mixture was stirred for two hours. Redissolving the solid in THF (100 mL) turned the color light green. After filtration and concentration to small volume, the resulting solution was allowed to stand at -78°C for two days upon which a mixture of colorless crystals $[\text{Al}(\text{acac})_2(\text{THF})_2][\text{AlCl}_4]$ (**2.5**) and light green crystals of $[\text{V}_2\text{Cl}_3(\text{THF})_6][\text{AlCl}_4]$ (**2.6**) separated. The large size of the crystals allowed in physical separation under microscope and to obtain analytically pure samples of **2.5** (0.5 g, 0.93 mmol, yield 10%) and **2.6** (0.7 g, 0.88 mmol, yield 29%). Both compounds were identified by comparison of their spectroscopic, crystallographic cell parameters and combustion analysis data with those of analytically pure samples prepared according to literature procedures.¹⁶

Synthesis of $[\text{V}_2\text{Cl}_3(\text{THF})_6][\text{AlCl}_4]$ (**2.6**):

Method A: see above description.

Method B: To a solution of $\text{VCl}_3(\text{THF})_3$ (3.3 g, 8.8 mmol) in THF (150 mL) the 18 mL of Et_3Al (1.0 M, hexane) was added at room temperature. The mixture was kept on stirring for 2 hours which color changed from purple/pink to light green, and then allowed to stand at -30°C for 2 days, upon which light green crystals of $[\text{V}_2(\mu\text{-Cl})_3(\text{THF})_6][\text{AlCl}_4]$ (**2.6**) (1.4 g, 1.7 mmol, yield 39%) separated.

Synthesis of $\text{V}(\text{acac})_2(\text{TMEDA})$ (**2.7**)

A solution of *acacH* (0.58 mL, 5.7 mmol) in THF (150 mL) was treated with a solution of MeLi in ether (4.1 mL, 1.4 M) at $-78\text{ }^{\circ}\text{C}$. Gas evolution took place, and the mixture was maintained under vigorous stirring for 1 hour while warming to room temperature. $\text{VCl}_2(\text{TMEDA})_2$ (0.88 g, 2.8 mmol) was added to the mixture. The resulting dark violet-blue solution was stirred for several hours. The solution was evaporated to dryness and the residual solid redissolved in hexane (50 mL). A small amount of insoluble and colorless material was eliminated by filtration and the filtrate was allowed to stand at $-30\text{ }^{\circ}\text{C}$ for 2 days. Dark violet-blue crystals of **2.7** separated (0.51 g, 1.4 mmol, yield 50%). Anal. Calcd (Found) for $\text{VC}_{16}\text{H}_{30}\text{N}_2\text{O}_4$: C 52.60 (52.68), H 8.28 (8.33), N 7.67 (7.34); I.R. (Nujol mull, cm^{-1}): 1576(s), 1522(s), 1457(s), 1376(s), 1283(s), 1190(s), 1124(m), 1017(s), 953(s), 924(s), 796(s), 756(s), 654(s). $\mu_{\text{eff}} = 3.58\ \mu_{\text{BM}}$.

Synthesis of (*t*-Bu-*acac*)₂V(TMEDA) (**2.7c**)

An identical procedure as per **2.7** was followed by using freshly distilled *t*-Bu-*acacH* (2.36 mL, 11.3 mmol) in THF (100 mL) and NaH (0.27 g, 11.3 mmol) at room temperature. Yield: 1.69 g, 3.16 mmol, 56%. Anal. Calcd (Found) for $\text{VC}_{28}\text{H}_{52}\text{N}_2\text{O}_4$: C 63.02 (62.99), H 10.20 (10.14), N 5.25 (5.17); I.R. (Nujol mull, cm^{-1}): 1559(s), 1510(s), 1456(m), 1398(s), 1376(s), 1285(m), 1256(m), 1188(m), 1125(m), 1099(m), 1058(m), 1005(s), 955(m), 920(m), 797(m), 755(m), 722(w), 652(m), 566(w); $\mu_{\text{eff}} = 3.82\ \mu_{\text{BM}}$

Reaction of (*acac*)₂V(TMEDA) with 1,1,1-trichloroethane.

Solid (Cy-*acac*)₂V(TMEDA) (2.0 g, 4.5 mmol) was dissolved in 100 mL of anhydrous toluene to give a dark blue solution, which in turn was treated with an excess of trichloroethane (1.9 mL, 13.5 mmol) with stirring. The blue solution immediately turned dark

brown. The reaction mixture was stirred at room temperature overnight, then filtered to eliminate a tiny amount of insoluble material. The solvent was evaporated to dryness and the residual solid redissolved in hexane. A brown solid (1.1 g) separated slowly upon standing at room temperature for one month. I.R. (Nujol mull, cm^{-1}): 1541(m), 1502(m), 1459(s), 1377(s), 1297 (w), 1260 (m), 1249 (m), 1225 (m), 1174 (m), 1144 (m), 1096 (m), 1021 (m), 961 (w), 937 (w), 930 (w), 874 (s), 794 (s), 761 (m), 740 (m), 722 (w), 628(m). $\mu_{\text{eff}} = 2.67 \mu_{\text{BM}}$

Synthesis of $[(t\text{-Bu-acac})_2\text{V}(\text{TMEDA})]_2[\text{ZnCl}_4]$ (2.8).

A mixture of $[(t\text{-Bu-acac})_2\text{V}(\text{TMEDA})]$ (1 g, 1.8 mmol) with excess $\text{ZnCl}_2(\text{THF})_2$ was added to a dry toluene solution (100 mL) containing three equivalents of reactivator (0.75 mL, 5.4 mmol). Stirring for 12 hours resulted in a drastic color change from dark blue to reddish brown. After partial removal of the solvent *in vacuo*, the solution separated red cubic crystals of 2.8 (0.22 g) upon standing at room temperature for a few hours. Anal. Calcd (found) for $\text{V}_2\text{C}_{56}\text{H}_{108}\text{O}_8\text{N}_4\text{ZnCl}_4$: C, 52.77 (52.82); H, 8.54 (8.55); N, 4.40 (4.41). I.R. (Nujol mull, cm^{-1}): 1561(s), 1510(s), 1456(m), 1376(s), 1286(m), 1186(m), 1125(m), 1098(m), 1057(m), 1003(s), 953 (m), 920(m), 798(m), 755(m), 722 (w), 654 (m), 566 (w); $\mu_{\text{eff}} = 2.82 \mu_{\text{BM}}$

Synthesis of $[(t\text{-Bu-acac})_2\text{V}(\text{TMEDA})][\text{CuCl}_2]$ (2.9).

A crystalline sample of 2.8 (2.00 g, 3.3 mmol) was dissolved in toluene (100 mL). Upon addition of excess anhydrous CuCl (0.49 g, 4.9 mmol) there was no immediate color change. The mixture was stirred and heated at 110°C for 12 hours upon which a dark burgundy red solution was formed. The solution was filtered to eliminate some colloidal copper and excess CuCl . The solution was concentrated *in vacuo* and allowed to stand overnight at room temperature. Burgundy red crystals of $[(t\text{-Bu-acac})_2\text{V}(\text{TMEDA})]^+[\text{CuCl}_2]^-$

separated (0.80 g, 1.2 mmol, yield 36%). Anal. Calcd. (Found) for $\text{VC}_{28}\text{H}_{54}\text{N}_2\text{O}_4\text{CuCl}_2$: C 50.33 (50.21), H 8.15 (8.09), N 4.19 (4.13); I.R. (Nujol mull, cm^{-1}): 1582(s), 1531(s), 1456(s), 1376(s), 1327(m), 1286(m), 1172(m), 1036(s), 921(m), 853(s), 722(m), 668 (m). $\mu_{\text{eff}} = 3.92$ B. M.

Synthesis of $\text{V}(\text{t-Bu-acac})_2\text{Cl}_2$ (2.10)

n-BuLi (3.2 ml, 2.5 M in hexane) was added to a stirred solution of t-Bu-acacH (1.7 ml, 8.1 mmol) in toluene (150 ml) at -78°C . The mixture was kept on stirring for 1 hour and allowed to warm up to room temperature. $\text{VCl}_4(\text{DME})$ (1.15 g, 4.1 mmol) was added under stirring to the mixture. The resulting solution was stirred for several hours which color changed from colorless to dark blue. The resulting solution was evaporated to dryness. The residual solid redissolved in ether (50 ml) and LiCl was removed by filtration. The filtrate was allowed to stand at -30°C for 2 days, upon which a blue crystal of $\text{V}(\text{t-Bu-acac})_2\text{Cl}_2$ (2.10) (1.0 g, 2.0 mmol, yield 50%) separated. Infrared Spectrum (Nujol mull, cm^{-1}): 1457(s), 1376(s), 1283(s), 1190(s), 1124(m), 1017(s), 953(s), 924(s), 796(s), 756(s), 654(s). $\mu_{\text{eff}} = 1.86$ B. M..

Synthesis of $[\text{VCl}_2(\text{THF})_4][\text{EtAlCl}_3]$ (2.11)

To a solution of $\text{VCl}_3(\text{THF})_3$ (3.7 g, 9.9 mmol) in THF (150 ml) was added the 20 ml of EtAlCl_2 (1.0 M, hexane) at room temperature. The mixture was kept on stirring for 2 hours which color changed from purple/pink to light yellow and allowed to stand at -30°C for 2 days, upon which light yellow crystals of $[\text{VCl}_2(\text{THF})_4][\text{EtAlCl}_3]$ (2.11) (4.3 g, 7.5 mmol, yield 76%) separated. Anal. Calcd (Found) for $\text{VAlCl}_5\text{C}_{18}\text{H}_{37}\text{O}_4$: C 37.75 (36.70), H 6.51

(6.40); Infrared Spectrum (Nujol mull, cm^{-1}): 1456(s), 1346(s), 1259(s), 1176(s), 1041(s), 1003(s), 958(s), 922(s), 839(s), 683(m), 615(m). $\mu_{\text{eff}} = 1.74$ B.M..

General Polymerization Procedure.

Catalysts were evaluated by copolymerizing ethylene-propylene in cyclohexane solutions at 2 bar total pressure and 22°C. Experiments were carried out in 200 mL cyclohexane in magnetically agitated glass reactors using a continuous flow of 1000 sccm ethylene and 1000 sccm propylene. After equilibration of the cyclohexane with the EP feed, 0.2 mmole of cocatalyst was added followed by 5 μmole $\text{V}(\beta\text{-diketonate})_3$. Reactivating substance (CHCl_3) was continuously added to the reaction mixture. Polymerization reactions were carried out for 30 minutes followed by addition of 5 mL ethanol and depressurization. The EP rubber was recovered by solvent evaporation, dried in a vacuum oven at 60°C. The polymer composition was determined by FTIR using the ratio of peak heights of the bands at 1155 and 720 cm^{-1} after calibration with standard samples. The molecular weights were determined by GPC at 140°C by using trichlorobenzene as a solvent. The molecular weights are reported as polystyrene equivalents. Each experiment and determination was conducted at least five times in order to obtain a reliable statistic. Table 2.1 summarizes the findings.

Structural studies

Data were collected for a suitable air-sensitive crystal mounted under the liquid nitrogen stream of a Siemens CCD X-ray diffractometer. The ω -2 θ scan technique was used. Data were collected to 57.0 deg. (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). Their positions were refined anisotropically. 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).

All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were assigned with idealized geometry, and constrained with an isotropic, riding model. Crystallographic details are presented in Table 2.3, 2.4, 2.5. Selected bond distances and angles are given in Table 2.3a, 2.4a, 2.5a. All scattering factors are contained in the SHELXTL 5.03 program library (Sheldrick, 1997, WI).

Complex 2.3 and 2.4. The structure of **2.3** (Fig. 2.1) and **2.4** (Fig. 2.2) is identical to that of $V(acac)_3$ ²⁰. The average V-O bond distance (1.98 Å) is in both **2.3** and **2.4** is very similar to that of $V(acac)_3$ (1.97 Å). The octahedron formed by the oxygen atoms about vanadium center is trigonally distorted in both **2.3** (O2A-V1-O2 = 176.2(3)°, O2A-V1-O3 = 90.3(2)°, O3-V1-O2 = 92.4(2)°, O3-V1-O3A = 87.7(3)°, O2-V1-O1 = 85.7(2)°, O2-V1-O1 = 85.7(2)° and **2.4** (O3-V-O5 = 88.62(11)°, O3-V-O6 = 91.15(11)°, O6-V-O5 = 87.81(11)°, O3-V-O1 = 178.29(12)°). The O-V-O interring angles are different from that of $V(acac)_3$ (O1-V-O6 = 91.7(2)°, O1-V-O5 = 89.8(2)°, O5-V-O6 = 88.86(14)°).

Complex 2.5. The structure consists of two distinct ionic fragments (Figure 2.3). The cation is formed by an octahedral aluminum atom surrounded by two *acac* ligands [Al(1)-O(3) =

1.846(4)Å, Al(1)-O(4) = 1.843(4)Å] and two molecules of THF [Al-O(6) = 1.953(4)Å] in an overall regular octahedral coordination geometry [O(3)-Al(1)-O(4) = 92.8(2)°, O(3)-Al-O(6) = 90.1(2)°, O(4)-Al-O(6) = 90.1(2)°, O(3)-Al(1)-O(4a) = 87.2(2)°]. The two *acac* ligands define the symmetry generated equatorial plane of the octahedron [O(3)-Al(1)-O(3a) = 180.0°, O(4)-Al(1)-O(4a) = 179.997(1)°] while the two molecules of THF are lying *trans* to each other on the vertical axis [O(6)-Al(1)-O(6a) = 180.0°]. The anion is a regular tetrahedral AlCl₄⁻ anion [Al(3)-Cl(1) = 2.100(3)Å°, Cl(1)-Al(3)-Cl(2) = 109.6(2)°]. The structure of **2.5** is rather unique and provides the third example of a cationic aluminum species.^{3,19}

Complex 2.7. The crystal structure is composed by discrete monomeric units containing a vanadium atom in a slightly distorted octahedral environment. Two *acac* ligands [V-O(1) = 2.057(4)Å, V-O(2) = 2.051(4)Å, V-O(3) = 2.065(4)Å, V-O(4) = 2.042(4)Å] and one TMEDA [V-N(1) = 2.243(5)Å, V-N(2) = 2.239(4)Å] defined the coordination octahedron [O(1)-V-O(2) = 88.0(2)°, O(1)-V-N(1) = 92.2(2)°, O(1)-V-O(3) = 92.0(2)°, O(1)-V-O(4) = 94.2(2)°, O(1)-V-N(1) = 92.2(2)°, O(1)-V-N(2) = 171.9(2)°] (Figure 2.4).

Complex 2.8. The structure consists of three separate ionic units. The two identical cationic vanadium moieties are octahedral with two *acac* ligands and one TMEDA defining the vertices of a distorted octahedron [O(1)-V-O(2) = 87.31(18)°, O(1)-V-O(3) = 96.03(18)°, O(1)-V-O(4) = 88.71(18)°, N(1)-V-N(2) = 82.4(2)°, O(1)-V-N(1) = 91.3(2)°, O(1)-V-N(2) = 173.3(2)°]. Both the V-N and V-O bond distances [V-N(1) = 2.172(6)Å, V-O(1) = 1.963(4)Å, V-O(2) = 1.961(4)Å] and angles are as expected and compare well with those of (acac)₃V.¹⁵ The anion is formed by a zinc atom surrounded by four chlorine atoms defining a rather regular tetrahedron with normal bond distances [Zn-Cl(1) = 2.277(2)Å] and angles [Cl(1)-Zn-Cl(2) = 11.07(8)°] (Figure 2.5).

Complex 2.9. The complex is isomorphous with **8** except for the anionic fragment which consists of a linear CuCl_2 anion [$\text{Cu}-\text{Cl}(1) = 2.0863(13)\text{\AA}$, $\text{Cl}(1)-\text{Cu}-\text{Cl}(1a) = 180.00(8)^\circ$] (Figure 2.6).

Complex 2.10. The structure of $\text{trans-V}(\text{t-Bu-acac})_2\text{Cl}_2$ is very similar to that of $\text{trans-V}(\text{acac})_2\text{Cl}_2$. The expected octahedral coordination around the vanadium is defined by two chlorine and four oxygen atoms of the t-Bu-acac groups ($\text{Cl}-\text{V}-\text{Cl}(\text{A}) = 180^\circ$, $\text{O}(1)-\text{V}-\text{O}(1\text{A}) = 180^\circ$, $\text{O}(2)-\text{V}-\text{Cl}(1\text{A}) = 89.79^\circ$, $\text{O}(2)-\text{V}-\text{Cl} = 90.21^\circ$, $\text{O}(1)-\text{V}-\text{O}(1\text{A}) = 180^\circ$, $\text{O}(2)-\text{V}-\text{O}(1) = 86.56^\circ$). The mean V-O bond distance ($1.888\text{ \AA}$) is comparable with that of $\text{trans-V}(\text{acac})_2\text{Cl}_2$ ($1.91\text{ \AA}$) (Figure 2.7).

Complex 2.11. The unit cell contains two independent fragments. The first unit is $[\text{VCl}_2(\text{THF})_4]^+$ (Fig. 2.7). The octahedral geometry around vanadium is defined by two atoms of chlorine which are placed in *trans* position ($\text{Cl}(1)-\text{V}-\text{Cl}(2) = 179.56(13)$) and four molecules of THF which define the equatorial plane ($\text{O}(1)-\text{V}-\text{O}(2) = 90.4(3)$, $\text{O}(1)-\text{V}-\text{O}(4) = 91.1(3)$, $\text{O}(1)-\text{V}-\text{O}(3) = 179.6(3)$, $\text{O}(1)-\text{V}-\text{Cl}(2) = 90.0(2)$). The second unit is a $[\text{EtAlCl}_3]^-$ anion (Fig. 2.8). The aluminum atom is placed in the center of a distorted tetrahedron defined by three chlorine atoms and one alkyl group ($\text{Cl}(4)-\text{V}-\text{Cl}(5) = 105.6(2)$, $\text{Cl}(4)-\text{V}-\text{Cl}(3) = 106.6(2)$, $\text{C}(17)-\text{V}-\text{Cl}(4) = 111.4(4)$, $\text{C}(17)-\text{V}-\text{Cl}(5) = 111.3(4)$). The Al-C bond distance is $[\text{Al}-\text{C}(17) = 1.958(10)\text{ \AA}]$.

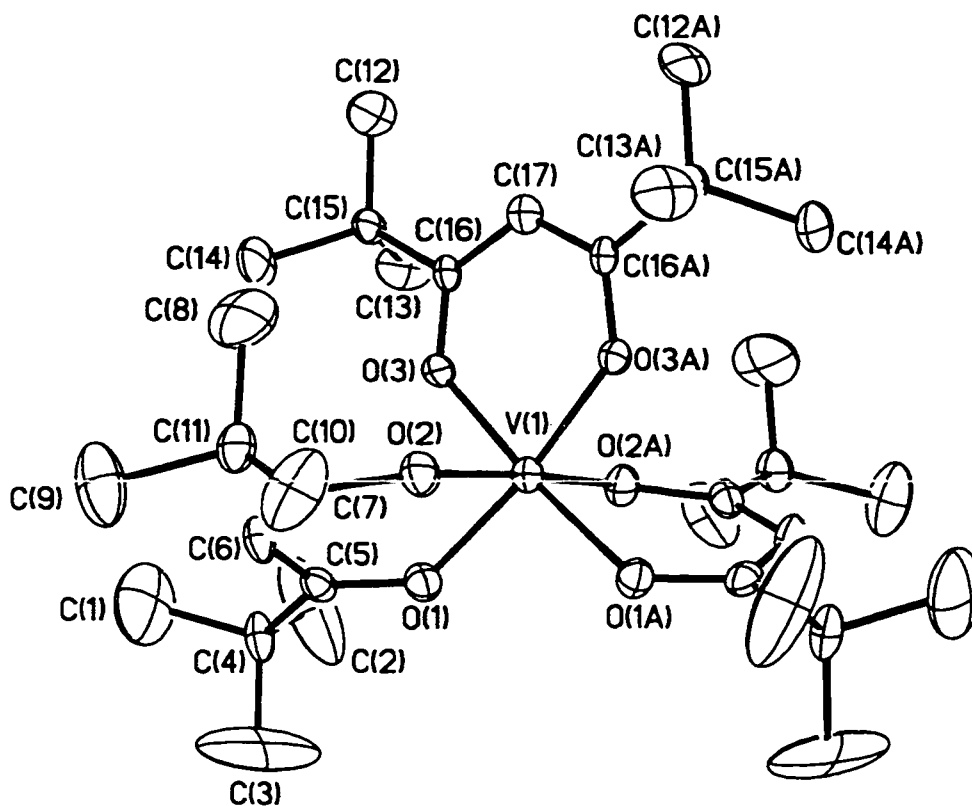


Fig. 2.1 ORTEP drawing of $V(t\text{-Bu-acac})_3$ (**2.3**) Bond distances ($\text{\AA}$) and angles (deg) are as follows: $V1-O2\#1 = 1.962(5)$, $V1-O2 = 1.962(5)$, $V1-O3 = 1.970(5)$, $V1-O3\# = 1.970(5)$, $V1-O1\# = 2.013(5)$, $V1-O1 = 2.013(5)$, $O2\#1-V1-O2 = 176.2(3)$, $O2\#1-V1-O3 = 90.3(2)$.

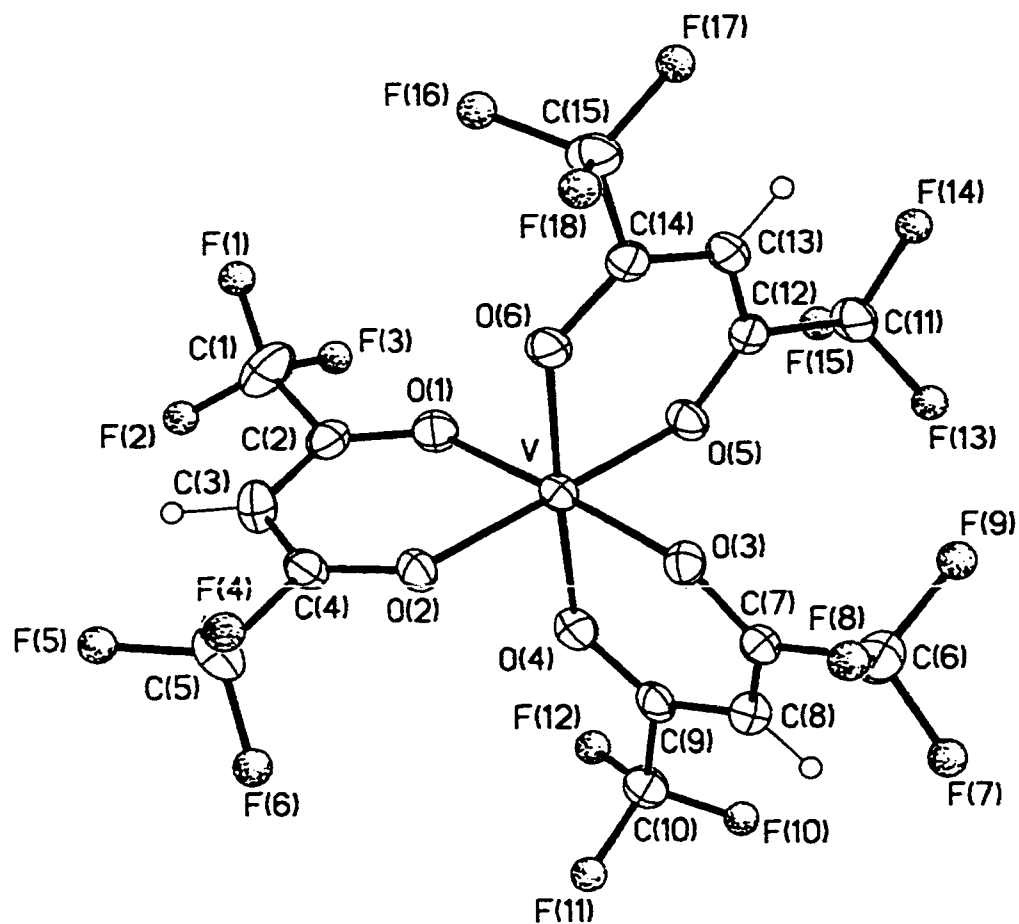


Fig. 2.2 ORTEP drawing of $V(F\text{-}acac)_3$ (2.4) Bond distances ($\text{\AA}$) and angles (deg) are as follows: $V\text{-}O3 = 1.960(3)$, $V\text{-}O5 = 1.966(4)$, $V\text{-}O6 = 1.973(3)$, $V\text{-}O1 = 1.986(3)$, $V\text{-}O4 = 1.991(3)$, $O3\text{-}V\text{-}O5 = 88.62(11)$, $O3\text{-}V\text{-}O6 = 91.15(11)$.

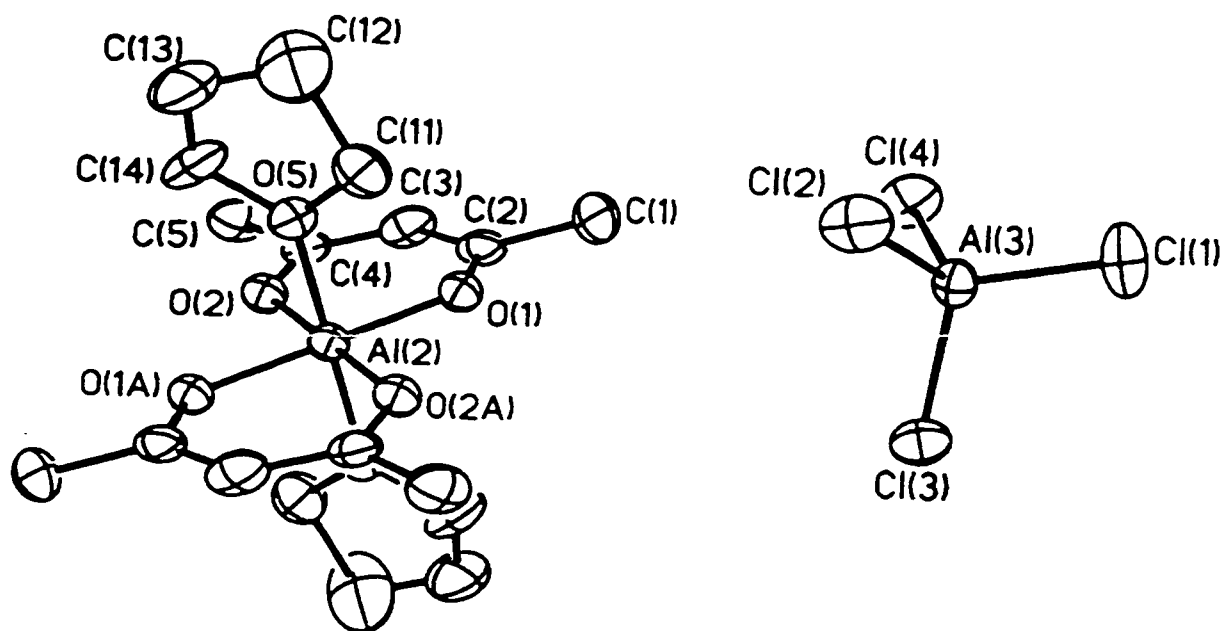


Fig. 2.3 ORTEP drawing of $[\text{Al}(\text{acac})_2(\text{THF})_2][\text{AlCl}_4]$ (2.5) Bond distances (Å) and angles (deg) are as follows: $\text{Al}(1)\text{-O}(4) = 1.843(4)$, $\text{Al}(1)\text{-O}(3) = 1.846(4)$, $\text{Al}(1)\text{-O}(6) = 1.953(4)$, $\text{Al}(3)\text{-Cl}(1) = 2.100(3)$, $\text{Al}(3)\text{-Cl}(2) = 2.119(3)$, $\text{Al}(3)\text{-Cl}(3) = 2.125(3)$, $\text{O}(4\text{a})\text{-Al}(1)\text{-O}(4) = 179.997(1)$, $\text{O}(4\text{a})\text{-Al}(1)\text{-O}(3) = 92.8(2)$, $\text{O}(4)\text{-Al}(1)\text{-O}(3\text{a}) = 87.2(2)$.

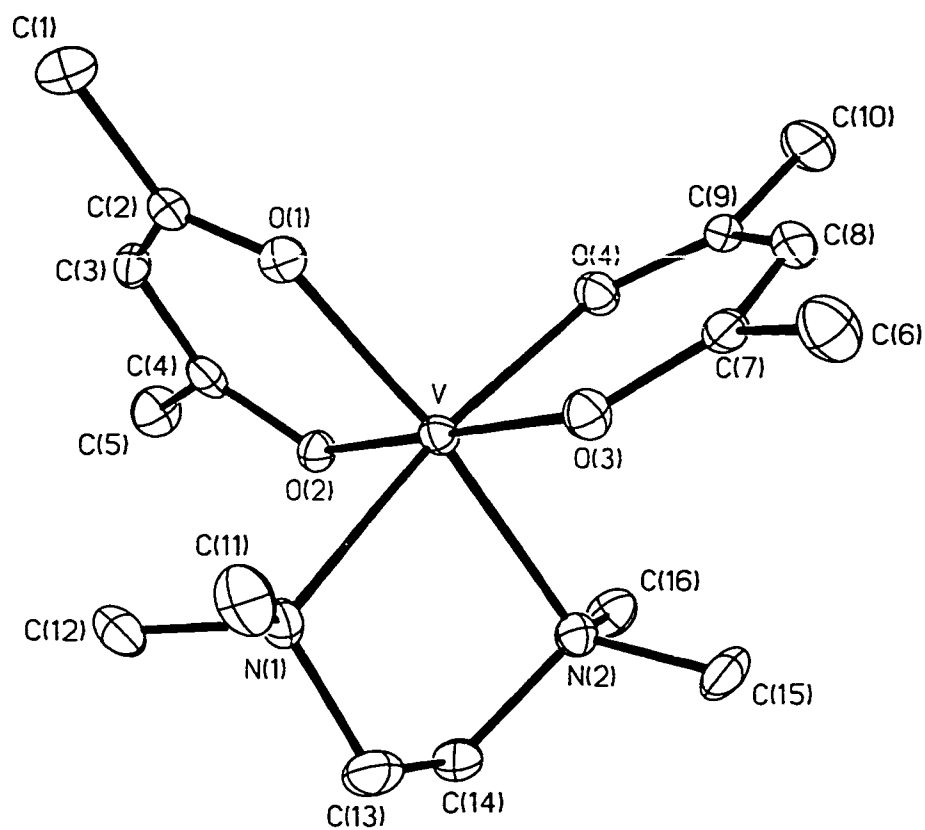


Fig. 2.4. ORTEP drawing of $V(acac)_2(TMEDA)$ (**2.7**) Bond distances ($\text{\AA}$) and angles (deg) are as follows: $V-O(4) = 2.042(4)$, $V-O(2) = 2.051(4)$, $V-O(1) = 2.057(4)$, $V-O(3) = 2.065(4)$, $V-N(2) = 2.239(4)$, $O(2)-V-O(3) = 179.8(2)$, $O(4)-V-O(3) = 88.4(2)$, $O(2)-V-O(1) = 88.0(2)$.

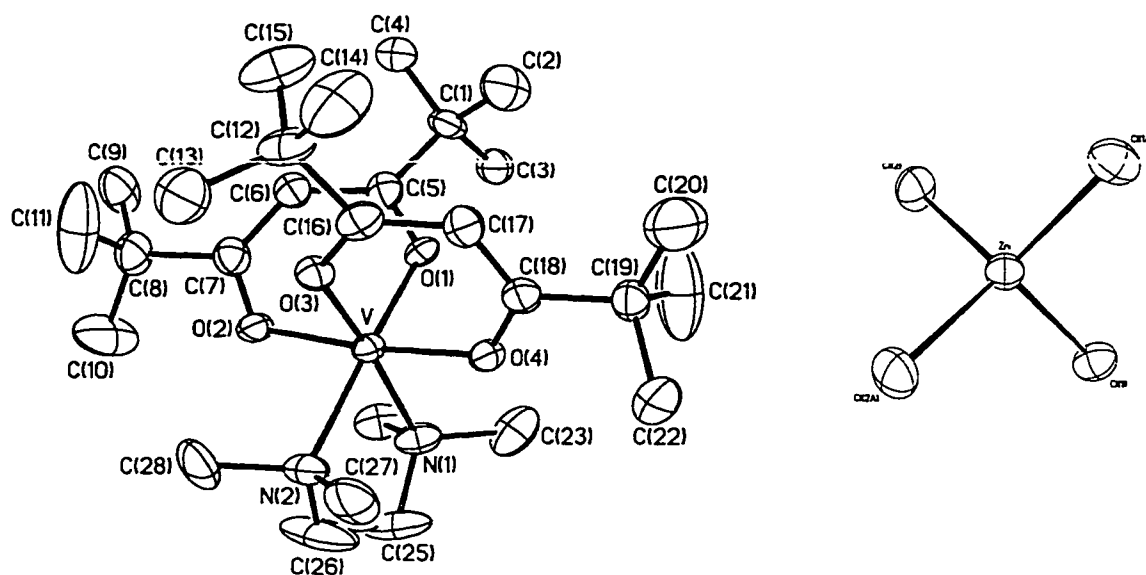


Fig. 2.5. ORTEP drawing of $[(t\text{-Bu-acac})_2\text{V(TMEDA)}]_2[\text{ZnCl}_4]$ (**2.8**) Bond distances (Å) and angles (deg) are as follows: V-O(3) = 1.936(4), V-O(4) = 1.957(4), V-O(2) = 1.961(4), V-O(1) = 1.963(4), V-N(1) = 2.172(6), O(1)-C(5) = 1.272(8), O(2)-C(7) = 1.307(8), O(3)-C(16) = 1.285(9), O(3)-V-O(4) = 87.82(18).

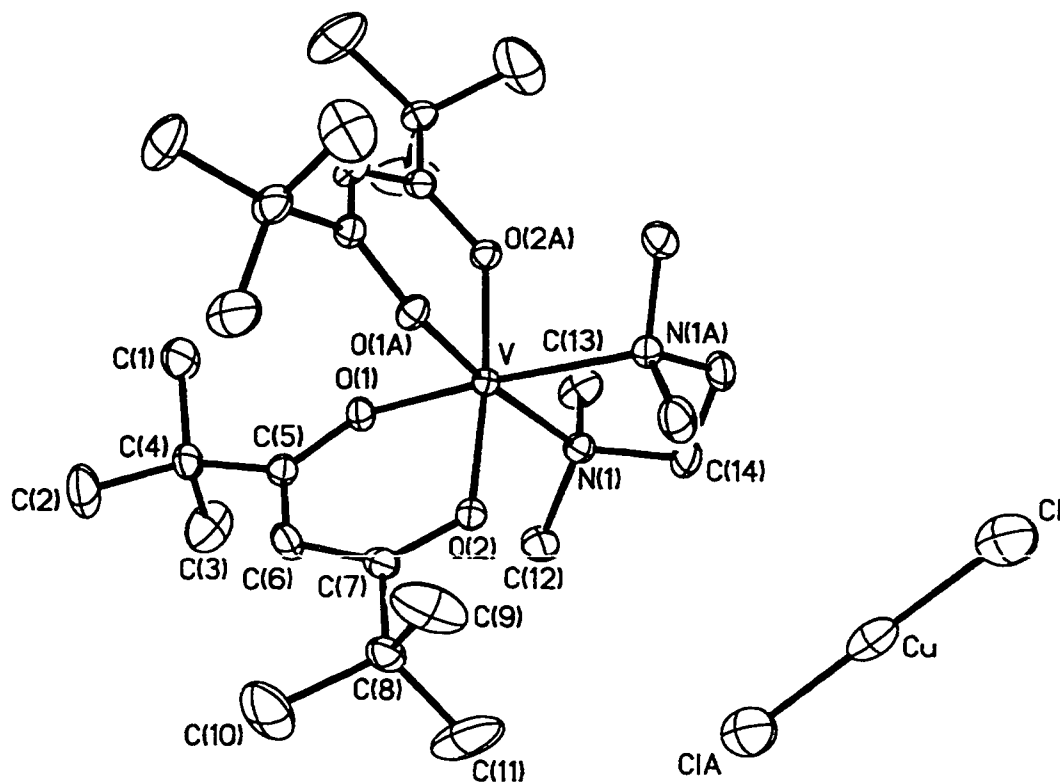


Fig. 2.6. ORTEP drawing of $[(t\text{-Bu-acac})_2\text{V(TMEDA)}][\text{CuCl}_2]$ (**2.9**) Bond distances ($\text{\AA}$) and angles (deg) are as follows: $\text{V-O1} = 1.9497(17)$, $\text{V-O1\#} = 1.9497(16)$, $\text{V-O2} = 1.9601(17)$, $\text{V-O2\#} = 1.9601(17)$, $\text{V-N1} = 2.188(2)$, $\text{O2-V-O1\#} = 88.89(7)$, $\text{O2-V-O1} = 87.28(7)$, $\text{Cu-Cl2\#} = 2.0863(12)$, $\text{Cu-Cl} = 2.0863(13)$, $\text{O1-V-O1\#} = 94.62(10)$.

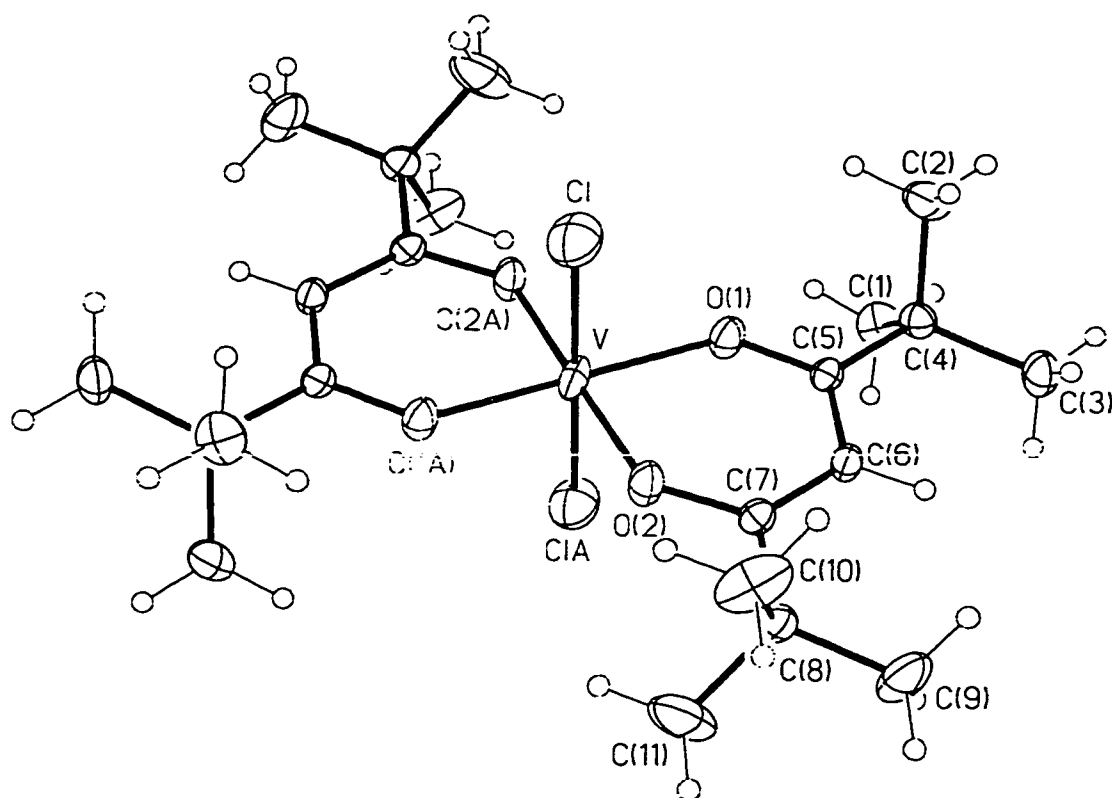


Fig 2.7. ORTEP drawing of $V(\text{t-Bu-acac})_2\text{Cl}_2$ (**2.10**) Bond distances (Å) and angles (deg) are as follows: $V\text{-O}2 = 1.8846(13)$, $V\text{-O}2\# = 1.8847(13)$, $V\text{-O}1 = 1.8904(13)$, $V\text{-O}1\# = 1.8904(13)$, $V\text{-Cl}1 = 2.265(3)$, $V\text{-Cl}2 = 2.264(3)$, $\text{O}2\text{-V-O}2\# = 180.0$, $\text{O}1\text{-V-O}1\# = 93.44(5)$.

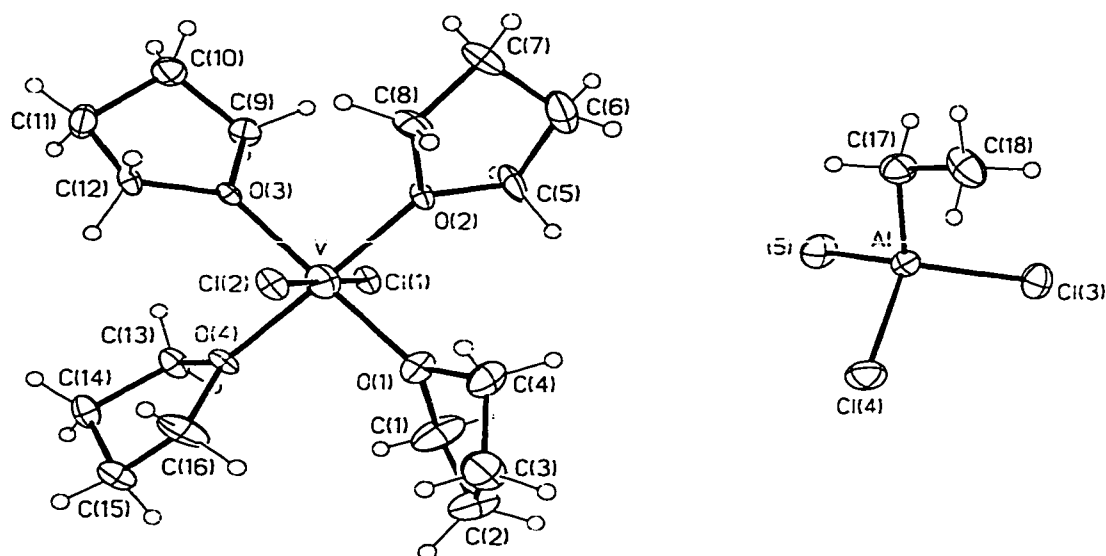
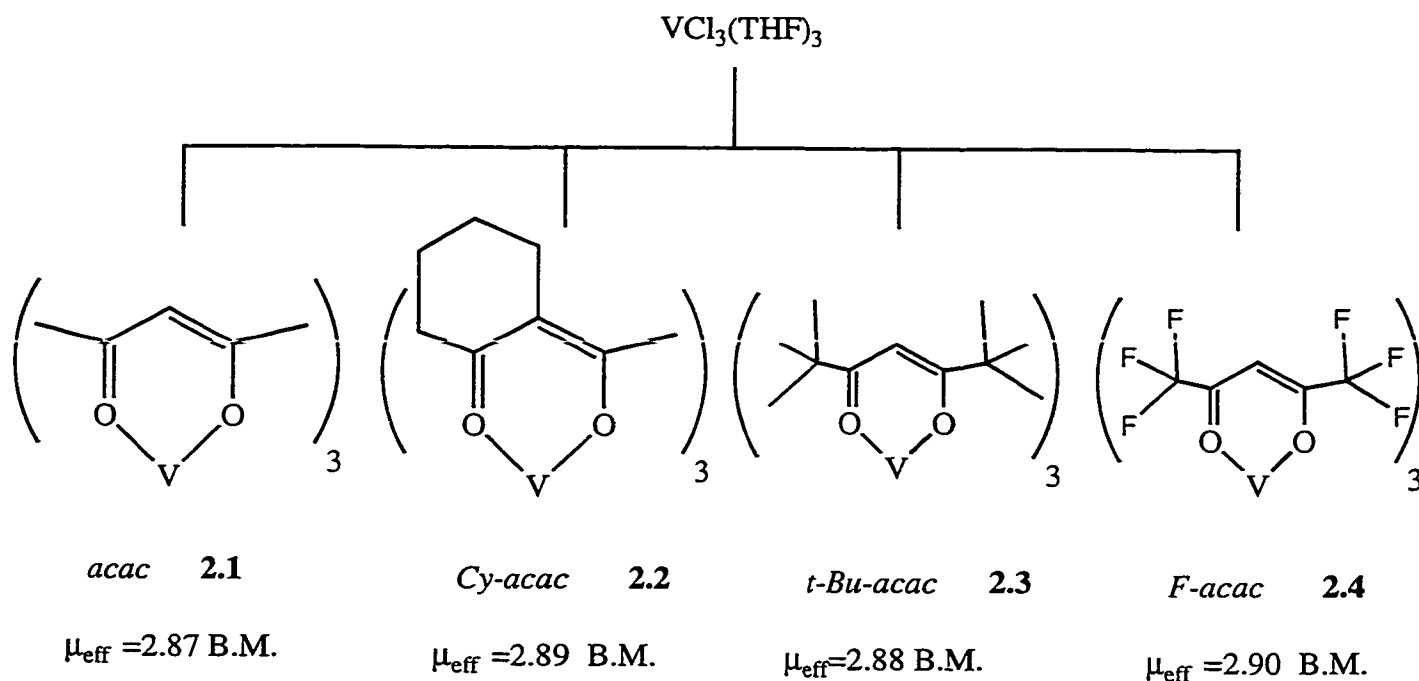


Fig 2.8. ORTEP drawing of $[\text{VCl}_2(\text{THF})_4][\text{EtAlCl}_3]$ (2.11) Bond distances ($\text{\AA}$) and angles (deg) are as follows: $\text{V-O1} = 1.955(6)$, $\text{V-O4} = 1.974(5)$, $\text{V-O2} = 1.985(5)$, $\text{Al-C17} = 1.958(10)$, $\text{Al-Cl3} = 2.155(4)$, $\text{Al-Cl2} = 2.155(4)$, $\text{O4-V-O2} = 178.5(3)$, $\text{V-Cl2} = 2.264(3)$, $\text{O1-V-O2} = 90.4(3)$, $\text{Al-Cl5} = 2.1167(4)$, $\text{O1-V-O4} = 91.1(3)$.

Results and Discussion



Scheme 2.1

Four $(\text{R-acac})_3\text{V}$ complexes were prepared (Scheme 2.1) in order to study the effect of the steric and electronic features of the various ligands on catalyst activity. By selecting the *Cy-acac* ligand we expected to obtain higher solubility while nearly preserving the steric and electronic properties of the basic *acac* ligand. It was hoped that higher solubility would heighten the possibility of isolating the catalytically active species in crystalline form. By using the *t-Bu-acac* ligand we expected to be able to evaluate the influence of steric factors on

the catalytic process. The fluorinated *F-acac* was expected to modify mainly the electronic features of the ligand while keeping the steric bulk of the catalyst almost comparable to that of *t-Bu-acac*. The vanadium dionate complexes employed in this study were prepared following standard procedures and were characterized by combustion analysis, IR spectroscopy and single crystal X-ray analysis. Magnetic moments consistent with the high spin d^2 electronic configuration were obtained in all cases.

The catalytic activity of the various complexes was tested for ethylene-propylene copolymerization in the presence of catalyst reactivator (i.e. CHCl_3). The results are summarized in Table 2.1.

Table 2.1	V(acac)₃ (2.1)		V(Cy-acac)₃ (2.2)		V(<i>t</i>-Bu-acac)₃ (2.3)		V(<i>F</i>-acac)₃ (2.4)	
	DEAC	EASC	DEAC	EASC	DEAC	EASC	DEAC	EASC
Activity*	994	980	10168	990	746	622	762	800
M_w x 10³	219	702	218	716	290	1265	277	801
% ethylene	62	52	59	53	65	57	63	54

* Kg EP elastomer produced in 30 minutes by one mole of vanadium catalyst; DEAC = Et_2AlCl , EASC = $\text{Et}_3\text{Al}_2\text{Cl}_3$

The results clearly indicate that the activities of **2.1** and **2.2** are comparable in the presence of DEAC and EASC, and are slightly higher with respect to the more crowded **2.3** and **2.4**. However, these effects are only minor and we can conclude that in general the activity is relatively insensitive to both the chlorine content of the cocatalyst and to the R-*acac* ligand

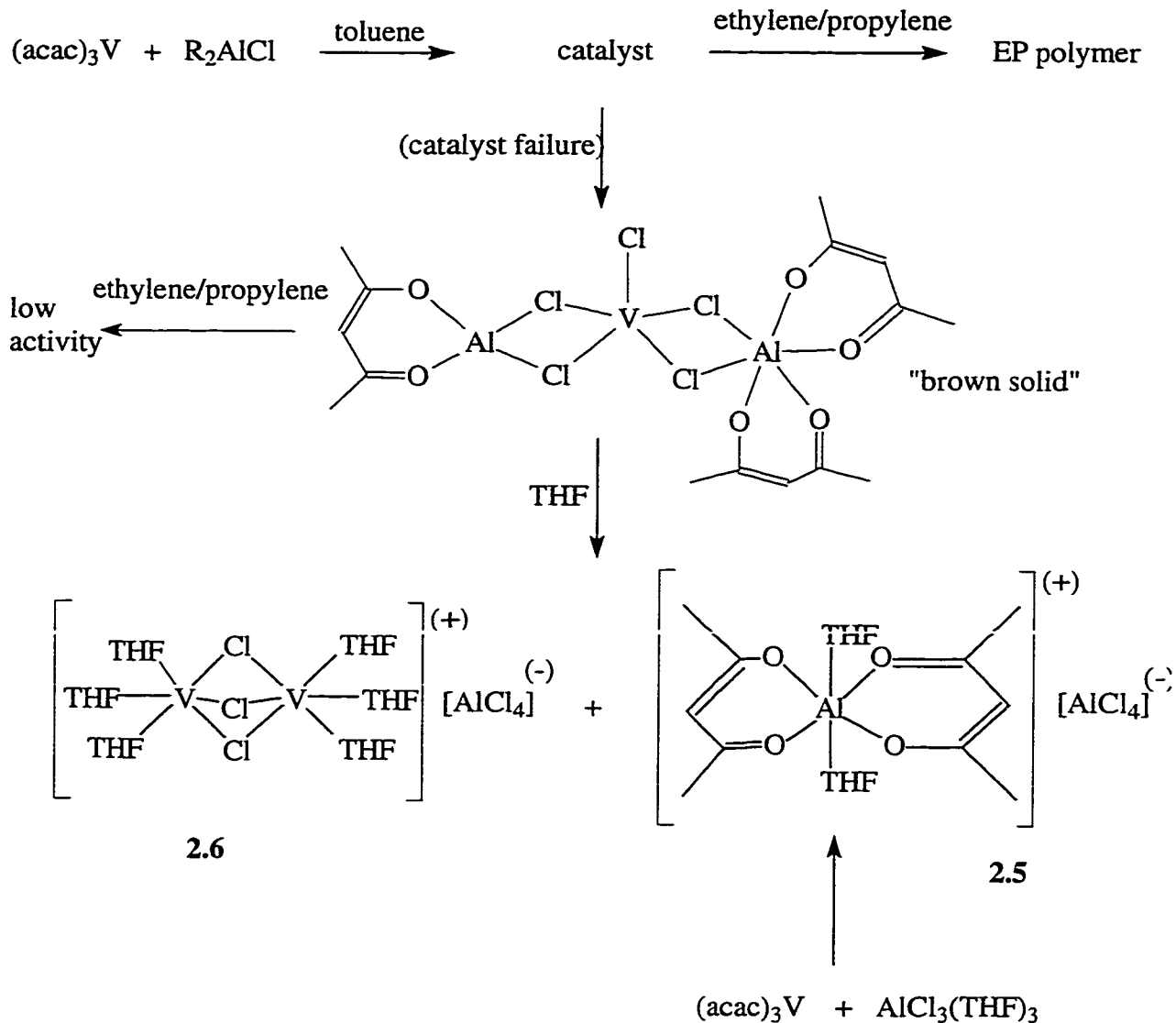
steric hindrance. Even more surprising, the two bulky *t*-Bu-acac and *F*-acac ligands show comparable activities in spite of their considerably different electronegativities. Examination of the data in Table 2.1 reveals that the propylene content in the EP elastomers decreases in the case of the sterically encumbered **2.4** and **2.3** catalysts but only to a surprisingly modest extent.

The relative insensitivity of both the catalyst activity and polymer composition to large a variation in ligand steric hindrance and electronic features strongly indicates that the catalytic site is widely open and probably far from the β -diketonate ligand. Thus, a primary role of the aluminum cocatalyst is that of abstracting at least two if not all of the three *acac* ligands from the vanadium center. The variation of about 5-10% in polymer composition observed by changing the cocatalyst Lewis acidity is also in line with this rationale. A relatively minor increase of the Lewis acidity of the cocatalyst as in the case of EASC probably increases the extent of migration of the *acac* ligand from vanadium thus decreasing further the selectivity.

Different from the catalyst activity and polymer composition, the polymer molecular weight was strongly affected by the nature of the cocatalyst. The higher molecular weights consistently observed with the more acidic EASC cocatalyst are perhaps explained by a diminished tendency to perform destructive C-H σ -bond metathesis or reductive elimination reactions while in the presence of a lower concentration of alkyl functions. The fact that the nature of the *R*-acac ligand indeed plays a role in determining the molecular weight of the polymer, indicates that the ligand determines the stability and the life-time of the active species.

The polymerization reactions were typically carried out in hydrocarbon solvents since the employment of coordinating solvents such as ethers are well known to quench the

polymerization. For this reason, attempts to isolate and characterize the catalytically active species were carried out by mixing together catalyst and cocatalyst in toluene with variable ratios and without exposure to reactivators. This was of course an oversimplification of the real catalytic system which *requires* the presence of reactivators for higher catalyst productivity. Nevertheless, we felt that this strategy might help to evaluate the intriguing roles of these substances and to shed some light on the structure of the catalyst.



Scheme 2.2

Different from the catalytic system where a large excess cocatalyst is imperative to enhance catalyst efficiency, the nature of the catalyst produced in toluene proved to be rather insensitive to the stoichiometric ratio employed. Typically, reactions carried out with a ratio of 1:1 and 1:3 (V:Al) produced the same poorly soluble, brown and paramagnetic material in high yield (Scheme 2.2). This solid is pyrophoric and reacts with moisture to yield a small

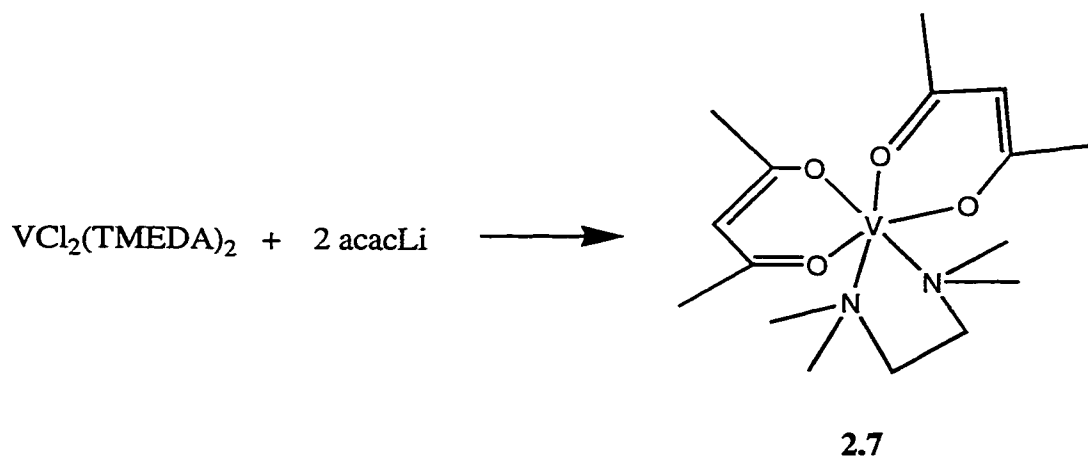
amount of ethane (5%). Although combustion analysis data were inconclusive due to the extreme air-sensitivity of this solid, XRF data consistently yielded a V/Cl/Al ratio of 1:5:2. The IR spectrum clearly indicated the presence of the *acac* ligand. Once placed in cyclohexane or toluene and exposed to a mixture of ethylene and propylene, this solid displayed a minimal polymerization activity without the need of additional cocatalyst or of catalyst reactivator. We simply noticed that the catalytic activity was well below the normal level. Further addition of cocatalyst did not affect the catalytic activity. Unfortunately, repeated attempts to grow suitable crystals for X-ray analysis were hampered by the low solubility of the species in hydrocarbon solvents. Therefore, we have attempted to indirectly identify the nature of this species via degradation (Scheme 2.2). Treatment of the “brown solid” obtained from the direct reaction of the catalyst with the aluminum cocatalyst, with THF yielded a bright green solution from which a green crystalline mass, mixed together with white crystals, was obtained in good yield. In the case of the *acac* ligand (complex 2.1) the structures of both compounds were elucidated by X-ray analysis. The green crystals were found to be $[V_2Cl_3(THF)_6][AlCl_4]$ which contains vanadium in the formal oxidation state +2 and whose crystal structure has been previously reported.¹⁶ The white crystals are the unprecedented ionic $[(acac)_2Al(THF)_2][AlCl_4]$ complex. This species was also conveniently prepared in large scale and analytically pure form by reacting $(acac)_3V$ with $AlCl_3$ or through direct synthesis via treatment of $AlCl_3(THF)_3$ with 1 eq. of *acac*Na in THF.

These findings suggest that the cocatalyst plays the dual role of: 1) *completely* abstracting the *acac* ligands from the vanadium center, and 2) reducing vanadium to its divalent state.^{11a} In fact, treatment of the “brown solid” with THF is unlikely to trigger a redox process although the possibility that the divalent 2.4 might be generated by a disproportionation reaction cannot be categorically excluded at this stage. However, the good

yield of **2.4**, the neatness of the reaction and the consistency of the characteristic bright green color of the mother liquor with that of the isolated solid, discourage the idea that other high-valent vanadium species may be present in significant amount in the reaction mixture. On the basis of the XRF and degradation experiment results we speculate that the brown, poorly active solid obtained from the reaction of the catalyst with cocatalyst in toluene has the formulation $\{[(\beta\text{-diketonate})\text{AlCl}_2][\text{VCl}_2][(\beta\text{-diketonate})_2\text{AlCl}]\}$ (Scheme 2.2). Obviously the structure is purely speculative. However, it is consistent with all the finding described above. It contains the appropriate ratio of heavy elements and arises from simple reduction of the adduct obtained by adding two equivalents of cocatalyst to one equivalent of catalyst. The absence of *acac* ligands on the vanadium center is further consistent with the relative insensitivity of the catalyst activity and polymer composition to the nature of the *acac* ligand.

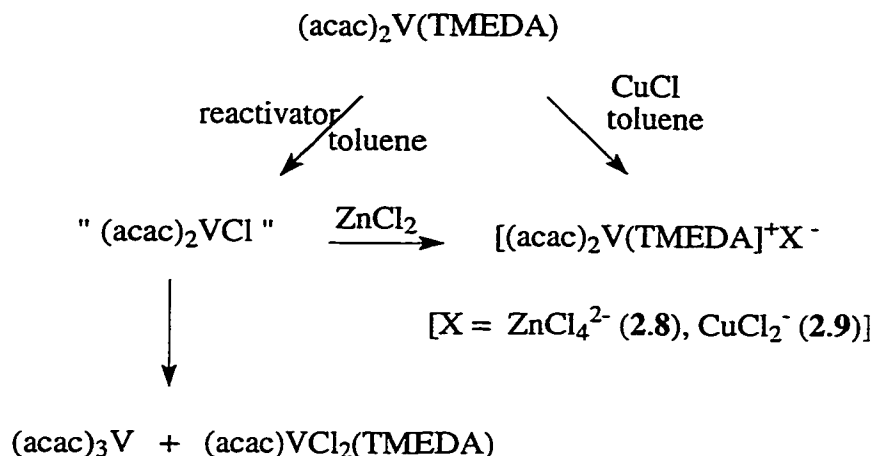
Since the brown product isolated from the reaction catalyst/cocatalyst is itself a very poor catalyst, at first glance this seems to contradict the recent claim that a V(II) species might be the active species responsible for the catalytic activity.^{11b} Actually, V(II) complexes indeed are poorly active towards olefin polymerization. We have tested the activity of $[\text{V}_2\text{Cl}_3(\text{THF})_6][\text{AlCl}_4]$ under the usual reaction conditions finding only negligible amount of polymerization in comparison to the β -diketonate V(III) complexes used in this work. Some activity was observed in the presence of reactivator, but the overall polymerization capability always remained very low. While it is well possible that the presence of THF in the coordination sphere of vanadium is responsible in this particular case for the lack of catalytic activity, on the other hand, the “brown solid” is a much less efficient catalyst in comparison to the catalysts prepared *in situ*. Therefore, the “brown solid” is some deactivated form of catalyst and since vanadium is present in this species in the oxidation state +2, reduction of the metal center indeed corresponds to catalyst deactivation. In an attempt to substantiate this

hypothesis, we have attempted the preparation of a V(II) complex containing the *acac* ligand, and to study its behavior in the presence of cocatalysts with or without reactivators. The (*R-acac*)₂V(TMEDA) complexes (**2.7**) were prepared as described in Scheme 2.3 via



Scheme 2.3

straightforward chlorine replacement reaction on $\text{VCl}_2(\text{TMEDA})_2$ by the corresponding β -diketonate lithium salt. The complex was isolated in good yield and crystalline form after suitable work up. This unprecedented species was characterized on the basis of combustion analysis data while the connectivity was elucidated by an X-ray crystal structure. The complex displays a value for its the magnetic moment as expected for the d^3 electronic configuration.



Scheme 2.4

Complex **2.7** is certainly not an ideal substrate to model the catalyst reactivation process. Two ligands are still attached to the vanadium atom while this is unlikely to happen during the catalytic cycle where the transition metal probably retained no more than one *acac* (if any). Furthermore, the presence of coordinated TMEDA in the coordination sphere of vanadium, necessary to prevent rapid disproportionation towards the formation of $(\text{acac})_3\text{V}$, could be detrimental to the catalytic process. Nevertheless, we expected that TMEDA would be easily abstracted by the excess cocatalyst, thus overturning its undesirable presence. Also, the presence of the β -diketonate ligand is certainly necessary to the catalytic cycle since simple vanadium (II) and (III) halide salts display far lower activity.

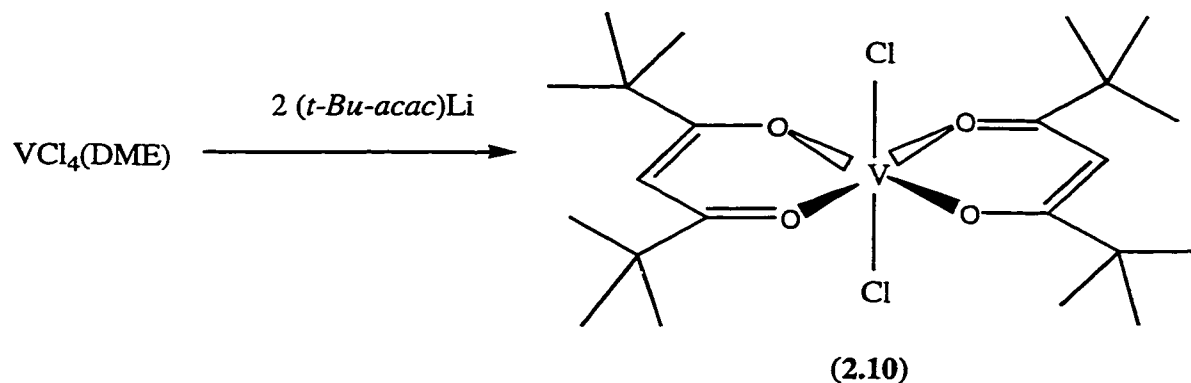
As expected, complex **2.7** does not polymerize olefins under the usual reaction conditions in the presence of cocatalyst but in the absence of reactivating substances. This reinforces the idea that V(II) species, formed during the catalytic cycle, are unreactive or only poorly reactive towards polymerization and thus their formation indeed accounts for the catalyst failure during the cycle. Conversely, treatment of toluene solutions of complex **2.7a** with reactivators suddenly changed the color from blue to brown-red and subsequent addition of excess DEAC gave a moderate polymerization activity (153 Kg/mole/20 min) in spite of the

detrimental presence of one equivalent of TMEDA in the mixture. Attempts to isolate the product of the reaction of **2.7a** with reactivators yielded a red-brown solid formulated as $(acac)_2VCl(TMEDA)$ (scheme 2.4). The formulation was demonstrated on the basis of analytical, spectroscopic and magnetic data. Since this species contains trivalent vanadium, it is legitimate to conclude that the primary role of the reactivator is that of reoxidizing the metal to the trivalent state and to provide in the process chlorine atoms. In agreement with this proposal, a similar reaction of **2.7** with reactivators carried out in the presence of $ZnCl_2$ allowed for the isolation of red crystals of $[(acac)_2V(TMEDA)]_2[ZnCl_4]$ (**2.8**) in good yield. This new compound is paramagnetic and provides satisfactory analytical data consistent with the formulation revealed by the X-ray crystal structure.

Similarly, oxidation of **2.7** with excess $CuCl$ in hot toluene led to the formation of an ionic complex $[(acac)_2V(TMEDA)][CuCl_2]$ **2.9** also containing the same cation of complex **2.8**.

By reforming $V(acac)_3$ through reactivation of the "reduced" catalytic species, the original V(III) catalyst is restored and polymerization is renewed. In view of the general inactivity of V(II) species towards olefin polymerization and corresponding remarkable efficiency of V(III)-based systems, the question arises concerning the behavior of V(IV) in terms of catalysis. Thus, in order to explore a possible alternative to $V(acac)_3$, we embarked on the preparation of *trans*- $V(t-Bu-acac)_2Cl_2$ **2.10** (Scheme 2.5) and assessed its catalytic activity.

The choice of this particular complex was based principally on its favorable solubility properties with respect to the previously reported $V(acac)_2Cl_2$. Its preparation was conveniently carried out by reacting $VCl_4(DME)$ with 2 eq. of a substituted (t-Bu-) 1,3-dionate lithium salt. The compound (**2.10**) was characterized by routine spectroscopy, elemental analysis, magnetic moment and X-ray analysis (Fig. 2.3).



Scheme 2.5

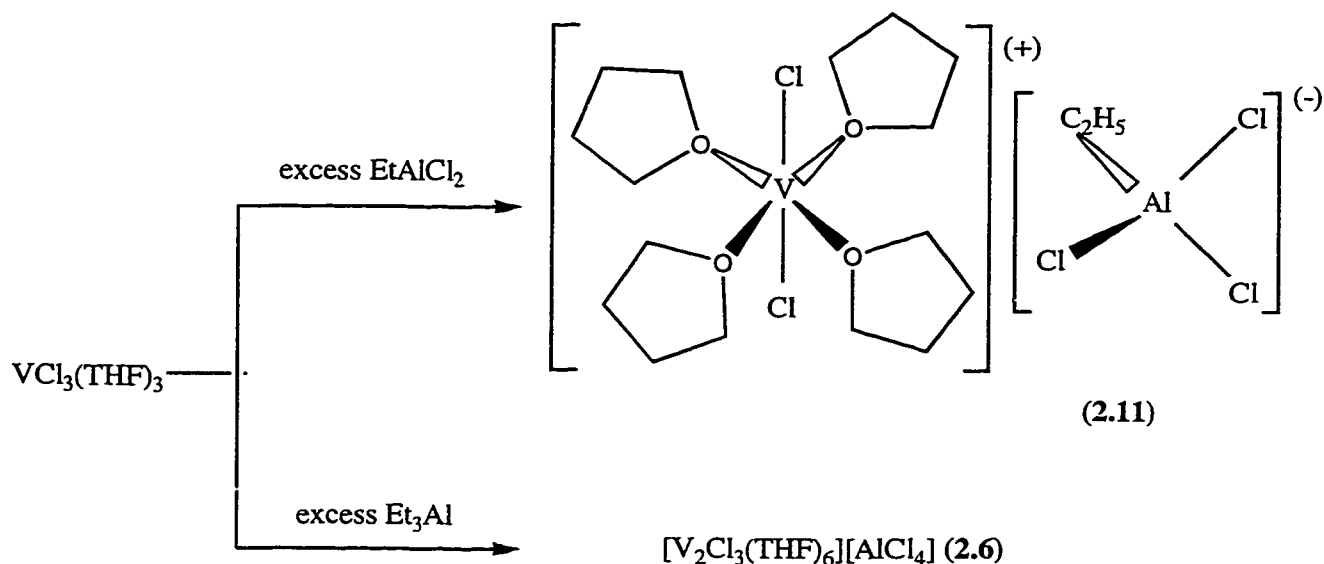
A comparison of the catalytic activity of $\text{V}(\text{t-Bu-acac})_3$ (**2.3**), and $\text{V}(\text{t-Bu-acac})_2\text{Cl}_2$ (**2.10**) in Table 2.2 (kg EP/mole V/hr) reveals that complex (**2.10**) is even more reactive towards ethylene polymerization.

Table 2.2	$\text{V}(\text{t-Bu-acac})_3$	$\text{V}(\text{t-Bu-acac})_2\text{Cl}_2$
	(2.1)	(2.10)
	DEAC	DEAC
Activity*	1.80	2.30

kg EP/mole V/hr, DEAC = Et_2AlCl

As mentioned before, our efforts to isolate the catalytically active species produced by the reaction of the vanadium catalyst with cocatalyst were not successful. Therefore, to approach this problem from another direction we attempted to identify the nature of the catalytic species using $\text{VCl}_3(\text{THF})_3$ as the starting material. The reaction of $\text{VCl}_3(\text{THF})_3$ with

an excess of EtAlCl_2 in THF formed a yellow solution (Scheme 2.6). Paramagnetic, yellow crystals of $[\text{VCl}_2(\text{THF})_4][\text{EtAlCl}_3]$ (**2.11**) were obtained in good yield. The formulation of (**2.11**) was confirmed by X-ray analysis.



Scheme 2.6

A similar reaction of $\text{VCl}_3(\text{THF})_3$ with excess Et_3Al in THF formed a green solution (Scheme 2.6). Paramagnetic, green crystals of $[\text{V}_2(\eta^2\text{-Cl})(\text{THF})_6][\text{AlCl}_4]$ (**2.6**) were obtained in good yield. The formulation of (**2.6**) was also confirmed by X-ray analysis. As expected for a V(II) species, this complex proved to be unreactive towards ethylene polymerization. It would indicate that excess Et_3Al more easily reduces V(III) to V(II) than does EtAlCl_2 . The comparison between these two reactions clearly indicates that 1) a primary role of the Al cocatalyst is that of performing as a Lewis acid to "cationize" the neutral starting complex 2) the balance between the alkyl groups and chlorine atoms is crucial to the stability of the

vanadium oxidation state. For example, excess alkyl groups were found to reduce the metal and deactivate the catalyst.

Conclusions

Unfortunately, the ambitious target of elucidating the structure of the catalyst and fully understanding the reactivation process was not reached with this work. However, it was at least possible to prove that $(acac)_3V$ indeed undergoes reduction to the divalent state during the catalytic cycle. A major ligand scrambling and perhaps a complete removal of the *acac* ligand from the metal center was also observed as a result of the interaction of catalyst and cocatalyst. The role of the reactivator is certainly that of restoring the trivalent state of vanadium.

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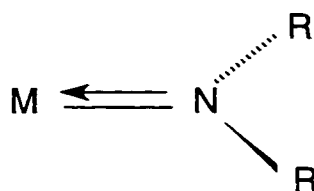
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Chapter 3

Preparation and Characterization of Tetra-Valent Vanadium Amide Complexes and Their Activity as Olefin Polymerization Catalysts

Introduction

Anionic organic amides are proven to be versatile supporting ligands. Transition metal derivatives of these species have shown an impressive variety of reactivity which spans from dinitrogen fixation¹ and cleavage², formation of carbenes³, metallacycles⁴, nitriles⁵, deoxygenation and fragmentation of THF solvent⁶, formation of unsupported M-M bonds⁷, coupling reactions⁸, hydrogenolysis of M-N bonds⁹, and formation of active intermediates in catalytic cycles^{1c,10}.



Given the above, literature scenario, anionic organic amide (R_2N^-) ligands with nitrogen-based donor atoms show potential for V(III) chemistry on account of some unique

characteristics of these ligand system. They are (a) easily accessible by simple deprotonation of secondary and primary amines; (b) widely available in large selection from commercial sources or via simple organic preparation; (c) sterically tunable by appropriate selection of organic substituents connected to the nitrogen donor atom; (d) versatile in terms of bonding modes since they may act as monodentate, bidentate, terminally bonded or bridging ligands; (e) electronically flexible since nitrogen's lone pair of electrons may participate in bonding, when necessary, through extensive π -donation from nitrogen to the metal center, and finally (f) optically active, when their alkyl substituents are selected to contain one or more chiral centers.

The employment of anionic organic amides as ancillary ligands has proven to be a viable alternative for the stabilization of a wide range of oxidation states for first-row transition metals Ti and Cr. However, much less information is available in the literature for the structure and reactivity of V(IV) amides.

Moreover, recent work in our lab has demonstrated that tetravalent vanadium amides may work as efficient catalysts for the production of elastomers^{11a}. In order to better understand this behavior and to expand this chemistry we have explored the possibility of extending the availability of V(IV) amides.

As a matter of fact, aside from early reports claiming the preparation of V(IV) amides, their structural characterization was not conclusively demonstrated until recently^{11,12}. For example, the treatment of $\text{VCl}_3(\text{THF})_3$ with one equivalent of R_2NLi [$\text{R} = i\text{-Pr, Cy}$] resulted in a unusual disproportionation to form $(\text{R}_2\text{N})_2\text{VCl}_2$ ^{11a}. In another example, 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 $\text{VCl}_4(\text{DME})$ ($\text{DME} = 1,2\text{-dimethoxyethane}$) to give the corresponding $[\text{N}_3\text{N}]\text{VCl}$ derivative^{11b}.

In this chapter, the synthesis and characterization of mononuclear V(IV) amides is described along with a preliminary discussion of the factors which influence their stability and make V(IV) species potential catalysts for olefin polymerization.

Experimental Section

All operations were performed under an inert atmosphere (N_2) using standard Schlenck techniques or in a nitrogen-filled drybox. $VCl_3(THF)_3$ was prepared according to published procedures. Solvents were dried by following standard procedures. NMR spectra were recorded on a Varian Gemini 200 spectrometer by using vacuum-sealed samples prepared in a drybox. C_6D_6 for NMR spectroscopy was dried over the appropriate agent. Infrared spectra were recorded on Mattson 3000 FTIR spectrometer. Nujol mulls were prepared in the drybox. MeLi (Aldrich) was used as received. Samples for magnetic susceptibility measurements were prepared inside the drybox and measurements were carried out at room temperature using a Gouy balance (Johnson Matthey). Elemental analyses were carried out using a Perkin Elmer Series II CHN/O 2400-analyzer.

Preparation of $Bz_2NLi \cdot Et_2O$

A solution of Bz_2NH (35.62 g, 0.1802 mol) in hexane (300 mL) was treated with a solution of MeLi in Et_2O (129.0 mL, 1.4 M, 0.18 mol) at $-78^\circ C$. Gas evolution took place, and the mixture was stirred for 1 hour and allowed to warm up to room temperature. After partial evaporation of the solvent, the resulting light yellow solution was allowed to stand overnight at $-30^\circ C$ upon which colorless crystals of $Bz_2NLi \cdot Et_2O$ (41.73 g, 0.1512 mol, 84%) precipitated. Infrared Spectrum (Nujol mull, cm^{-1}): 2749(sh, m), 1596(sh, m), 1457(s),

1377(s), 1308(s), 1086(s), 1063(s), 1024(s), 907(s), 804(s), 745(s), 700(s), 611(s). $^1\text{H-NMR}$ (C_6D_6 , 200 MHz, $\delta(\text{ppm})$): 7.15(m, 10H phenyl), 3.74(s, 4H CH_2 benzyl), 3.10(q, 4H CH_2 Et_2O), 0.88(t, 6H CH_3 Et_2O).

Preparation of $\text{Bz(Ph)NLi}\cdot\text{Et}_2\text{O}$

A solution of MeLi in Et_2O (106.0 mL, 1.4 M, 0.15 mol) was slowly added to a solution of Bz(Ph)NH (27.10 g, 0.1479 mol) in hexane (300 mL) at -78°C . Gas evolution took place, and the mixture was stirred for 1 hour and allowed to warm up to room temperature. The resulting light yellow solution was allowed to stand overnight at -30°C upon which colorless crystals of $\text{Bz(Ph)NLi}\cdot\text{Et}_2\text{O}$ (33.8 g, 0.129 mol, 86%) precipitated. Infrared Spectrum (Nujol mull, cm^{-1}): 1586(sh, m), 1537(sh, m), 1461(s), 1311(br), 1059(br), 975(s), 913(s, w), 868(s, w), 847(w), 797(s), 742(s), 697(s), 661(s), 630(s). $^1\text{H-NMR}$ (C_6D_6 , 200 MHz, $\delta(\text{ppm})$): 7.40(m, 5H benzyl), 6.45(m, 5H phenyl), 4.30(s, 2H CH_2 benzyl), 3.05(q, 4H CH_2 Et_2O), 0.75(t, 6H CH_3 Et_2O).

Preparation of $(\text{Bz}_2\text{N})_4\text{V}$ (3.1)

Addition of solid $\text{Bz}_2\text{NLi}\cdot\text{Et}_2\text{O}$ (1.5 g, 5.4 mmol) to a suspension of $\text{VCl}_3(\text{THF})_3$ (1.0 g, 2.7 mmol) in THF (100mL) turned the color from purple/pink to reddish brown at room temperature after stirring overnight. The solvent was evaporated in vacuum and the residual solid redissolved in hexane (50 mL). After removal of LiCl by filtration, reddish brown crystals of $(\text{Bz}_2\text{N})_4\text{V}$ (3.1) (0.79 g, 0.94 mmol, 35%) separated upon allowing the filtrate to stand overnight at -30°C . Anal. Calcd(found) for $\text{C}_{52}\text{H}_{52}\text{N}_4\text{V}$: C, 65.38(64.59), H, 5.49(5.37), N, 5.45(5.18). Infrared Spectrum (Nujol mull, cm^{-1}): 1599(m), 1492(s), 1456(s), 1377(s), 1343(s), 1145(s), 1033(s), 935(w), 892(w), 802(w), 750(s), 732(s), 699(s). $\mu_{\text{eff}} = 1.63$ B. M..

Preparation of [Bz(Ph)N]₄V (3.2)

The addition of Bz(Ph)NLi·Et₂O (1.4 g, 5.4 mmol) at room temperature to a stirred solution of VCl₃(THF)₃ (1.0 g, 2.7 mmol) in THF (100mL) turned the color to purple. Stirring was continued overnight followed by removal of the solvent in vacuum. The residual solid was redissolved in hexane (50 mL). Followed by removal of LiCl by filtration. Light purple crystals of [Bz(Ph)N]₄V (3.2) (0.63 g, 0.81 mmol, 30%) separated upon allowing the filtrate to stand overnight at - 30 °C. Anal. Calcd(found) for C₅₂H₄₈N₄V: C, 80.08(79.56), H, 6.20(6.05), N, 7.18(7.46). Infrared Spectrum (Nujol mull, cm⁻¹): 1587(m), 1483(s), 1458(s), 1377(s), 1263(br), 1219(s), 1176(w), 1084(s), 1047(s), 1025(s), 902(w), 811(br), 760(s), 729(s), 691(s). $\mu_{\text{eff}} = 1.79 \text{ M.B.}$

Preparation of (Bz₂N)₃VCl (3.3)

A stirred suspension of VCl₃(THF)₃ (1.2 g, 3.2 mmol) in ether (100mL) was treated with Bz₂NLi·Et₂O (0.89 g, 3.2 mmol) at room temperature. The color changed to reddish brown after stirring overnight. Following filtration of LiCl and solvent concentration, the filtrate was allowed to stand overnight at -30 °C, upon which reddish brown crystals of (Bz₂N)₃VCl (3.3) (0.43 g, 0.64 mmol, 20%) separated. Anal. Calcd(found) for C₄₂H₄₂N₃ClV: C, 74.71(73.83), H, 6.27(6.43), N, 6.22(5.94). Infrared Spectrum (Nujol mull, cm⁻¹): 1598(m), 1456(d, st), 1378(s), 1347(s), 1261(s), 1086(t), 1024(s), 937(s, w), 889(w), 804(m), 751(s), 730(s), 696(s). $\mu_{\text{eff}} = 1.77 \text{ B. M.}$

Preparation of {[Bz(Ph)N]₃VCl}·[VCl₃(THF)₃] (3.4)

The addition of Bz(Ph)NLi·Et₂O (0.77 g, 2.9 mmol) to a stirred suspension of VCl₃(THF)₃ (1.1 g, 2.9 mmol) in ether (100mL) at room temperature changed the color to purple after stirring overnight. Following removal of LiCl by filtration and partial removal of the solvent in vacuum, purple crystals of {[Bz(Ph)N]₃VCl}·[VCl₃(THF)₃] (**3.4**) (0.27 g, 0.43 mmol, 15%) separated upon allowing the filtrate to stand overnight at - 30 °C. Anal. Calcd(found) for C₅₁H₆₀N₃O₃Cl₄V₂: C, 60.85(62.18), H, 6.01(5.30), N, 4.17(3.88). Infrared Spectrum (Nujol mull, cm⁻¹): 1584(t), 1460(s), 1378(s), 1345(w), 1261(s), 1209(s), 1084(s), 1020(s), 824(br), 755(s), 695(s). $\mu_{\text{eff}} = 2.72$ B.M..

X-ray crystallography

Data were collected using a Siemens CCD X-ray diffractometer for a suitable air-sensitive crystal mounted under a liquid nitrogen stream. The ω -2 θ scan technique was used. Data were collected to 57.0 deg. for (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). Their positions were refined anisotropically. Hydrogen atom positions were calculated and refined. 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). Details on the data collections and structure refinement are listed in Table 3.2 and 3.3. Selected bond distances and angles are given in Table 3.2a and 3.3a.

General Polymerization Procedure

Catalysts were tested for ethylene polymerization activity in hexane solution at 2 bar total pressure and 25°C with EtAlCl₂ as the cocatalyst. Polymerization was carried out in 200 mL of hexane in magnetically agitated glass reactors at a 2 pressure of bar using a continuous flow of 1000 sccm ethylene. After equilibration of the hexane with the EP feed at 25°C, 0.2 mmol of cocatalyst was added followed by the addition of 5 μ mol of vanadium catalyst. These conditions led a final concentration of 25 μ M [catalyst] and a 4/1 ratio of Al/V. Polymerization was carried out for 15 minutes followed by depressurization and quenching with 100 ml of ethyl alcohol. The polyethylene produced was washed with several portions of ethyl alcohol (200 ml) and recovered by solvent evaporation at room temperature.

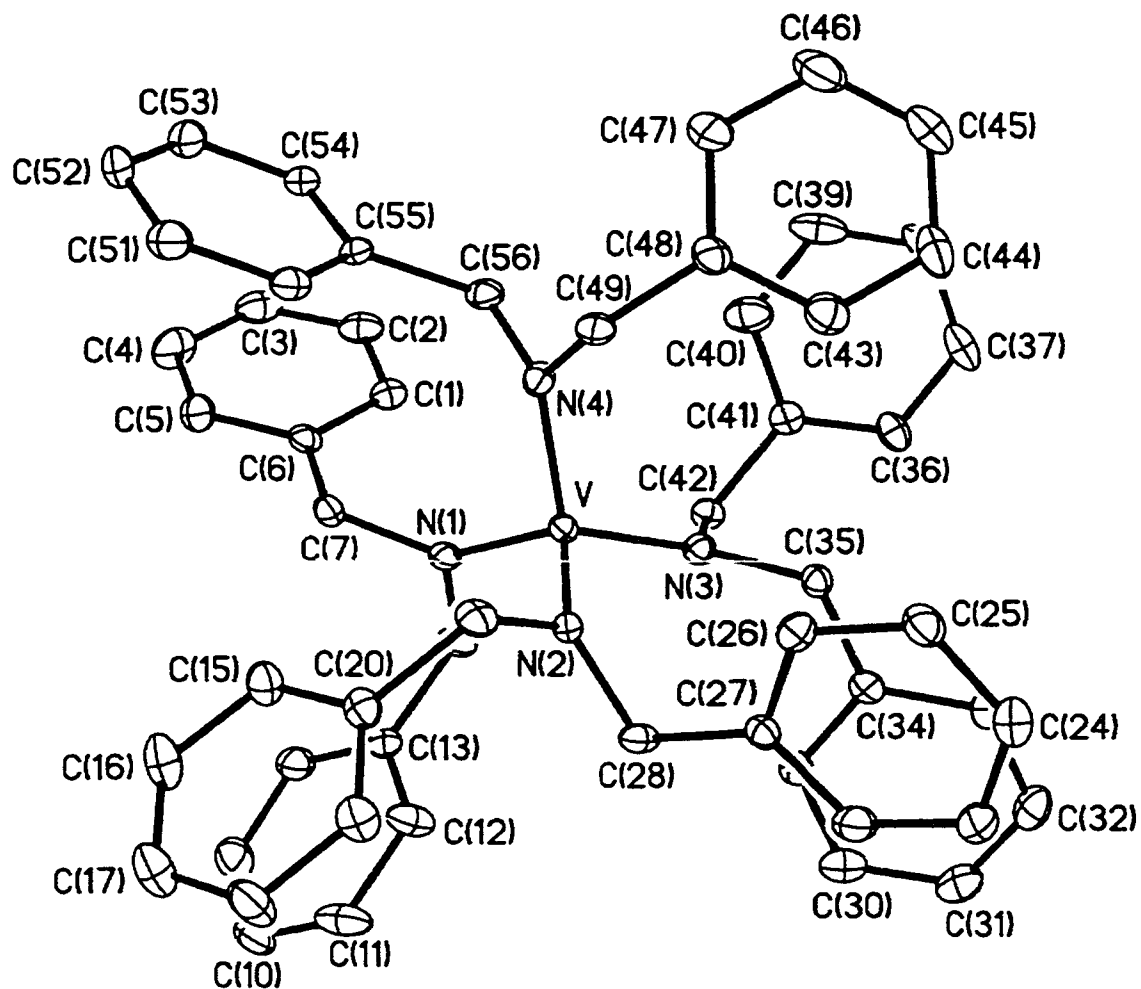


Fig 3.1. ORTEP drawing of $(\text{Bz}_2\text{N})_4\text{V}$ (3.1) Bond distances ($\text{\AA}$) and angles (deg) are as follows: $\text{V-N1} = 1.887(5)$, $\text{V-N2} = 1.891(5)$, $\text{V-N3} = 1.893(6)$, $\text{V-N4} = 1.898(6)$, $\text{N3-V-N4} = 115.8(2)$, $\text{N3-V-N2} = 108.5(2)$, $\text{N4-V-N2} = 103.8(2)$, $\text{N3-V-N1} = 103.6(2)$, $\text{N4-V-N1} = 108.2(2)$.

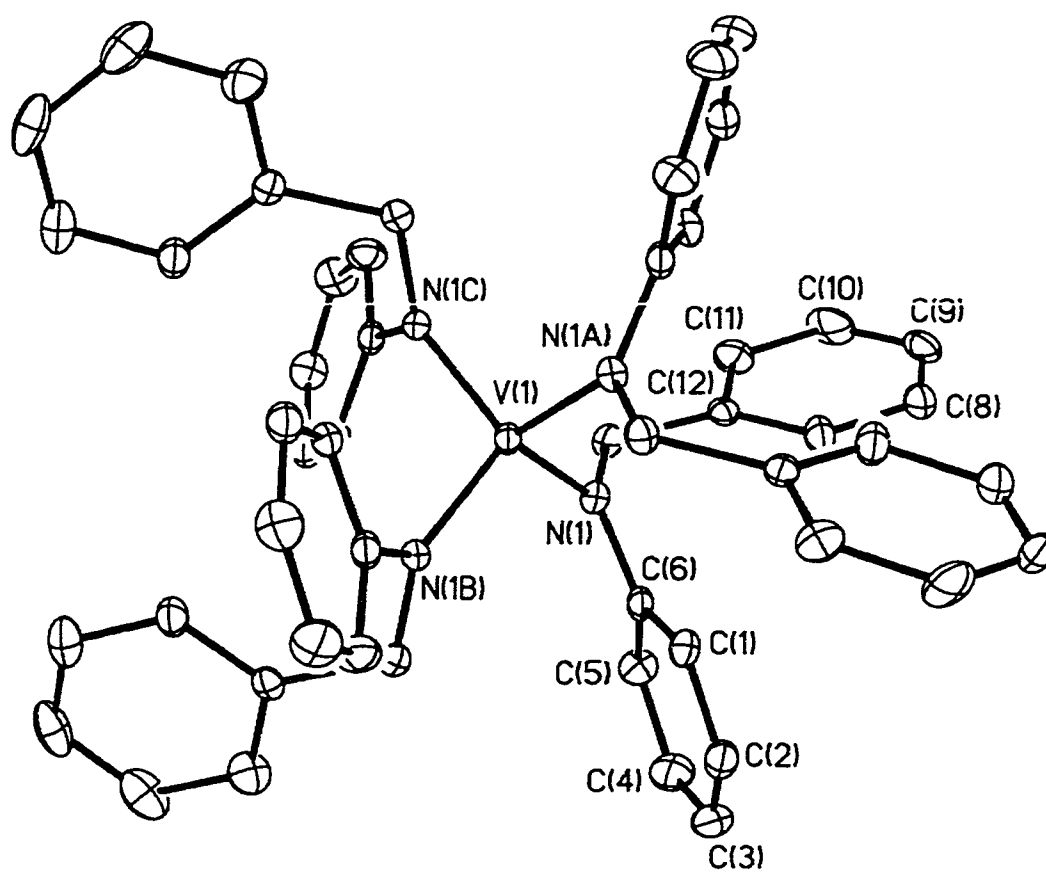


Fig 3.2. ORTEP drawing of $[\text{Bz(Ph)N}]_4\text{V}$ (3.2) Bond distances ($\text{\AA}$) and angles (deg) are as follows: $\text{V1-N1} = 1.897(2)$, $\text{V1-N1A} = 1.897(2)$, $\text{V1-N1B} = 1.897(2)$, $\text{N1-V-N1B} = 108.95(7)$, $\text{V1-N1C} = 1.897(2)$, $\text{N1-V-N1A} = 108.95(7)$.

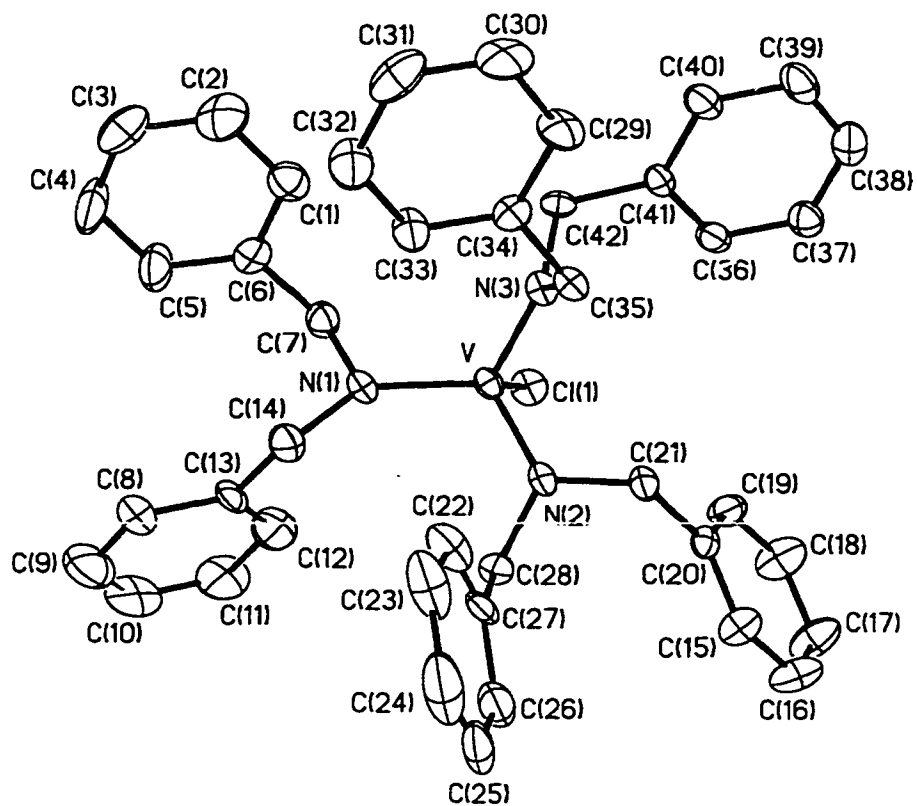


Fig 3.3 ORTEP drawing of $(\text{Bz}_2\text{N})_3\text{VCl}$ (3.3) Bond distances ($\text{\AA}$) and angles (deg) are as follows: $\text{V-N2} = 1.813(7)$, $\text{V-N3} = 1.843(8)$, $\text{V-N1} = 1.846(7)$, $\text{V-Cl} = 2.251(3)$, $\text{N2-V-N3} = 101.7(3)$, $\text{N1-V-N2} = 112.8(3)$, $\text{N3-V-N1} = 114.1(3)$.

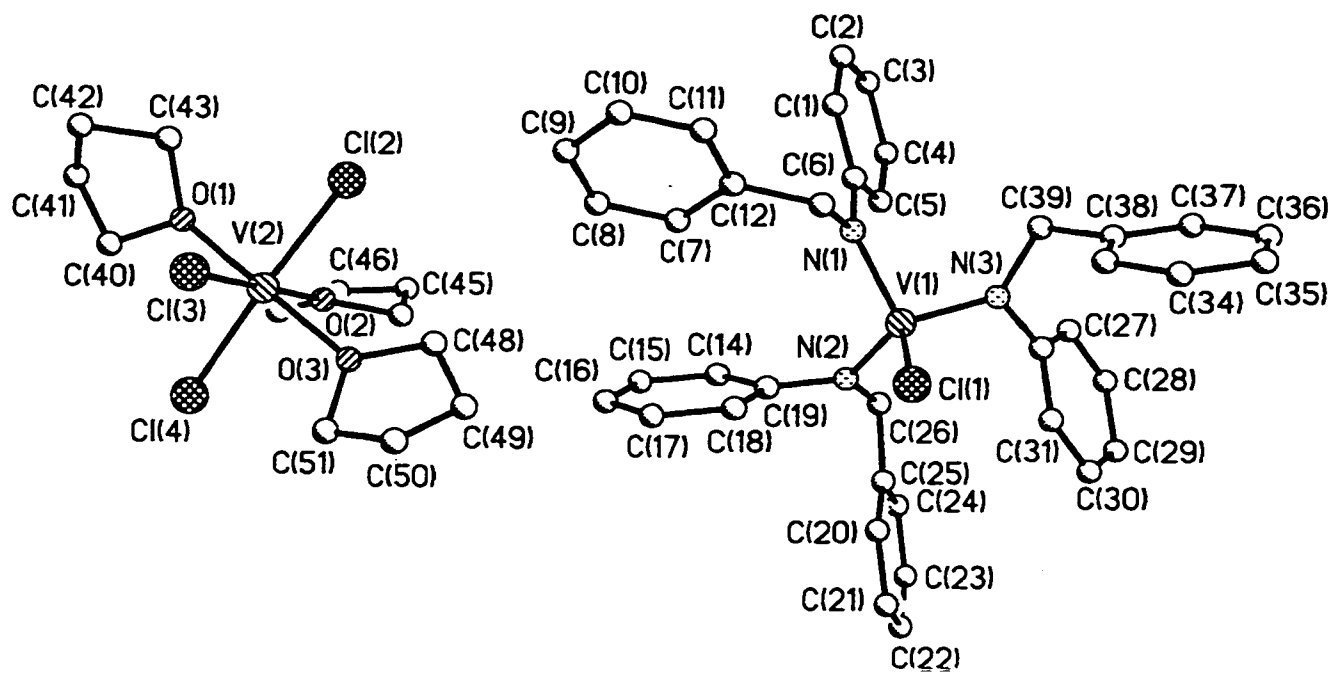
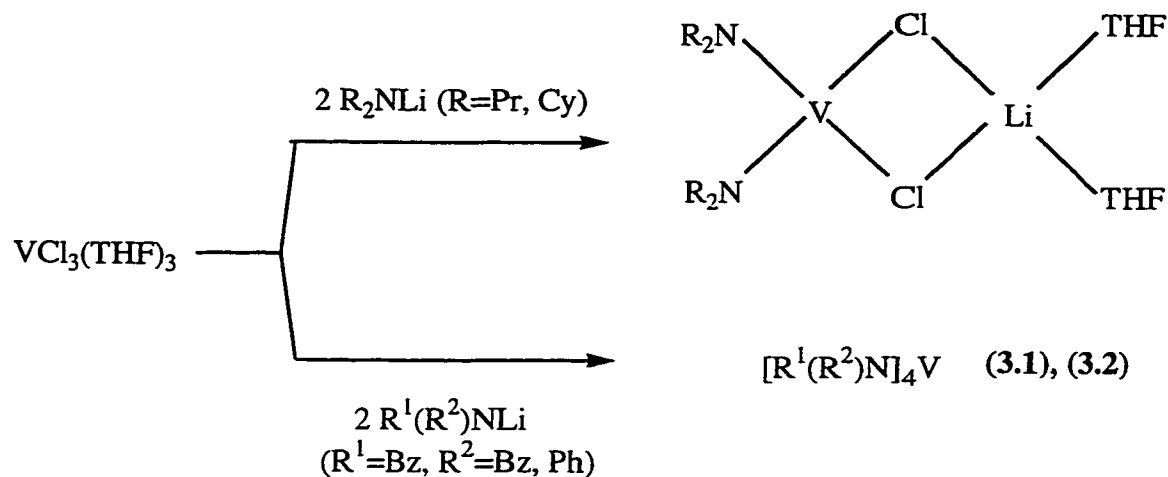


Fig 3.4. ORTEP drawing of $\{[\text{Bz}(\text{Ph})\text{N}]_3\text{VCl}\}[\text{VCl}_3(\text{THF})_3]$ (3.4) Bond distances ($\text{\AA}$) and angles (deg) are as follows: $\text{V1-N3} = 1.804(9)$, $\text{V1-N1} = 1.844(9)$, $\text{V1-N2} = 1.804(8)$, $\text{V1-Cl1} = 3.216(3)$, $\text{N3-V1-N1} = 100.8(4)$, $\text{N3-V1-N2} = 115.3(4)$, $\text{N1-V1-N2} = 108.2(4)$, $\text{N3-V1-Cl1} = 107.4(3)$.

Results and Discussion

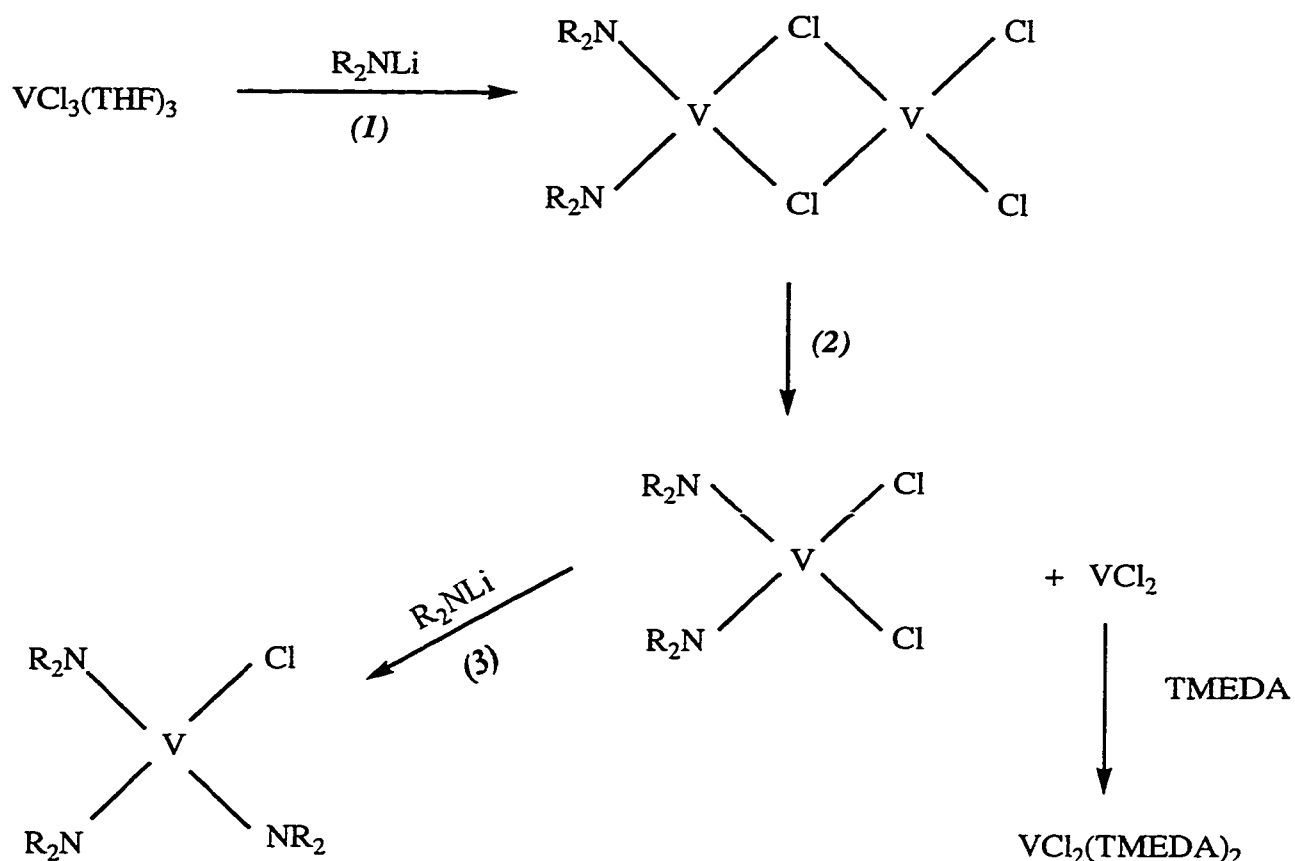
The reaction of $\text{VCl}_3(\text{THF})_3$ with 2 eq of $\text{R}^1(\text{R}^2)\text{NLi}$ ($\text{R}^1 = \text{Bz, Ph}$; $\text{R}^2 = \text{Bz}$) afforded the paramagnetic crystalline $[\text{R}^1(\text{R}^2)\text{N}]_4\text{V}$ (**3.1**) $(\text{Bz}_2\text{N})_4\text{V}$ and (**3.2**) $[\text{Bz}(\text{Ph})\text{N}]_4\text{V}$ (Fig 3.1, 3.2) (Scheme 3.1). The formulation of both products was confirmed by X-ray analysis. Combustion analysis data were consistent with the proposed formulation while the magnetic moments, calculated on the basis of these formulae, were also as expected for the d^1 electronic configuration of tetravalent vanadium. The two complexes are almost isomorphous. Both complexes are monomeric and are formed by a vanadium atom surrounded by four amide groups which define an almost regular tetrahedral coordination geometry around the metal center [$\text{V-N1} = 1.887(5)$, $\text{V-N2} = 1.891(5)$, $\text{V-N3} = 1.893(6)$, $\text{V-N4} = 1.898(6)$, $\text{N3-V-N4} = 115.8(2)$, $\text{N3-V-N2} = 108.5(2)$, $\text{N4-V-N2} = 103.8(2)$, $\text{N3-V-N1} = 103.6(2)$, $\text{N4-V-N1} = 108.2(2)$ in the case of (**3.1**) and $\text{V1-N1} = 1.897(2)$, $\text{V1-N1A} = 1.897(2)$, $\text{N1-V-N1A} = 108.95(7)$, $\text{N1-V-N1A} = 108.95(7)$, $\text{N1-V-N1B} = 108.95(7)$, $\text{N1-V-N1C} = 110.51(13)$ in the case of (**3.2**)]. Conversely, reaction of $\text{VCl}_3(\text{THF})_3$ with 2 eq. of R_2NLi ($\text{R} = \text{Cy, } i\text{-Pr}$) formed the paramagnetic and crystalline trivalent $[\text{R}_2\text{N}]_2\text{VCl}_2\text{Li}(\text{THF})_2$ ¹³. The remarkable difference between these reactions is likely to be ascribed to steric factors. We propose that ligands of modest steric hindrance (benzyl/phenyl groups) cannot stabilize V(III) species and result in the V(IV) species *via* disproportionation.



Scheme 3.1

The reactions of $\text{VCl}_3(\text{THF})_3$ with 1 eq of Bz(Ph)NLi and Bz_2NLi formed paramagnetic crystals of $[\text{R}^1(\text{R}^2)\text{N}]_3\text{VCl}$ ($\text{R}^1 = \text{Bz}$, $\text{R}^2 = \text{Ph}$) (3.3) and $[\text{R}_2\text{N}]_3\text{VCl}$ ($\text{R} = \text{Bz}$) (3.4). The formulations of these two products were also confirmed by X-ray analysis. Combustion analysis data were consistent with the proposed formulations. The complexes are monomeric and are formed by a vanadium atom surrounded by three amide groups and one chlorine atom which together define a distorted tetrahedral coordination geometry around the metal center [$\text{V-N2} = 1.813(7)$, $\text{V-N3} = 1.843(8)$, $\text{V-N1} = 1.846(7)$, $\text{V-Cl} = 2.251(3)$, $\text{N2-V-N3} = 101.7(3)$, $\text{N2-V-Cl} = 107.1(2)$, $\text{N3-V-N1} = 114.1(3)$ in the case of 3.3 and $\text{V1-N3} = 1.804(9)$, $\text{V1-N1} = 1.844(9)$, $\text{V1-N2} = 1.804(8)$, $\text{V1-Cl1} = 3.216(3)$, $\text{N3-V1-N1} = 100.8(4)$, $\text{N1-V1-N2} = 108.2(4)$, $\text{N2-V1-Cl1} = 111.5(3)$ in the case of 3.4] (Fig 3.3, 3.4). Conversely, reaction of $\text{VCl}_3(\text{THF})_3$ with only 1 eq of R_2NLi ($\text{R} = \text{Cy}$, *i*-Pr) formed paramagnetic crystals of $[\text{R}_2\text{N}]_2\text{VCl}_2$.^{14a} The difference between these reactions suggests that relatively minor changes

in ligand steric hindrance influence the chemical behavior of the corresponding vanadium complexes and lead to different final products.



Scheme 3.2

The reaction sequence illustrated in Scheme 3.2 proposes a possible rationalization of these results. The notion of an asymmetric binuclear intermediate was first proposed by our group^{14a}. The complexes $(\text{R}_2\text{N})_2\text{VCl}_2$ ($\text{R} = \text{Cy}, i\text{-Pr}$) were obtained only in the case of very large ligand steric hindrance. In the case of less encumbered ligands the reaction proceeded further towards the formation of $[\text{R}^2(\text{R}^1)\text{N}]_3\text{VCl}$ ($\text{R}^1 = \text{Bz}, \text{R}^2 = \text{Ph}, \text{Bz}$), or $[\text{R}^2(\text{R}^1)\text{N}]_4\text{V}$ ($\text{R}^1 = \text{Bz}, \text{R}^2 = \text{Ph}, \text{Bz}$) in the case of the smaller amides.

The tetravalent complexes **3.1**, **3.2**, **3.3** and **3.4** act as modest ethylene polymerization catalysts at room temperature in conjunction with EtAlCl_2 cocatalysts. Activity data are listed in table 3.1.

Catalyst	Co-catalyst	Activity kg EP/mole V/0.25 hr
$(\text{R}_2\text{N})_2\text{VCl}_2^{14a}$ R = i-Pr	EtAlCl_2	12
$(\text{R}_2\text{N})_2\text{VCl}_2^{14a}$ R = Cy	EtAlCl_2	11
$(\text{R}_2\text{N})_3\text{VCl}$ R = Bz	EtAlCl_2	5.1
$[\text{R}_1(\text{R}_2\text{N})_3\text{VCl} \cdot \text{VCl}_3(\text{THF})_3]$ $\text{R}_1 = \text{Bz}, \text{R}_2 = \text{Ph}$	EtAlCl_2	1.0
$(\text{R}_2\text{N})_4\text{V}$ R = Bz	EtAlCl_2	0.1
$[\text{R}_1(\text{R}_2\text{N})_4\text{V}]$ $\text{R}_1 = \text{Bz}, \text{R}_2 = \text{Ph}$	EtAlCl_2	0.1

Table 3.1 Ethylene Polymerization Activity of $(\text{R}_2\text{N})_n\text{VCl}_{4-n}$

Under the conditions employed, activity decreased upon diminishing the number of chlorine atoms or increasing the number of amide ligands around the vanadium center. This probably indicates that large hindrance, as in the case of vanadium tetraamide, results not only in a diminished possibility of formation of a chlorine bridge between vanadium and aluminum

in the active intermediates, but also in a diminished probability of having monomer coordination to the vanadium center. On the basis of these observations, the failure of vanadium(IV) tetra-amide systems to act as catalysts is probably caused by the absence of chlorine. The large difference in activity between complexes **3.3** and **3.4** may be attributed to quenching by the THF present in **3.4**.

Conclusion:

- (1) The synthesis, characterizations and properties of novel V(IV) amide compounds from $\text{VCl}_3(\text{THF})_3$ have been described. The amide ligand steric hindrance ($\text{R}_1(\text{R}_2)\text{N}^-$, $\text{R}_1 = \text{Bz}$, $\text{R}_2 = \text{Bz, Ph}$) directly determines the stability of V(III) species with respect to disproportionation to V(IV).
- (2) These novel V(IV) amide compounds have been employed as catalysts for the polymerization of ethylene. Unfortunately, these compounds did not show significant activity for the polymerization of ethylene under Ziegler-Natta conditions. Nevertheless, this suggests that high activity observed with $\text{amide}_2\text{VCl}_2$ catalysts does not imply amide abstraction by the Al cocatalyst as it may be argued on the basis of our finding in the chemistry of $(\text{acac})_3\text{V}$ (see chapter two).

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Chapter 4

Preparation and Characterization of Vanadium(II) borohydride Complexes

Introduction

Organotransition metal hydrides have been intensively studied and have been the topic of many reviews¹ since the successful preparation and characterization of Cp_2ReH^2 , the first compound where the presence of a metal-hydrogen bond was established. The enormous diversification of chemical reactivity and the variety of transformations displayed by transition-metal hydrides make this class of compounds one of the most important in inorganic and organometallic chemistry. The main reactivity patterns may be summarized as follows: (1) addition to unsaturated functions such as alkene to form alkyls (basic step in the catalytic polymerization of olefins³), alkyne to give vinyl compounds⁴, and carbonyl groups to form alkoxide derivatives⁵, (2) molecular activation, (typically, a metal hydride may metathesize a single A-B bond (C-N, C-O, C-Cl, etc.) to afford the complex M-A and B-H derivatives⁶), (3) catalytic H/D exchange⁷, (4) diene and olefin isomerization⁸, (5) catalytic hydrogenation of alkenes and alkynes⁹, (6) metal-promoted organic synthesis¹⁰, (7) hydroformylation¹¹, etc. The utilization of "acidic" early transition metal hydrides in high oxidation states was traditionally regarded as a possible way of increasing and ultimately boosting the reactivity of these compounds. Among early transition metal hydrides, group 5 metals occupy a very unique

place given the remarkable wealth of transformations discovered for Nb and Ta in a variety of oxidation states. By contrast, only little information is available for vanadium complexes. Only very few vanadium hydride species like $[\text{CpVH}(\text{CO})_3]^{-12}$, $\text{HV}(\text{CO})_4(\text{PP})$ (PP = chelating diphosphine)¹³, $[\text{CpV}(\mu\text{-H})_2(\mu\text{-C}_6\text{H}_6)]^\ddagger$, $\text{V}_2\text{Zn}_2\text{H}_4(\text{BH}_4)_2(\text{PMePh}_2)_4$ ¹⁵, $\text{Cp}^*\text{V}(\text{CO})\text{H}$ ¹⁶, $[\text{CpV}(\mu\text{-H})\text{dmpe}]_2$ ¹⁷ and $[\text{CpV}(\text{H})\text{dmpe}]_2(\mu\text{-dmpe})$ ¹⁷, $[\text{V}_2\text{H}_3(\text{PMe}_3)_6]^+{}^{18}$ are reported in the literature. This paucity is likely to be ascribed to an intrinsic instability of the V-H bond and also to the facility with which vanadium affords, in contrast to Nb and Ta, reduction reactions.

Borohydrides are widely used in transition-metal chemistry as precursors for the preparation of hydride species or as substitutes where hydrides display an intrinsic instability. For examples, the reaction of $\text{RuCl}_2(\text{PPh}_3)_2$ with NaBH_4 in $\text{MeOH}/\text{C}_6\text{H}_6$ gives $\text{RuH}_4(\text{PPh}_3)_2$ ¹⁹, the Re derivative $\text{ReH}_7(\text{PPh}_3)_2$ is obtained from the reaction of $\text{ReO}(\text{OEt})\text{Cl}_2(\text{PPh}_3)_2$ with NaBH_4 ²⁰ in EtOH, NaBH_4 reacts with $\text{ReCl}_5(\text{PPh}_3)_4$ to afford $\text{ReH}_5(\text{PPh}_3)_3$ ²⁰, while the reaction of MoCl_5 with $\text{Ca}(\text{BH}_4)_2$ in presence of PMePh_2 yields $\text{MoH}_4(\text{PMePh}_2)_4$ ²¹, a similar Mo product was obtained using a chelating phosphine (dppe = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) by reaction of $\text{Mo}_2\text{Cl}_4(\text{dppe})_2$ with NaBH_4 in EtOH to afford the corresponding $\text{MoH}_4(\text{dppe})_2$ ²².

One of the most remarkable structural characteristics of transition metal tetrahydroborates is the variety of bonding modes by which the BH_4^- group can be attached to the metal center (uni-, bi- or tridentate)^{23,24} (Fig. 4.1).

Vibrational spectroscopy data have been compiled for a large number of borohydride complexes and provide trends which can be used to determine the metal borohydride bonding mode^{23,24}. Bidentate complexes are characterized by a strong broad band centered at around 2415 cm^{-1} and a sharp singlet at 2125 cm^{-1} , whereas tridentate complexes exhibit a sharp band at 2420 cm^{-1} and a strong broad band centered at around 2230 cm^{-1} .

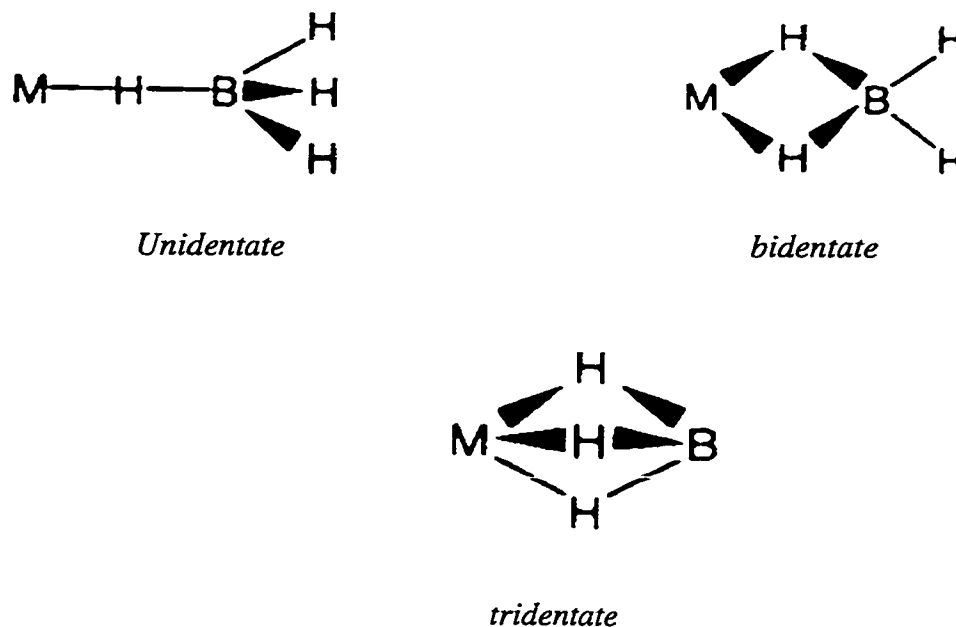


Fig 4.1 Bonding Modes of BH_4 ligand

There are very few examples of tetrahydroborates of group 5 elements, particularly for vanadium. A report appearing in the literature in 1972 claimed that treatment of vanadium alkoxides with diborane afforded the molecular species $\text{V}(\text{BH}_4)_3$ ²⁴. However this result was never confirmed by structural data. It was only in 1975 that the trivalent $\text{Cp}_2\text{V}(\text{BH}_4)$ complex was fully characterized, including elucidation of its formula by X-ray diffraction²⁵. The complex was prepared *via* reaction of bis(cyclopentadienyl)vanadium(IV) dichloride with a threefold excess of lithium tetraborate in DME. The authors proposed a structure where the BH_4^- unit adopted a bidentate bonding fashion (Fig. 4.2), similar to that of $\text{Cp}_2\text{Ti}(\text{BH}_4)$ ²⁶. Similarly, $\text{CpVCl}(\text{dmpe})$ is readily converted into the corresponding $\text{CpV}(\text{BH}_4)(\text{dmpe})$ ²⁷. The

use of $[\text{V}_2\text{Cl}_3(\text{THF})_6]_2(\text{Zn}_2\text{Cl}_6)$ and NaBH_4 in the presence of dmpe produces a light green crystalline and zinc free complex $[\text{V}(\mu\text{-O})(\mu\text{-dmpe})\text{BH}_4]_2$ where the metal is present in the oxidation state +2²⁸.

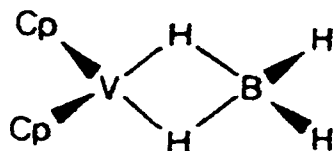
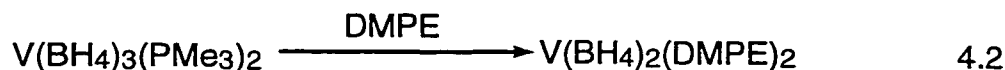
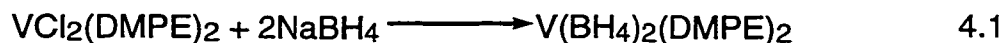


Fig. 4.2 The structure of $\text{Cp}_2\text{V}(\text{BH}_4)$



The first tetrahydroborate complex of vanadium(III), $[\text{Na}(\text{dme})][\text{V}(\text{BH}_4)_4]$, was obtained from the reaction of $\text{VCl}_3(\text{THF})_3$ with excess NaBH_4 in DME²⁹. Another literature example of tetrahydroborate vanadium(III) is $\text{V}(\text{BH}_4)_3(\text{PMe}_3)_2$, obtained from reaction of $\text{VCl}_3(\text{THF})_3$ with LiBH_4 in the presence of PMe_3 ³⁰. As per vanadium(II) tetrahydroborates, there is only one example reported, $\text{V}(\text{BH}_4)_2(\text{DMPE})_2$, where the DMPE [DMPE = 1,2-bis(dimethylphosphino)ethane] was used as a stabilizing ligand (eq. 4.1 and eq. 4.2)³⁰.

The X-ray crystal structure of $\text{V}(\text{BH}_4)_2(\text{DMPE})_2$ revealed that both tetrahydroborate groups are unidentate, in contrast to the case of the titanium analogue, $\text{Ti}(\text{BH}_4)_2(\text{DMPE})_2$ ³¹, which has an eight-coordinate geometry around the metal center and bidentate BH_4^- ligands.

All above-mentioned vanadium borohydride compounds are of interest as part of molecules that contain V-H bonds. The reactivity of these compounds has been less known, particularly for $V(BH_4)_2(DMPE)_2$, because of the limitation arising from the poor availability of the expensive DMPE ligand.

In order to gain some insight into the structure and reactivity of divanadium systems containing BH_4^- groups, the chemistry of V(II) bistetrahydroborates with several supporting ligands such as THF, TMEDA and py was investigated.

The interest for this particular oxidation state (+2) was mainly stimulated by the remarkable performance of divalent vanadium complexes in terms of dinitrogen activation. It was hoped that the presence of hydride or borohydride may lead to further transformations.

Experimental Section

All operations were performed under an inert atmosphere (N_2) with use of standard Schlenck techniques or in a nitrogen-filled drybox. $VCl_2(TMEDA)_2$, $VCl_3(THF)_3$ and $[V_2(\mu-Cl)_3(THF)_6]_2[Zn_2Cl_6]$ were prepared according to published procedures. Solvents, *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) and Pyridine (py) were dried by following standard procedures. $NaBH_4$ (Aldrich) was used as received. Infrared spectra were recorded on a Mattson 3000 FTIR spectrometer. Nujol mulls for IR spectra were prepared in the drybox. Samples for magnetic susceptibility measurements were prepared inside the drybox and the measurements were carried out at room temperature using a Gouy balance (Johnson Matthey). Corrections for underlying diamagnetism were applied to the data. Elemental analyses were carried out using a Perkin Elmer Series II CHN/O 2400-analyzer.

Synthesis of $V(BH_4)_2(THF)_3$ (4.1)

Method A: A suspension of $VCl_3(THF)_3$ (1.5 g, 4.0 mmol) in THF (150 ml) was treated with an excess of $NaBH_4$ (0.91 g, 24.0 mmol). The resulting solution was stirred for 3 days during which time the color changed from purple/pink to blue. After filtration and partial removal of solvent in vacuum, the filtrate was allowed to stand at $-30\text{ }^{\circ}\text{C}$ for 2 days, whereupon green crystals of $V(BH_4)_2(THF)_3$ (0.58 g, 2.0 mmol, yield 49%) separated. Elem. Anal. Calcd(found) for $C_{12}H_{32}O_3B_2V$: C, 48.56(46.06), H, 10.86(9.01). IR (Nujol mull, KBr,

cm⁻¹) 2386 (m, br), 2148 (m, br), 1456 (s), 1575 (s), 1260 (s), 1042 (s), 921 (w), 871 (m), 801 (m), 722 (w). $\mu_{\text{eff}} = 3.58$ B.M..

Method B: A suspension of NaBH₄ (0.69 g, 18 mmol) in THF (50 ml) was stirred in the presence of [V₂(μ-Cl)₃(THF)₆]₂[Zn₂Cl₆] (1.2 g, 1.5 mmol) for four hours. The resulting solution slowly turned light green. After filtration and concentration of the solvent, the filtrate was allowed to stand at -30 °C for 2 days, upon which green crystals of V(BH₄)₂(THF)₃ (0.30 g, 1.0 mmol, yield 34%) separated. The product was identified by comparison of IR spectroscopic data with those of analytically pure samples.

Synthesis of V(BH₄)₂(TMEDA)₂ (4.2)

Method A: The addition of excess NaBH₄ (0.91 g, 24.0 mmol) and TMEDA (1.2 ml, 8.0 mmol) to a stirred suspension of VCl₃(THF)₃ (1.5 g, 4.0 mmol) in THF (150 ml) changed the color to violet from purple/pink during an overnight stirring. After filtration of the excess NaBH₄ and solvent concentration, the filtrate was allowed to stand at -30 °C for 2 days, upon which violet crystals of V(BH₄)₂(TMEDA)₂ (0.91 g, 2.9 mmol, yield 73 %) separated. Elem. Anal. Calcd(found) for C₁₂H₄₀N₄B₂V: C, 46.04(44.86), H, 12.88(12.01), N, 17.90(17.66). IR (Nujol mull, KBr, cm⁻¹): 2327(m, br), 2210 (m), 2130 (m, br), 1457 (s), 1377 (m), 1284 (w), 1087 (s), 1015 (s), 953 (s), 798 (s), 722(w). $\mu_{\text{eff}} = 3.68$ B.M..

Method B: Excess NaBH₄ (0.30 g, 7.9 mmol) was added to a suspension of VCl₂(TMEDA)₂ (1.0 g, 2.8 mmol) in THF (150 ml). The mixture was stirred overnight whereupon the color changed from blue to violet. After filtration of the excess NaBH₄ and

partial removal of solvent, the resulting solution was allowed to stand at $-30\text{ }^{\circ}\text{C}$ for 2 days, upon which violet crystals of $\text{V}(\text{BH}_4)_2(\text{TMEDA})_2$ (0.75 g, 2.4 mmol, yield 86%) separated.

Method C: TMEDA (1.2 ml, 8.0 mmol) was added to a clear solution of $\text{V}(\text{BH}_4)_2(\text{THF})_3$ (0.97 g, 3.3 mmol) in THF (150 ml). The resulting solution was stirred for 0.5 hours upon which the color changed from green to violet. After partial removal of the solvent of THF in vacuum, the mixture was allowed to stand at $-30\text{ }^{\circ}\text{C}$ for 2 days, upon which violet crystals of $\text{V}(\text{BH}_4)_2(\text{TMEDA})_2$ (0.92 g, 2.9 mmol, yield 89%) separated.

Synthesis of $[\text{V}(\text{BH}_4)_2(\text{py})_4](\text{THF})_2$ (4.3)

Method A: 1.2 ml of pyridine (15 mmol) was added to a solution of $\text{V}(\text{BH}_4)_2(\text{THF})_3$ (1.0 g, 3.4 mmol) or $\text{V}(\text{BH}_4)_2(\text{TMEDA})_2$ (1.1 g, 3.5 mmol) in THF (150 ml). The resulting solution was stirred for 0.5 hours during which time the color changed from green in the case of (4.1) or from violet in the case of (4.2) to reddish brown. After partial removal of the solvent, the mixture was allowed to stand at $-30\text{ }^{\circ}\text{C}$ for 2 days, upon which reddish brown crystals of $[\text{V}(\text{BH}_4)_2(\text{py})_4](\text{THF})_2$ (1.7 g, 3.3 mmol, yield above 90 % based on both $\text{V}(\text{BH}_4)_2(\text{THF})_3$ and $\text{V}(\text{BH}_4)_2(\text{TMEDA})_2$) separated. Elem. Anal. Calcd(found) for $\text{C}_{24}\text{H}_{40}\text{N}_4\text{B}_2\text{O}_2\text{V}$: C, 66.04(66.18), H, 8.71(8.30), N, 11.00(10.88). IR (Nujol mull, KBr, cm^{-1}): 2329 (m, br), 2216 (m, br), 1597 (m, sh), 1484 (s), 1461 (s), 1441 (s), 1377 (s), 1260 (w), 1216 (w), 1074 (s), 1040 (s), 802 (w), 765 (s), 701 (s). $\mu_{\text{eff}} = 3.73\text{ M.B.}$.

Method B: $\text{VCl}_3(\text{THF})_3$ (1.0 g, 2.7 mmol) was dissolved in THF (150 ml) and treated with excess NaBH_4 (0.62 g, 16 mmol) and pyridine (1.0 ml, 1.2 mmol). The resulting solution was stirred overnight during which time the color changed from purple/pink to reddish brown. After filtration and partial removal of solvent, the filtrate was allowed to stand at $-30\text{ }^\circ\text{C}$ for 2 days, upon which reddish brown crystals of $[\text{V}(\text{BH}_4)_2(\text{py})_4](\text{THF})_2$ (0.87 g, 1.7 mmol, yield 63 %) separated.

X-ray crystallography

Data were collected at -153°C for a suitable air-sensitive crystal mounted under the liquid nitrogen stream of a Siemens CCD X-ray diffractometer. The ω - 2θ scan technique was used. 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). Their positions were refined anisotropically. Hydrogen atom positions were calculated and refined. 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). Details on the data collections and structure refinement are listed in Table 4.1. Selected bond distances and angles are given in Table 4.1a.

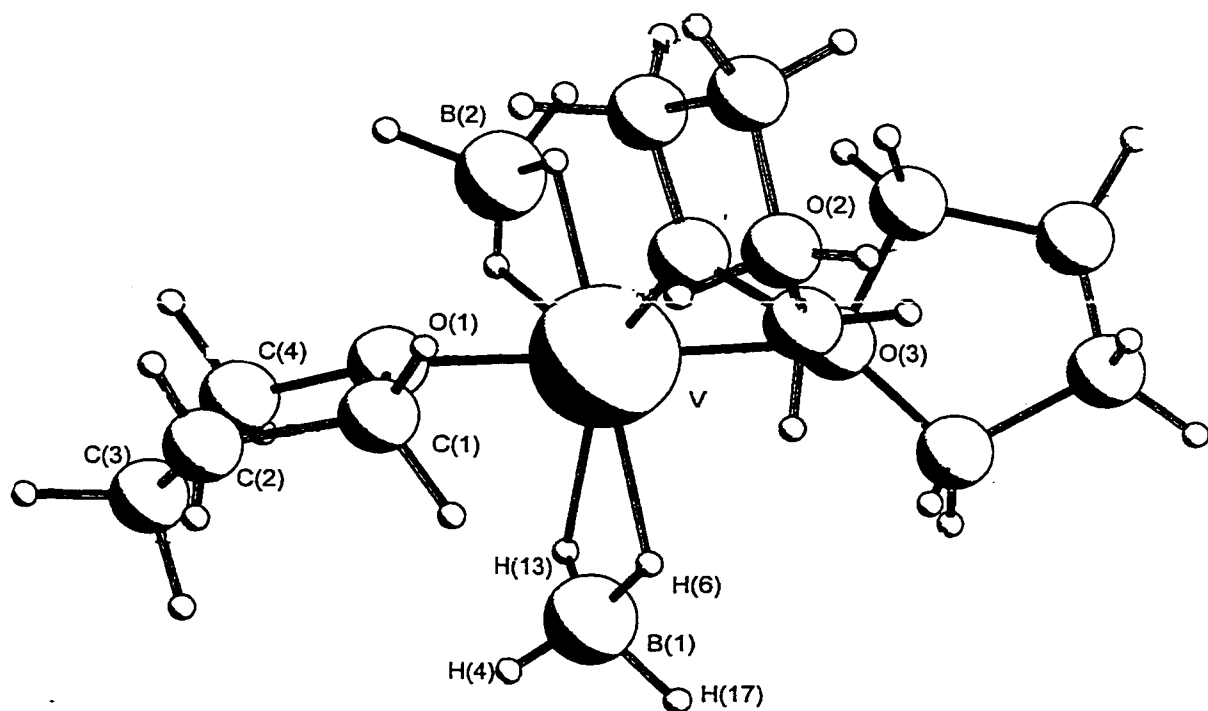


Fig. 4.3 ORTEP drawing of $V(BH_4)_2(THF)_3$ (4.1) Bond distances (Å) and angles (deg) are follows: V1-O1 = 2.219(3), V-O2 = 2.108(3), V-O3 = 2.134(3), V-H6 = 2.02(4), V-H13 = 2.08(5), B1-H4 = 1.02(6), B1-H6 = 1.12(5), O1-V1-O2 = 86.42(12), O1-V1-H13 = 92.4(14), B1-H13 = 1.06(5), O1-V1-O3 = 173.07(12), O1-V1-H6 = 92.4(14).

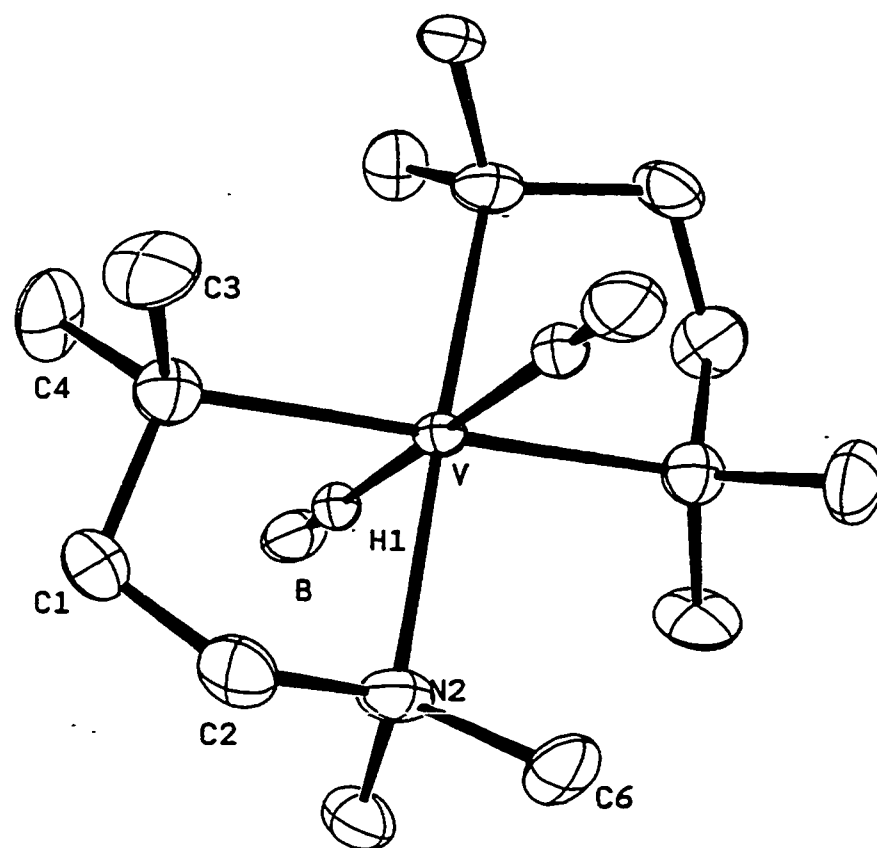


Fig. 4.4 ORTEP drawing of $V(BH_4)_2(TMEDA)_2$ (**4.2**) Bond distances ($\text{\AA}$) and angles (deg) are follows: $V-BH1 = 2.08(6)$, $B1-BH1 = 0.95(6)$, $N1-C1 = 1.491(10)$, $N1-C3 = 1.565(10)$, $C1-N1-C3 = 110.1(6)$, $C1-N1-C4 = 107.6(7)$, $C3-N1-C4 = 105.9(8)$, $V-BH1-B = 180.0$, $BH1-V-BH1a = 180.0$

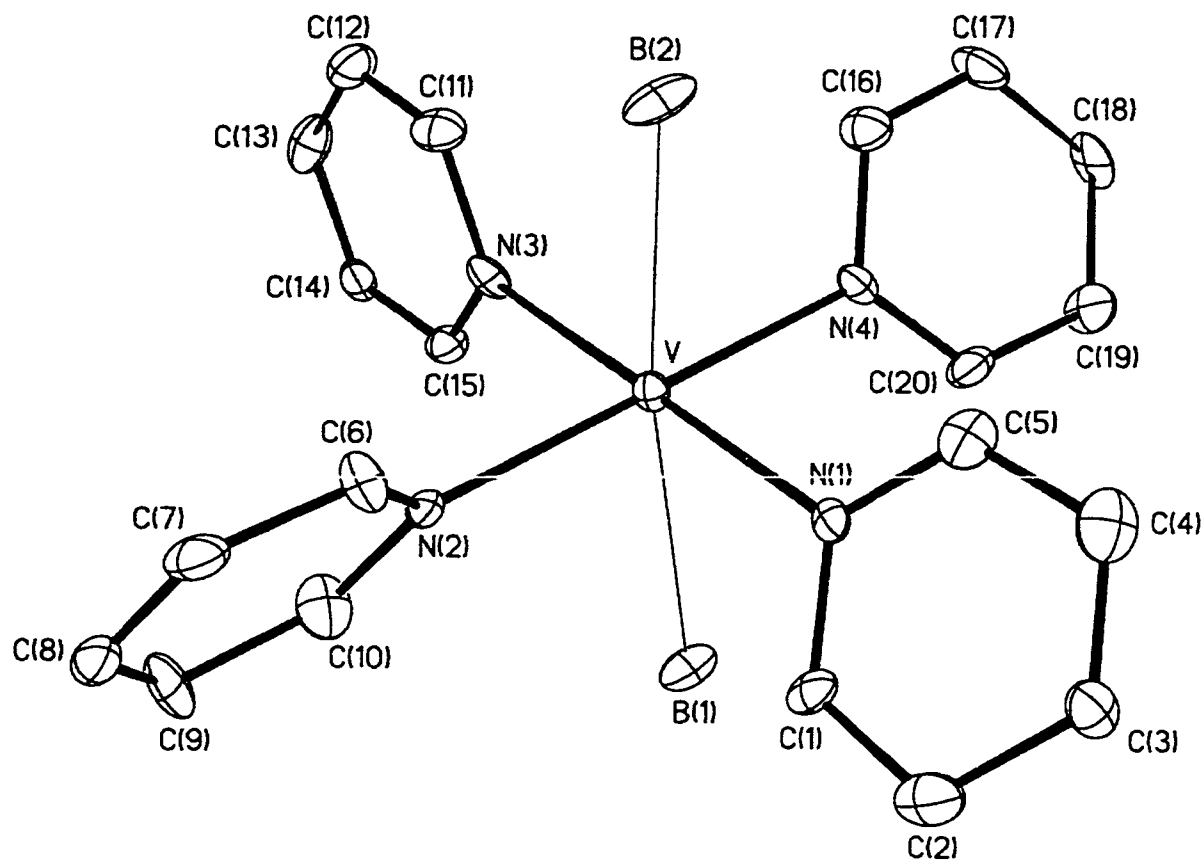


Fig. 4.5 ORTEP drawing of $[V(BH_4)_2(py)_4](THF)_2$ (**4.3**) Bond distances ($\text{\AA}$) and angles (deg) are follows: $V1-N4 = 2.198(9)$, $V1-N1 = 2.190(9)$, $V1-N2 = 1.194(9)$, $V1-N3 = 1.198(9)$, $N1-V-N2 = 90.5(3)$, $N1-V-N4 = 90.1(3)$, $N3-V-N2 = 89.4(3)$, $N3-V-N4 = 91.3(3)$.

Results and Discussion

The reaction of $\text{VCl}_3(\text{THF})_3$ with an excess of NaBH_4 in THF for 3 days afforded a blue suspension, from which paramagnetic, green $\text{V}(\text{BH}_4)_2(\text{THF})_3$ (**4.1**) was obtained in good yield and in crystalline form after suitable work-up. This unprecedented divalent vanadium borohydride derivative analyzes correctly for the formulation provided by the X-ray crystal structure. The infrared spectrum of (**4.1**) shows the absorption bands of the BH_4^- moiety as a broad singlet at 2386 cm^{-1} , a broad triplet around 2148 cm^{-1} and a singlet at 1368 cm^{-1} , which indicates a bidentate mode of the BH_4^- group.

The reaction is a perfectly reproducible process and can be carried out in large scale (up to 50 g) thus providing a valid synthetic method for the preparation of this promising V(II) precursor.

The same complex could be obtained upon reaction of $[\text{V}_2(\mu\text{-Cl})_3(\text{THF})_6]_2[\text{Zn}_2\text{Cl}_6]$ with an excess of NaBH_4 in THF. The reaction proceeds slowly in a few hours and at room temperature affording (**4.1**) in good yield and crystalline form. The result of this reaction is in striking contrast with that obtained from a similar reaction carried out in the presence of MePPh_2 ¹⁵. In that particular case, the reaction afforded $\text{V}_2\text{Zn}_2\text{H}_4(\text{BH}_4)_2(\text{PMePh}_2)_4$, where the vanadium was present in the formal oxidation state +1.

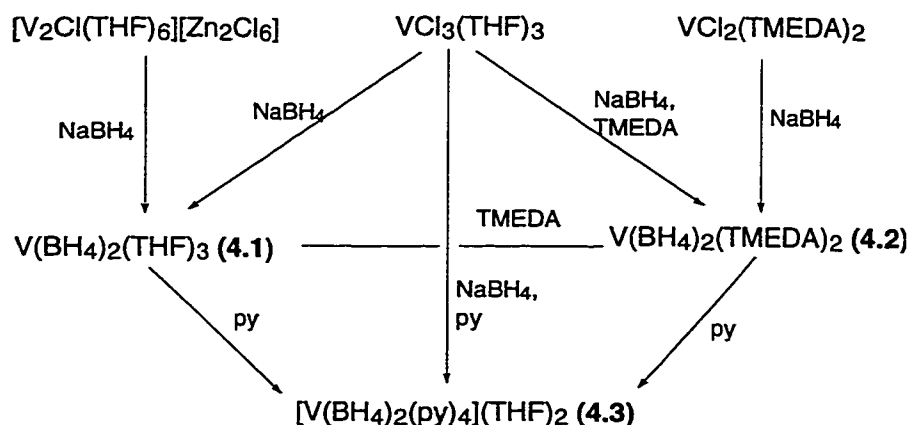
Mild Lewis bases such as Et_3N or py have been successfully used to abstract BH_3 groups from transition metal hydroborate and to prepare terminal or bridged hydride derivatives. We have tested the possibility of carrying out similar reactions on compound (**4.1**).

However, direct reaction of (4.1) with TMEDA afforded $V(BH_4)_2(TMEDA)_2$ (4.2) as violet crystals in good yield and through a fast reaction. This species was also obtained in much better yield by direct ligand-replacement reaction of $VCl_2(TMEDA)_2$ with $NaBH_4$.

Finally, reaction of $VCl_3(THF)_3$ with an excess of $NaBH_4$ in the presence of TMEDA yielded a violet suspension while stirring overnight. Paramagnetic, violet crystals of $V(BH_4)_2(TMEDA)_2$ (4.2) were isolated in good yield after work-up. The infrared spectrum of (4.2) shows the absorption bands of the BH_4^- moiety as a broad singlet at 2331 cm^{-1} , a doublet at around 2132 cm^{-1} and a strong singlet at 1092 cm^{-1} .

The reaction of $VCl_3(THF)_3$ with an excess of $NaBH_4$ in the presence of pyridine formed a reddish-brown suspension. Paramagnetic, reddish brown crystals of $[V(BH_4)_2(py)_4](THF)_2$ (4.3) were isolated in good yield. The infrared spectrum of (4.3) shows the absorption bands of the BH_4^- moiety as doublets at 2330 cm^{-1} and 2216 cm^{-1} and a strong singlet at 1073 cm^{-1} . $[V(BH_4)_2(py)_4](THF)_2$ (4.3) was also obtained in better yield when $V(BH_4)_2(THF)_3$ (4.1) or $V(BH_4)_2(TMEDA)_2$ (4.2) was treated with 4 eq. of pyridine.

The scheme 4.1 summarizes these findings:



Scheme 4.1

The molecular structure of $\text{V}(\text{BH}_4)_2(\text{THF})_3$ (**4.1**) was determined by an X-ray crystal structure (Fig. 4.3). The quality of the crystal of $\text{V}(\text{BH}_4)_2(\text{THF})_3$ (**4.1**) used for data collection at low temperature was sufficient to allow for successful location and refinement of the H atom positions, thus supporting the spectroscopic data indicating the bidentate bonding mode of the BH_4^- groups [$\text{V-H6}=2.03(4)$ Å; $\text{V-H13}=2.11(4)$ Å]. Accordingly, the V-H distances are significantly longer than in $\text{V}(\text{BH}_4)_2(\text{DMPE})_2$ [$\text{V-H}=1.88(3)$ Å] where the BH_4^- group is bound in a unidentate fashion. As a result of the bidentate mode, the distance of $\text{V1}\cdots\text{B1}$ is $2.437(5)$ Å is much shorter than in $\text{V}(\text{BH}_4)_2(\text{DMPE})_2$ ($\text{V1}\cdots\text{B1}=2.833(4)$ Å). The two bridging hydrogen atoms form a VH_2B planar moiety with the vanadium atom and the boron atoms in each BH_4^- unit.

The hepta-coordination of the vanadium center is defined by the four H atoms of two BH_4^- groups and three molecules of THF ($\text{O1-V1-O2}=86.51(11)$; $\text{O1-V1-O3}=173.17(11)$; $\text{O1-V1-H6}=91.2(14)$; $\text{O1-V1-H13}=93.9(12)^\circ$).

The molecular structure of $\text{V}(\text{BH}_4)_2(\text{TMEDA})_2$ (**4.2**) was determined by X-ray crystal structure determination (Fig. 4.4). The data collection for a crystal of $\text{V}(\text{BH}_4)_2(\text{TMEDA})_2$ (**4.2**) was carried out at low temperature in order to attempt to locate the H atoms.

The *trans* octahedral coordination environment of vanadium in $\text{V}(\text{BH}_4)_2(\text{TMEDA})_2$ (**4.2**) is in striking contrast with that of $\text{V}(\text{BH}_4)_2(\text{THF})_3$ (**4.1**), and is probably caused by the different steric hindrance between THF and TMEDA.

The molecular structure of $[\text{V}(\text{BH}_4)_2(\text{py})_4](\text{THF})_2$ (**4.3**) was determined by X-ray analysis (Fig. 4.5). Unfortunately, the quality of the crystals was not sufficient to successfully locate and refine the H atom positions in the core. The unidentate mode of the BH_4^- groups

was identified exclusively by IR spectroscopic data and shows the absorption bands at 2330 cm^{-1} , 2216 cm^{-1} , and 1078 cm^{-1} .

The vanadium center adopts a *trans*-octahedral geometry. The structure of $[\text{V}(\text{BH}_4)_2(\text{py})_4](\text{THF})_2$ (**4.3**) differs from that of the THF analogue, $\text{V}(\text{BH}_4)_2(\text{THF})_3$ (**4.1**), which possesses a hepta-coordinate geometry with bidentate BH_4^- ligands. The difference may be attributed to the smaller size of py and the shorter V-N bond distance in $[\text{V}(\text{BH}_4)_2(\text{py})_4](\text{THF})_2$ (**4.3**) than that in $\text{V}(\text{BH}_4)_2(\text{THF})_3$ (**4.1**).

In striking contrast to the formation of $\text{V}(\text{BH}_4)_3(\text{PMe}_3)_2$ ³⁰ previously reported in the literature, attempts to isolate a binary vanadium(III) borohydride species from reaction $\text{VCl}_3(\text{THF})_3$ with BH_4^- systematically led to divalent compounds. This result strongly suggests that binary vanadium(III) tris-borohydrides are unstable and spontaneously reduce to divalent species. On the other hand, there are only relatively few examples of V(II) complexes which have been fully characterized. It is believed that the scarcity of simple V(II) compounds able to work as starting materials is the main cause for the poor development of vanadium (II) chemistry. Besides $\text{VCl}_2(\text{TMEDA})_2$, vanadium bis-borohydride could be employed as a good starting material for pursuing V(II) chemistry. Furthermore, $\text{V}(\text{BH}_4)_2(\text{THF})_3$ (**4.1**) is the first example of a crystallographically characterized mononuclear V(II) species stabilized only by coordinated THF acting as the ancillary ligand.

As mentioned before, the goal of my thesis was to carry out a preliminary study on the polymerization activity of vanadium complexes in different oxidation states. Transition-metal hydrides are well known to be able to promote olefin polymerization⁸. Therefore, vanadium hydrides may be suitable substrates. However, the reducing ability of borohydride ligands allowed for the isolation of only divalent species. Unfortunately, these species did not display any catalytic activity under a variety of conditions and with a number of aluminum cocatalysts.

Furthermore, our work has demonstrated that V(II) species are in general inactive and their formation should be regarded as a deactivation process.

Conclusion

The following features have been demonstrated in this chapter:

- (1) Vanadium (II) forms a variety of stable covalent complexes with the BH_4^- ion. The synthesis, characterization and properties of these compounds have been described.
- (2) Coordination of BH_4^- to the vanadium center occurs through bridging hydrogens where the BH_4^- ligand adopts a bidentate or monodentate bonding mode depending on the nature of the supporting ligands.
- (3) These species are unreactive towards olefins.

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Chapter 5

Conclusion

This thesis deals with the synthesis, characterization and reactivity of vanadium complexes. During this work, a series of vanadium complexes with different ligand systems have been prepared and characterized. This was done with the hope of gaining some insight into the factors that promote dinitrogen fixation and olefin polymerization based on vanadium complexes.

In chapter two, a series of catalysts of V(III) with different substituted 1,3-dionates ($V(acac)_3$ **2.1**, $V(Cy-acac)_3$ **2.2**, $V(t-Bu-acac)_3$ **2.3** and $V(F-acac)_3$ **2.4**) were prepared and characterized and their activities were systematically compared. $V(acac)_2(TMEDA)$ **2.7** proved to be unreactive towards polymerization with respect to **2.1** under the usual reaction conditions carried out in the absence of reactivating substances, whereas products of reaction of **2.7** and reactivator proved to be reactive towards polymerization in the presence of cocatalyst. $V(t-Bu-acac)_2Cl_2$ **2.10** was more reactive towards polymerization with respect to **2.3** in the presence of cocatalyst. The isolation of $[(acac)_2Al(THF)_2][AlCl_4]$ **2.5** and $[V_2Cl_3(THF)_6][AlCl_4]$ **2.6** indicates that the primary role of the cocatalyst is not only that of *completely* removing the acac ligands from the vanadium center but also that of acting as a reducing agent. The isolation of $(t-Bu-acac)_2V(TMEDA)[X]$ [$X = ZnCl_4^-$ **2.8**, $CuCl_2^-$ **2.9**] indicates that the primary role of reactivating substances, commonly employed in the industrial processes, is to reoxidize V(II) to the trivalent state.

In chapter three, a series of catalysts of V(IV) with amide ligand were prepared and characterized and their activities were systematically compared. The novel V(IV) amide derivatives ((Bz₂N)₄V **3.1**, [Bz(Ph)N]₄V **3.2**, (Bz₂N)₃VCl **3.3**, [Bz(Ph)N]₃VCl·VCl₃(THF)₃ **3.4**) did not perform dinitrogen fixation, but were active towards olefin polymerization.

In chapter four, a series of vanadium (II) bisborohydrides was prepared and characterized and tested for activity towards olefin polymerization. Vanadium(II) bisborohydrides V(BH₄)₂(THF)₃ **4.1**, V(BH₄)₂(TMEDA)₂ **4.2**, [V(BH₄)₂(py)₄](THF)₂ **4.3** did not perform polymerization which indicate that V(II) is inactive towards the polymerization of olefins regardless of the ligand environment and the functional groups attached to vanadium.

APPENDIX

Table 2.3 Crystal Data and Structure Analysis Results for 2.3 and 2.4

	2.3	2.4
Formula	V ₂ C ₆₆ H ₁₃₄ O ₁₂	VC ₁₅ H ₃ F ₁₈ O ₆
Formula weight	1201.45	672.11
space group	Monoclinic P	Monoclinic, P2(1)/n
a (Å)	20.150(13)	8.8170(4)
b (Å)	17.42(2)	13.1756(7)
c (Å)	23.08(2)	19.2513(9)
α (deg)	90	90
β (deg)	112.60(8)	92.013(1)
γ (deg)	90	90
V (Å ³)	7480(10)	2235.0(2)
Z	4	4
Radiation (Kα Å)	0.71073	0.71073
T (°K)	203(2)	218(2)
D _{calcd} (g cm ⁻³)	1.067	1.997
μ _{calcd} (cm ⁻¹)	3.01	6.26
F ₀₀₀	645.28	1304
R, R _w ² , G.o.F	0.0919, 0.1836(R _w), 1.015	0.0514, 0.0592(R _w), 1.050

$$R = \sum \|F_0\| - \|F_c\| / \sum \|F_0\|$$

$$R_w = [(\sum (\|F_0\| - \|F_c\|)^2 / \sum w F_0^2)]^{1/2}$$

Table 2.3a Selected Bond Distances (Å) and Angles (deg) for **2.3** and **2.4**

2.3	2.4
V1-O2#1 = 1.962(5),	V-O3 = 1.960(3),
V1-O2 = 1.962(5),	V-O5 = 1.966(4),
V1-O3 = 1.970(5),	V-O6 = 1.973(3),
V1-O3# = 1.970(5),	V-O1 = 1.986(3),
V1-O1# = 2.013(5),	V-O4 = 1.991(3),
V1-O1 = 2.013(5),	V-O2 = 1.993(3),
O2#1-V1-O2 = 176.2(3),	O3-V-O5 = 88.62(11),
O2#1-V1-O3 = 90.3(2),	O3-V-O6 = 91.15(11),
O3-V1-O2 = 92.4(2),	O5-V-O6 = 87.81(11),
O2#1-V1-O3#1 = 92.4(2),	O3-V-O1 = 178.29(12),
O2-V1-O3#1 = 90.3(2),	O5-V-O1 = 92.89(12),
O3-V1-O3#1 = 87.7(3),	
O2#1-V1-O1#1 = 85.7(2),	
O2-V1-O1#1 = 91.8(2),	
O3-V1-O1#1 = 173.8(2),	
O1#1-V1-O3#1 = 87.7(2),	
O2#1-V1-O1 = 91.8(2),	
O2-V1-O1 = 85.7(2),	
O3-V1-O1 = 87.8(2),	
O3#1-V1-O1 = 173.8(2),	
O1#1-V1-O1 = 97.1(3),	

Table 2.4 Crystal Data and Structure Analysis Results

	2.5	2.7	2.8
formula	$\text{Al}_2\text{C}_{18}\text{H}_{30}\text{O}_6\text{Cl}_4$	$\text{VC}_{16}\text{H}_{30}\text{N}_2\text{O}_4$	$\text{C}_{56}\text{H}_{108}\text{N}_4\text{O}_8\text{V}_2\text{ZnCl}_4$
formula weight	538.18	365.36	1274.51
space group	Triclinic, P-1	Triclinic, P-1	Orthorhombic, Pbcn
a (Å)	8.916(3)	7.896(1)	18.723(7)
b (Å)	9.802(3)	10.032(2)	19.675(7)
c (Å)	15.390(5)	13.134(2)	18.836(7)
α (deg)	88.156(4)	75.265(2)	
β (deg)	86.041(4)	88.520(2)°,	
γ (deg)	82.710(4)	71.445(2)	
V (Å ³)	1330.7(7)	952.1(3)	6939(4)
Z	2	2	4
Radiation (K α Å)	0.71073	0.71073	0.71073
T (°K)	213(2)	173(2)	213(2)
D _{calcd} (g cm ⁻³)	1.343	1.274	1.220
μ_{calcd} (cm ⁻¹)	5.40	5.40	8.08
F ₀₀₀	560	390	2720
R, R _w ² , G.o.F	0.1288, 1.114	0.2114, 1.089	0.0786, 0.1921, 0.0636, 0.1722, 1.010

$$R = \sum \|F_0\| - \|F_c\| / \sum \|F_0\|$$

$$R_w = [(\sum (\|F_0\| - \|F_c\|)^2 / \sum w F_0^2)]^{1/2}$$

Table 2.4a Selected Bond Distances (Å) and Angles (deg) for **2.5**, **2.7** and **2.8**.

2.5	2.7	2.8
Al(1)-O(4) = 1.843(4),	V-O(4) = 2.042(4)	V-O(3) = 1.936(4)
Al(1)-O(3) = 1.846(4),	V-O(2) = 2.051(4)	V-O(4) = 1.957(4)
Al(1)-O(6) = 1.953(4),	V-O(1) = 2.057(4)	V-O(2) = 1.961(4)
Al(3)-Cl(1) = 2.100(3),	V-O(3) = 2.065(4)	V-O(1) = 1.963(4)
Al(3)-Cl(2) = 2.119(3),	V-N(2) = 2.239(4)	V-N(2) = 2.169(6)
Al(3)-Cl(3) = 2.125(3),	V-N(1) = 2.243(5)	V-N(1) = 2.172(6)
Al(3)-Cl(4) = 2.130(3),	O(4)-V-O(2) = 91.4(2)	O(1)-C(5) = 1.272(8)
O(4a)-Al(1)-O(4) = 179.997(1),	O(4)-V-O(1) = 94.2(2)	O(2)-C(7) = 1.307(8)
O(4a)-Al(1)-O(3) = 92.8(2),	O(2)-V-O(1) = 88.0(2)	O(3)-C(16) = 1.285(9)
O(4)-Al(1)-O(3a) = 87.2(2),	O(4)-V-O(3) = 88.4(2)	O(4)-C(18) = 1.289(8)
O(4a)-Al(1)-O(3) = 87.2(2),	O(2)-V-O(3) = 179.8(2)	Zn-Cl(1) = 2.277(2)
O(4)-Al(1)-O(3) = 92.8(2),	O(1)-V-O(3) = 92.0(2)	Zn-Cl(2) = 2.279(2)
O(3)-Al(1)-O(3) = 180.0,	O(4)-V-N(2) = 92.6(2)	O(3)-V-O(4) = 87.82(18)
Cl(1)-Al(3)-Cl(3) = 109.6(2),	O(2)-V-N(2) = 87.4(2)	O(3)-V-O(2) = 87.97(19)
Cl(1)-Al(3)-Cl(4) = 109.8(2),	O(1)-V-N(2) = 171.9(2)	O(4)-V-O(2) = 173.87(18)
Cl(2)-Al(3)-Cl(4) = 108.23(13),	O(3)-V-N(2) = 92.6(2)	O(3)-V-O(1) = 96.03(18)
Cl(1)-Al(3)-Cl(3) = 110.08(14),	O(4)-V-N(1) = 173.3(2)	O(4)-V-O(1) = 88.71(18)
	O(2)-V-N(1) = 90.6(2)	O(2)-V-O(1) = 87.31(18)
	O(1)-V-N(1) = 92.2(2)	O(3)-V-N(2) = 90.3(2)
	O(3)-V-N(1) = 89.7(2)	O(4)-V-N(2) = 93.8(2)

$$\begin{array}{ll} \text{N(2)-V-N(1)} = 81.1(2) & \text{O(2)-V-N(2)} = 90.7(2) \\ & \text{O(1)-V-N(2)} = 173.3(2) \\ & \text{O(3)-V-N(1)} = 172.6(2) \\ & \text{O(4)-V-N(1)} = 91.5(2) \\ & \text{O(2)-V-N(1)} = 93.3(2) \\ & \text{O(1)-V-N(1)} = 91.3(2) \\ & \text{N(2)-V-N(1)} = 82.4(2) \end{array}$$

Table 2.5 Crystal Data and Structure Analysis Results **2.9**, **2.10** and **2.11**

	2.9	2.10	2.11
formula	VCuC ₂₈ H ₅₄ N ₂ O ₄ Cl ₂	VC ₂₂ H ₃₈ Cl ₂ O ₄	VAI ₅ C ₁₈ H ₃₇ O ₄
formula weight	668.11	488.36	572.65
space group	Monoclinic, C2/c	Monoclinic, P2(1)/n	Monoclinic, P2(1)/c
a (Å)	13.676(5)	12.1147(7)	9.041(1)
b (Å)	19.521(3)	9.1690(5)	20.066(2)
c (Å)	13.206(3)	12.1818(7)	14.877(2)
α (deg)	90	90	90
β (deg)	98.47(3)	92.879(1)	90.900(2)
γ (deg)	90	90	90
V (Å ³)	3487.2(9)	1351.4(1)	2698.6(5)
Z	4	2	4
Radiation (Kα Å)	0.71073	0.71073	0.71073
T (°K)	203(2)	223(2)	203(2)
D _{calcd} (g cm ⁻³)	1.273	1.200	1.409g
μ _{calcd} (cm ⁻¹)	10.62	5.86	9.16
F ₀₀₀	1416	518	1192
R, R _w ² , G.o.F	0.0345, 1.096	0.0918, 1.034	0.0602, 0.1465(R _w), 0.1151, 0.2538(R _w), 1.035

$$R = \sum \|F_0\| - \|F_c\| / \sum \|F_0\|$$

$$R_w = [(\sum (\|F_0\| - \|F_c\|)^2 / \sum w F_0^2)]^{1/2}$$

Table 2.5a Selected Bond Distances (Å) and Angles (deg) for **2.9**, **2.10** and **2.11**

2.9	2.10	2.11
V-O1 = 1.9497(17),	V-O2 = 1.8846(13),	V-O1 = 1.955(6),
V-O1# = 1.9497(16),	V-O2# = 1.8847(13),	V-O4 = 1.974(5),
V-O2 = 1.9601(17),	V-O1 = 1.8904(13),	V-O2 = 1.985(5),
V-O2# = 1.9601(17),	V-O1# = 1.8904(13),	V-O3 = 1.987(4),
V-N1 = 2.188(2),	V-Cl1 = 2.3137(6),	V-Cl1 = 2.265(3),
V-N1# = 2.188(2),	V-Cl1# = 2.3137(6),	V-Cl2 = 2.264(3),
Cu-Cl2# = 2.0863(12),	O1-V-O1# = 180.0,	Al-C17 = 1.958(10),
Cu-Cl = 2.0863(13),	O2-V-O2# = 180.0,	Al-Cl3 = 2.155(4),
O1-V-O1# = 94.62(10),	O2-V-O1 = 86.56(5),	Al-Cl2 = 2.155(4),
O2-V-O1 = 87.28(7),	O1-V-O1# = 93.44(5),	Al-Cl5 = 2.1167(4),
O2-V-O1# = 88.89(7),	O1-V-Cl2 = 89.79(5),	O1-V-O4 = 91.1(3),
Cl#2-Cu-Cl = 180.00(8),		O1-V-O2 = 90.4(3),
		O4-V-O2 = 178.5(3),
		O1-V-O3 = 179.6(3),
		O1-V-Cl2 = 90.0(2),
		C17-Al-Cl4 = 111.4(4),
		C17-Al-Cl3 = 112.1(4),
		C17-Al-Cl5 = 111.3(4),
		Cl3-Al-Cl5 = 109.4(2),
		Cl4-Al-Cl5 = 105.6(2),

Table 3.2 Crystal Data and Structure Analysis Results for (3.1) and (3.2)

	(3.1)	(3.2)
formula	C ₅₆ H ₅₆ N ₄ V	C ₅₂ H ₄₈ N ₄ V
formula weight	835.99	779.88
space group	triclinic, P-1	Tetragonal, I-4
a (Å)	10.87(1)	19.243(3)
b (Å)	13.82(4)	19.243(3)
c (Å)	16.67(1)	11.292(2)
α (deg)	107.6 (1)	90
β (deg)	97.62(9)	90
γ (deg)	82.42(2)	90
V (Å ³)	112.3(1)	4181.4(12)
Z	2	4
Radiation (Kα Å)	0.71073	0.71073
T (°K)	293(2)	293(2)
D _{calcd} (g cm ⁻³)	1.199g	1.239
μ _{calcd} (cm ⁻¹)	2.56	2.78
F ₀₀₀	886	1644
R, R _w ² , G.o.F	0.2145, 0.2914, 1.038	0.0897, 0.1184(R _w), 1.106
$R = \sum F_0 - F_c / \sum F_0 \quad R_w = [(\sum (F_0 - F_c)^2 / \sum w F_0^2)]^{1/2}$		

Table 3.2a Selected Bond Distances (Å) and Angles (deg) for (3.1) and (3.2)

(3.1)	(3.2)
V-N1 = 1.887(5),	V1-N1 = 1.897(2),
V-N2 = 1.891(5),	V1-N1A = 1.897(2),
V-N3 = 1.893(6),	V1-N1B = 1.897(2),
V-N4 = 1.898(6),	V1-N1C = 1.897(2),
N3-V-N4 = 115.8(2),	N1-V-N1A = 108.95(7),
N3-V-N2 = 108.5(2),	N1-V-N1B = 108.95(7),
N4-V-N2 = 103.8(2),	N1A-V-N1B = 110.51(13),
N3-V-N1 = 103.6(2),	N1-V-N1C = 110.51(13),
N4-V-N1 = 108.2(2),	N1A-V-N1C = 108.95(7),

Table 3.3 Crystal Data and Structure Analysis Results for (3.3) and (3.4)

	(3.3)	(3.4)
formula	C ₄₂ H ₄₂ N ₃ ClV	C ₅₁ H ₆₀ N ₃ O ₃ Cl ₄ V ₂
formula weight	705.20	1006.7
space group	Triclinic, P-1	Triclinic, P-1
a (Å)	11.169(1)	9.200(2)
b (Å)	14.045(1)	13.857(3)
c (Å)	14.939(1)	19.753(4)
α (deg)	82.997(2)	74.988(3)
β (deg)	88.181(2)	87.838(3)
γ (deg)	75.746(2)	81.882(2)
V (Å ³)	2254.4(3)	2407.8(8)
Z	2	2
Radiation (Kα Å)	0.71073	0.71073
T (°K)	203(2)	218(2)
D _{calcd} (g cm ⁻³)	1.039	1.389
μ _{calcd} (cm ⁻¹)	3.08	6.56
F ₀₀₀	740	1050
R, R _w ² , G.o.F	0.1962, 0.3556(R _w),.	0.1789, 0.2305(R _w),.
	0.962	0.983
$R = \Sigma F_0 - F_c / \Sigma F_0 \quad R_w = [(\Sigma (F_0 - F_c)^2 / \Sigma w F_0^2)]^{1/2}$		

Table 3.3a Selected Bond Distances (Å) and Angles (deg) for (3.3), and (3.4)

(3.4)	(3.4)
V-N2 = 1.813(7),	V1-N3 = 1.804(9),
V-N3 = 1.843(8),	V1-N1 = 1.844(9),
V-N1 = 1.846(7),	V1-N2 = 1.804(8),
V-Cl = 2.251(3),	V1-Cl1 = 3.216(3),
N2-V-N3 = 101.7(3)	N3-V1-N1 = 100.8(4)
N1-V-N2 = 112.8(3)	N3-V1-N2 = 115.3(4)
N3-V-N1 = 114.1(3)	N1-V1-N2 = 108.2(4)
N2-V-Cl = 107.1(2)	N3-V1-Cl1 = 107.4(3)
N3-V-Cl = 113.2(2)	N1-V1-Cl1 = 113.3(3)
N1-V-Cl = 107.8(2)	N2-V1-Cl1 = 111.5(3)

Table 4.1 Crystal Data and Structure Analysis Results for (4.1), (4.2), and (4.3)

	(4.1)	(4.2)	(4.3)
formula	VO ₃ B ₂ C ₁₂ H ₃₂	VN ₄ C ₁₂ B ₂ H ₃₄	VN ₄ C ₂₈ B ₂ H ₄₄
formula weight	296.94	306.99	541.23
space group	Orthorhombic, P	Tetragonal, I 41/acd	Monoclinic, P2(1)/n
a (Å)	10.60460(10)	13.737(18)	11.846(2)
b (Å)	11.18060(10)	-	15.735(3)
c (Å)	14.07570(10)	20.445(4)	15.887(3)
α (deg)			90
β (deg)			90.10(3)
γ (deg)			90
V (Å ³)	1668.896(25)	3858(5)	2961.3(10)
Z	4	8	4
Radiation (Kα Å)	0.70930	0.70930	0.71073
T (°K)	140(2)	140(2)	140(2)
D _{calcd} (g cm ⁻³)	1.182	1.057	1.214
μ _{calcd} (cm ⁻¹)	5.7		3.66
F ₀₀₀	645.28	1338.50	3864
R, R _w ² , G.o.F	0.035, 0.041(R _w),	0.061, 0.055(R _w),	0.1498, 0.3308(R _w),
	1.22	11.23	1.163

$$R = \sum \|F_0\| - \|F_c\| / \sum \|F_0\|$$

$$R_w = [(\sum (\|F_0\| - \|F_c\|)^2 / \sum w F_0^2)]^{1/2}$$

Table 4.1a Selected Bond Distances (Å) and Angles (deg) for (4.1), (4.2), and (4.3)

(4.1)	(4.2)	(4.3)
V1-O1 = 2.219(3),	V-BH1 = 2.08(6)	V1-N4 = 2.198(9)
V-O2 = 2.108(3),	B1-BH1 = 0.95(6)	V1-N1 = 2.190(9)
V-O3 = 2.134(3),	N1-C1 = 1.491(10)	V1-N2 = 1.194(9)
V-H6 = 2.02(4),	N1-C3 = 1.565(10)	V1-N3 = 1.198(9)
V-H13 = 2.08(5),	BH1-V-BH1a = 180.0	N1-V-N2 = 90.5(3)
B1-H4 = 1.02(6),	C1-N1-C3 = 110.1(6)	N1-V-N4 = 90.1(3)
B1-H6 = 1.12(5),	C1-N1-C4 = 107.6(7),	N3-V-N2 = 89.4(3)
B1-H13 = 1.06(5),	C3-N1-C4 = 105.9(8)	N3-V-N4 = 91.3(3)
O1-V1-O2 = 86.42(12),	V-BH1-B = 180.0	
O1-V1-O3 = 173.07(12),		
O1-V1-H6 = 92.4(14),		
O1-V1-H13 = 92.4(14),		
O2-V1-O3 = 86.91(12),		
O2-V1-H6 = 96.6(14),		
O2-V1-H13 = 148.9(14),		
O3-V1-H6 = 86.4(14),		
H4-B1-H6 = 107(4),		
H4-B1-H13 = 110(4),		
O2-V1-H17 = 115(4),		
V1-DH-B1 = 97(3),		