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Abstract

Reactions of *trans*-$TiCl_2(TMEDA)_2$ with two equivalents of RONa gave the paramagnetic linear trimeric $[Ti_3(PhO)_9(TMEDA)_2]$ **(2.1)** , dimeric $[Ti(OR)Cl(TMEDA)]_2(\mu\text{-}OR)_2$ **(2.2)** [R = 3,5-$(t\text{-}Bu)_2C_6H_3$] or monomeric $[Ti(OR)_4][Li(TMEDA)_2]$ **(2.7)** [R = 2,6-$(iPr)_2C_6H_3$], indicating that the role of steric hindrance not only controls the geometry and the nuclearity of the complex, but also stabilizes the +3 oxidation state.

Conversely, in the case of vanadium, it was possible to isolate and characterize monomeric and neutral V(II) aryloxides with a variety of coordination geometries like square-planar and saddle-shaped. Less bulky phenols give monomeric or dimeric products after disproportionation and oxidation. Similar to the case of titanium, vanadium aryloxides do not show any interaction with dinitrogen. Reaction of $V[(2\text{-}OMe)C_6H_4O]_2(TMEDA)$ **(4.7)** with Me_3SiCHN_2 gave $\{[(2\text{-}OMe)C_6H_4O]_2V\}_2[\mu\text{-}NNCHSiMe_3]_2$ co-crystallized with $\{[(2\text{-}OMe)C_6H_4O]_2V\}_2[\mu\text{-}(2\text{-}OMe)\ C_6H_4O]_2$ **(4.14)**. The structures of these complexes were determined by X-ray analysis.

The synthesis and reactions of ionic Ti(III) amides with RLi are discussed. Sterically demanding alkyl groups [R = CH_2CMe_3, CH_2SiMe_3, CH_2CMe_2Ph] led to disproportionation and isolation of Ti(IV) complexes of the formulation $[(Cy_2N)_2TiR_2]$ whereas with MeLi & BzLi, $(Cy_2N)_2TiR_2Li(TMEDA)$ [R = Bz **(3.4a)**,

Me **(3.4b)**] was formed, thus retaining the +3 oxidation state of titanium. Thermolysis of $(Cy_2N)_2TiNf_2$ gave $(Cy_2N)_2TiCH_2C(Me)_2C_6H_4$ **(3.10)** after losing a molecule of neophane.

The ability of three-center chelating ligands (such as formamidinates or benzamidinates) to form dinuclear complexes with a short M-M contact was studied in order to understand the role of bridging ligands in promoting or disfavoring the dinuclear aggregation and to determine the extent of intermetallic separation in such species.

The reaction of Li amidinates with *trans*-$VCl_2(TMEDA)_2$ gave dinuclear $[(CyNC(H)NCy)_2V]_2$ **(5.3)**, monomeric $[CyNC(Me)NCy]_2V(THF)_2$ **(5.7)** and $[Me_3SiNC(Ph)NSiMe_3]_2V(THF)_2$ **(5.9)** depending upon the steric interaction between Cy or Me_3Si with H, Me or Ph substituents of the ligands. Attempts to remove THF from $[CyNC(Me)NCy]_2V(THF)_2$ resulted in the formation of V(III) complex $[CyNC(Me)NCy]_3V$ **(5.6)** whereas in the case of $[Me_3SiNC(Ph)NSiMe_3]_2V(THF)_2$ a novel dinitrogen complex $[\{Me_3SiNC(Ph)NSiMe_3\}_2V]_2(N_2)$ **(5.12)** was formed. All these complexes could also be synthesized *via* reduction of V(III) amidinates.

Reactions of $LiNR_2$ with $SmCl_3(THF)_3$ in a 2:1 molar ratio gave Sm(III) amides with different formulations and structures depending upon the R group of the amide. Dimeric $[(Cy_2N)_2Sm(THF)(\mu\text{-}Cl)]_2$ **(6.1)** was obtained from the reaction of

$SmCl_3(THF)_3$ with Cy_2NLi whereas $[(i\text{-}Pr_2N)_2SmCl_3(Li.TMEDA)_2]$ **(6.2)** was obtained from the amide, iPr_2NLi under similar reaction conditions but in the presence of TMEDA. The reactivity of these amides was studied which gave another variety of Sm(III) amides like $[(Cy_2N)_6Sm_4Cl_6(THF)_2]$ **(6.3)** and $[(Cy_2N)_4SmLi(THF)]$ **(6.4)**. Attempts to reduce **(6.1)** gave either metallic samarium or $Sm(Cy_2N)_3(THF)$ **(6.5)** . The direct synthesis of a Sm(II) amide was possible only with Ph_2N^-, the salt having no α-hydrogen. Using Ph_2N^- as the ligand, both ionic $[Sm(Ph_2N)_4Na_2(TMEDA)_2]$ **(6.6)** and neutral $[Sm(Ph_2N)_2(THF)_4]$ **(6.7)** complexes were obtained. The structures of all these complexes are demonstrated by X-ray analysis.

Publications

1) **Ravinder K. Minhas, Robbert Duchateau, Sandro Gambarotta and Corinne Bensimon.** Linear Trimeric, Dimeric and Monomeric Titanium (III) Aryloxides. *Inorg.Chem.* Vol.31, 4933, **1992.**

2) **Ravinder K. Minhas, Jilles J.H. Edema, Sandro Gambarotta and Auke Meetsma.** Stability of Vanadium (II) Aryloxides: Synthesis and Characterization of Sterically Protected Neutral and Monomeric V(II) Aryloxides. Reactivity with the N-N Bond of $(Me_3Si)CH=N=N$. *J.Am.Chem.Soc.* 115, 6710-6717, **1993.**

3) **Sandro Gambarotta, Jilles J.H. Edema and Ravinder K. Minhas.** Isolation and Characterization of a Vanadium Ethylidyne Complex. The Crystal Structure of $[(Cy_2N)_2V]_2Li(\mu^3\text{-}O)(\mu^2,\eta^1\text{:}\eta^2\text{-}CMe)$: An Unusual V_2LiO Cluster. *J.Chem. Soc., Chem.Comm.*, 19, 1503-1504, **1993.**

4) **Pietro Berno, Shoukang Hao, Ravinder K. Minhas and Sandro Gambarotta.** Dinitrogen Fixation Versus Metal- Metal Bond Formation in the Chemistry of Vanadium (II) amidinates. *J.Am.Chem.Soc.* 116, 7417-7418, **1994.**

5) **Pietro Berno, Ravinder K. Minhas, Shoukang Hao and Sandro Gambarotta.** Preparation, Characterization and Reactivity of the Binuclear Vanadium (III)

compound $\{[(Me_3Si)_2N]V[\mu\text{-}CH_2SiMe_2N(SiMe_3)]\}_2$. C-H σ- Bond Metathesis promoted by an Amido Function. *Organometallics*, 13, 1052-1054, **1994.**

6) **Ludmila Scoles, Ravinder K. Minhas, Rob Duchateau, Jayne Jubb and Sandro Gambarotta.** Synthesis and Characterization of Novel Titanium (III) and (IV) Alkyls and Carbenes Supported by Amide Ligands. Crystal Structure of $[(Cy_2N)_2Ti(\mu\text{-}CH_2)]_2$. *Organometallics*, 13, 4978-4983, **1994.**

7) **Shoukang Hao, Pietro Berno, Ravinder K. Minhas and Sandro Gambarotta.** The Role of the Ligand Steric Hindrance in Determining the Stability of Very Short V-V Contacts. Preparation and Characterization of a Series of V(II) and V(III) Amidinates. *Inorganica Chimica Acta.* Publication in Press.

8) **Ravinder K. Minhas, Ludmila Scoles, Sandro Gambarotta.** Tri- and Tetravalent Titanium Alkyls Supported by Organic Amides. *Organometallics.* Publication in Press.

9) **Ravinder K. Minhas, Sandro Gambarotta.** Synthesis, Reactivity and Stability of Di- and Trivalent Samarium Amides. *Inorg. Chem.* Publication in Press.

10) **Ravinder K. Minhas, Sandro Gambarotta.** Synthesis and Characterization of Sm(II) and Sm(III) Borohydrides. Manuscript in Preparation.

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Dedicated to Hardit Singh and Tanvir Singh

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List Of Abbreviations

Å	angstroms
δ	chemical shift
μ_{eff}	effective magnetic moment in Bohr magnetons
χ_g	magnetic susceptibility
Bz	benzyl
cm^{-1}	wave number
Cp	cyclopentadienyl
Cy	cyclohexyl
dipy	dipyridyl
dmpe	dimethylphosphinoethane
g	grams
Guo	2-$(OCH_3)C_6H_4O$
i-Pr	isopropyl
Me	methyl
Mes	mesityl
MHz	frequency in megahertz
ml	milliliter
mmol	millimoles
Mz	o-$Me_2NCH_2C_6H_4$
Nf	-CH_2CMe_2Ph

NMR	nuclear magnetic resonance
Np	$-CH_2CMe_3$
Ph	phenyl
ppm	parts per million
Py	Pyridine
R	alkyl group
t-Bu	tert-butyl
THF	tetrahydrofuran
TMEDA	N,N,N',N'-tetramethylethylenediamine
X	halogen

CHAPTER I

Introduction

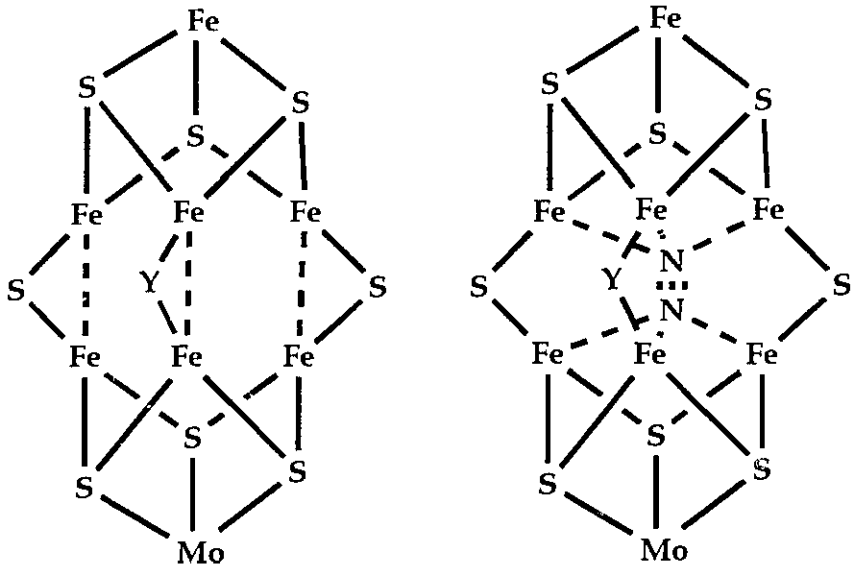
Dinitrogen fixation is the process of converting the highly inert and most abundant component of the atmosphere, N_2, into ammonia and/or nitrogenous compounds. In nature, nitrogenase[1] is the enzyme which catalyses the reduction of dinitrogen to ammonia and which plays a pivotal role in maintaining the nitrogen cycle on earth. Earlier in this century[2], it was shown that Mo is an essential element for dinitrogen fixation by bacteria and since then scientists assumed that transition metal complexes can activate dinitrogen. However, until the sixties, little was reported in the literature about the ability of transition metals to interact with dinitrogen. In 1962, studies on dinitrogen fixing enzymes (nitrogenases) showed the existence of two distinct proteins[3], one containing Mo and Fe, the other containing Fe as the only transition metal. The stoichiometry of the biological N_2 fixation reaction is :

$$N_2 + 8H^+ + 8e^- \longrightarrow 2NH_3 + H_2$$

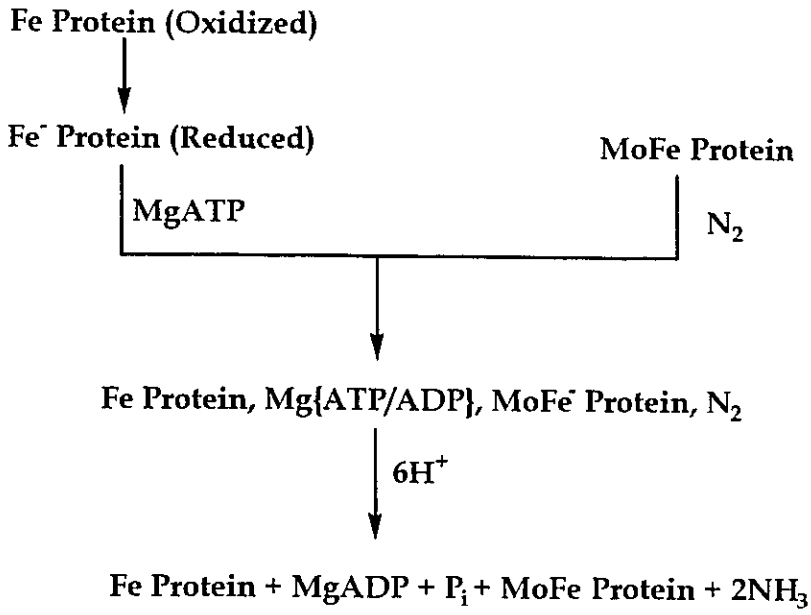
It should be noted that the process also results in the reduction of the hydrogen ion to dihydrogen. The formation of elemental hydrogen is responsible for the other performances of nitrogenase such as its ability to reduce substrates like ethylene[4]. The Fe protein cofactor of nitrogenase is a dimer of two identical subunits with a

total molecular mass of ~60K and which coordinates a single 4Fe:4S cluster. The MoFe protein is an $\alpha_2\beta_2$ tetramer of relative molecular mass 240K, the α- and β-subunits being composed of 491 and 522 amino acids respectively. The tetramer contains 30 Fe and 2 Mo atoms which are present as two types of metal clusters ($MoFe_3S_3$ and Fe_4S_3). In both these proteins, sulphide ions are present and are approximately equal to the number of iron atoms.

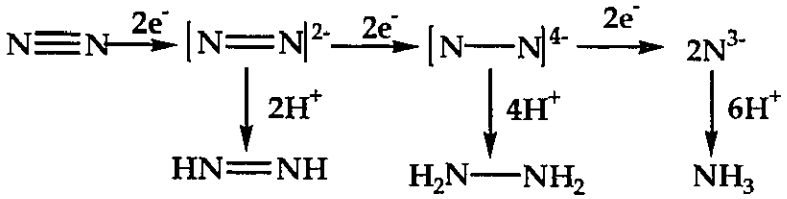
The recently reported crystal structures of the Fe protein and the MoFe protein of nitrogenases[5] do not provide any information regarding the location or the geometry of the bonding site. However, it is almost certain that the fixation of N_2 occurs at the MoFe cofactor. The X-ray diffraction study of the MoFe protein has confirmed the presence of two MFe_3S_3 (M = Fe, Mo) cubane clusters linked together by two disulphide bridges between Fe atoms of each cubane clusters. According to the electron density maps, a third ligand designated as Y, possibly O or N atom, was also found linked to the two cubane units. The difference Fourier maps exclude the presence of a sulphur atom in the center of the cluster. The cofactor contains three Fe-Fe bonds which are quite weak and further destabilized by the distortion of the tetrahedral geometry. This observation has suggested that the bonding of dinitrogen in the FeMo cofactor might involve the Fe-Fe bond, which originates a Fe-N2-Fe moiety. The cooperative interaction of two metal centers with N_2 probably weaken the N-N bond thus lowering the activation barrier for dinitrogen reduction.



The electrons necessary for dinitrogen reduction are provided by a small protein which acts as a specific carrier of electrons from the reducing agent to the large protein. The reducing agent is $Na_2S_2O_4$ or reduced forms of ferredoxins or flavodoxins. The hydrolysis of the monomagnesium salt of ATP to ADP and inorganic phosphate provides the energy required for each electron transfer step. According to **Scheme 1.1**, the proposed sequence of steps based on spectroscopic studies[6] is that the reduced Fe protein forms a complex with large protein and MgATP. It transfers its reducing electron to the MoFe protein and then to the dinitrogen bound on the active site. The reduction of dinitrogen occurs in three steps, (**Scheme 1.2**) requiring 6 electrons in total, to completely reduce one molecule of N_2. The first step forms diazene, followed by reduction to hydrazine, further cleaving the N-N bond to form a nitride which, in the presence of protic medium, gives ammonia. After a series of electron transfer steps, with simultaneous transfer



Scheme 1.1



Scheme 1.2

of protons from water to dinitrogen, MgADP, inorganic phosphate and NH_3 are produced with the regeneration of the proteins at their original oxidation states.

In 1986, the existence of another natural nitrogen fixation system, called vanadium nitrogenase[7] was demonstrated. In this system, the conventional molybdoprotein is replaced by a vanadoprotein, which functions under conditions of absence or deficiency of Mo. The discovery of this vanadium nitrogenase implies that a wide range of transition metals possibly facilitate the reactions of dinitrogen in their coordination sphere. Therefore the studies of the syntheses and reactions of

dinitrogen complexes of transition metals became of particular interest.

In striking contrast to the naturally occurring nitrogenase, synthetic systems have been able to show only a very few transformations of elemental nitrogen. In 1965, the study of the chemistry of dinitrogen fixation marked a milestone when Allen & Senoff[8] isolated the first dinitrogen complex $[Ru(NH_3)_5(N_2)]_2^+$. This result catalyzed further the research into this field and synthesis and reactivity of dinitrogen complexes of various transition metals was actively pursued by several groups around the world. This was also in the view of industrially important applications. For example, the existing Fe-catalyzed Haber-Bosch process, which is used worldwide for the production of NH_3, requires severe reaction conditions (ca. 200 atm. and 400 - 500°C) and is in striking contrast to the biological N_2-fixing system which can reduce N_2 gas into NH_3 under very mild conditions (1 atm., aq. medium, pH ~ neutral, RT). Therefore, one of the goals of this chemistry was to develop an alternate, industrially viable synthesis of NH_3 and of other nitrogenous compounds.

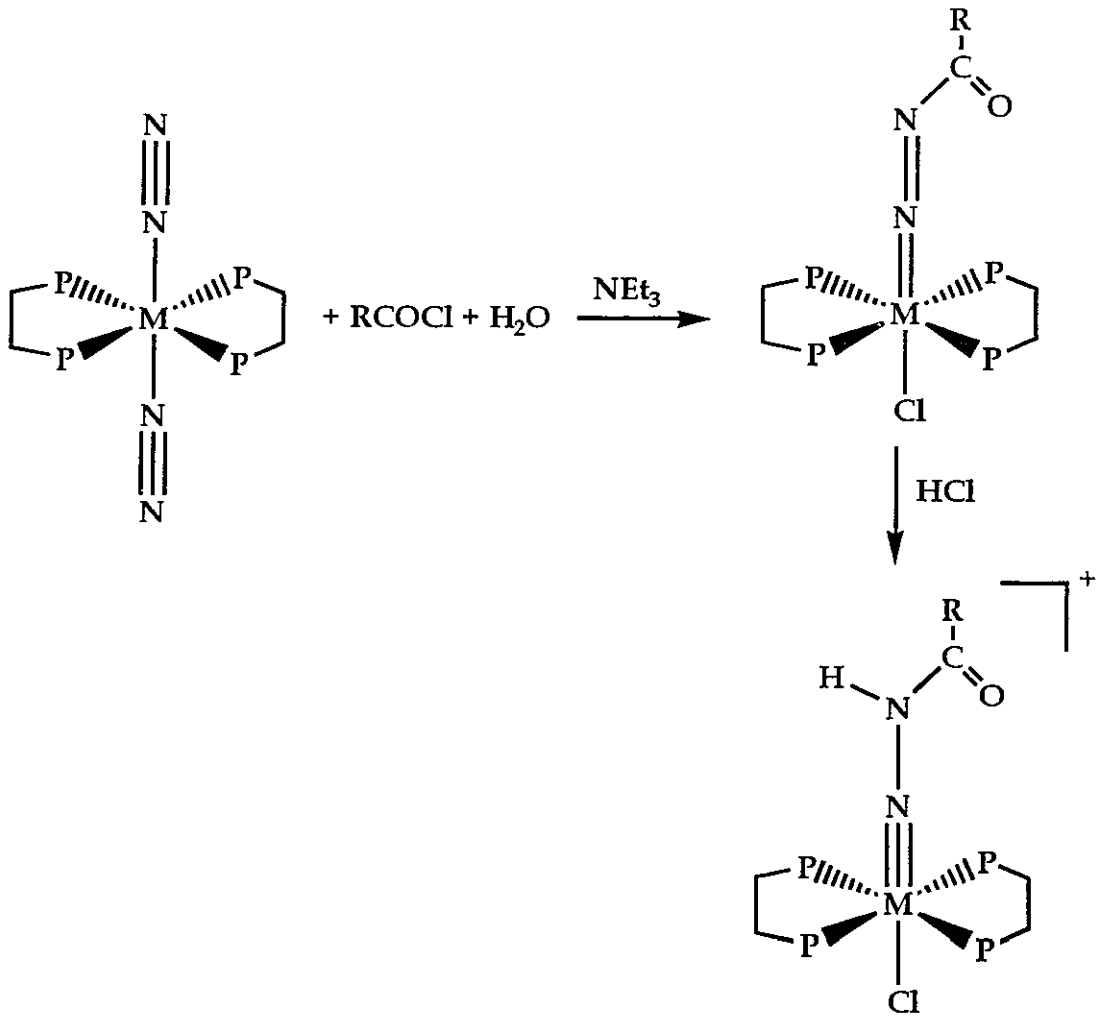
In spite of its abundance in the atmosphere, dinitrogen is not a useful raw material from the chemical synthesis point of view. Its stability under ambient conditions is caused by the presence of a N-N triple bond, which makes this substrate difficult to be either oxidized or reduced. The enthalpies of formation of NH_3 and of the intermediates[9] (Kcal/mole) in the reaction of dinitrogen with

dihydrogen shows that only the formation of 6 N-H bonds provides sufficient energy to compensate the rupture of the N-N multiple bond.

Table of Enthalpies of Formation of NH_3 and Intermediates

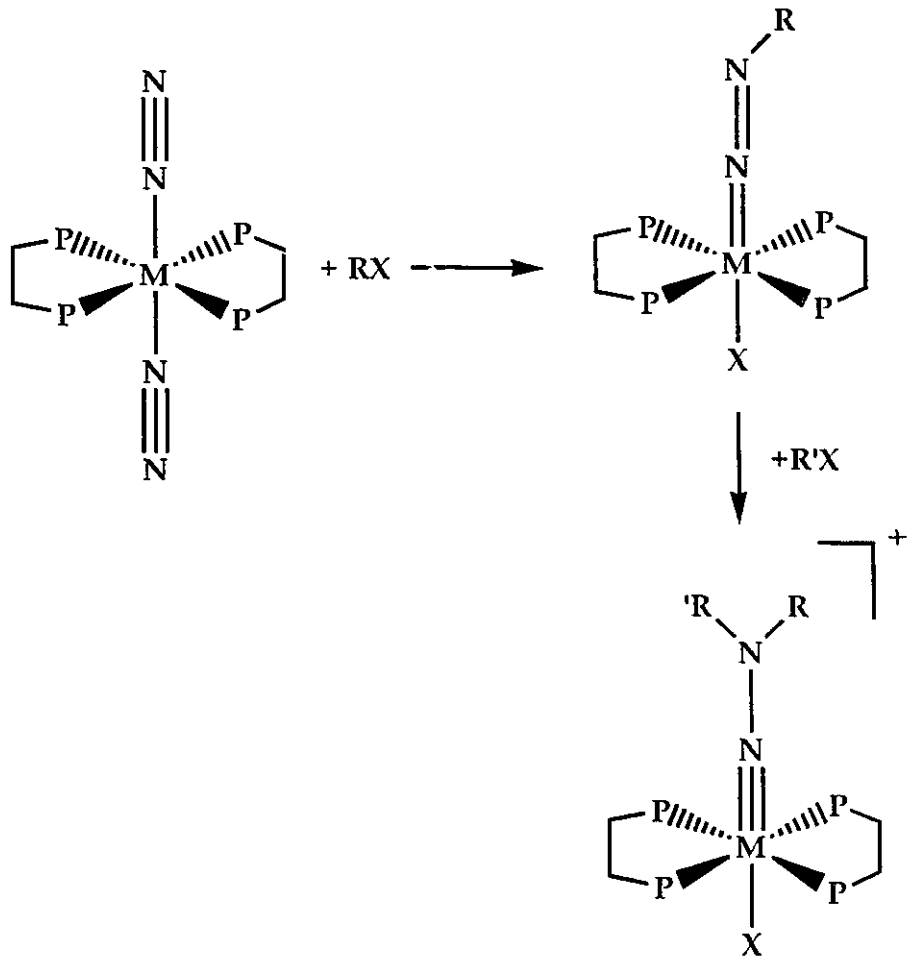
	$N_2 \longrightarrow$	$N_2H_2 \longrightarrow$	$N_2H_4 \longrightarrow$	$2NH_3$
ΔH_{298}	-	49	22.7	-22
ΔH_{298}(Soln./H_2O)	-	-	8.2	-38.4
ΔH_{298}(Soln./acid)	-	-	-1.8	-64

Dinitrogen complexes are known for almost all transition metals but those which react in a well defined manner to give nitrogenous compounds are relatively few. The dinitrogen complexes of Mo and W have been most intensively studied since the initial preparation of *trans*-$[Mo(N_2)_2(dppe)_2]$ by Chatt[10]. At the time of its discovery, this result generated enormous interest in both the scientific community and the media because of: (i) the possible relevance to the active site of FeMo nitrogenases studies, and (ii) the possibility to isolate and characterize reactive species which are formed as intermediates during the formation of NH_3 and/or N_2H_4. Formation of a C-N bond was also observed during the acylation/aroylation[11] or alkylation[12] reactions of Mo and W complexes, *trans*-$[M(N_2)_2(dppe)_2]$ with RCOCl or RX, forming *trans*-$[MCl(NNHCOR)(dppe)_2]^+$ and *trans*-$[MX(NNHR)(dppe)_2]^+$ respectively. The acylation reaction is believed to occur *via* nucleophilic attack of the



Scheme 1.3

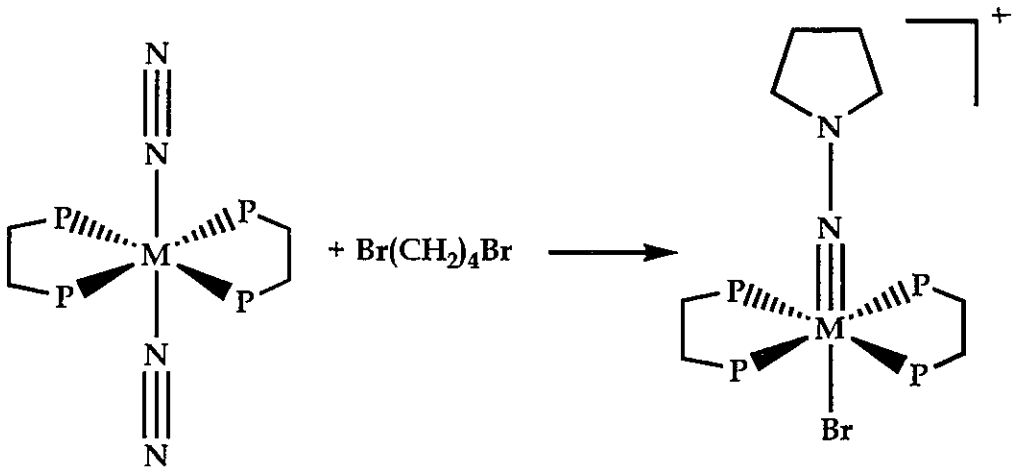
terminal N atom on the acyl carbon (**Scheme 1.3**). The X-ray structural analysis[13] of the Mo analogue has shown a linear Mo-N-N group with the carbonyl carbon attached to the terminal N atom. Conversely, the alkylation proceeds *via* homolysis of alkylhalide, generating the alkyl radical (**Scheme 1.4**) which attacks the N_2 ligand. Similar complexes of Mo and W have also been described to react with different alkyl/aryl halides such as MeI, MeBr, PhBr and PhI[14].



Scheme 1.4

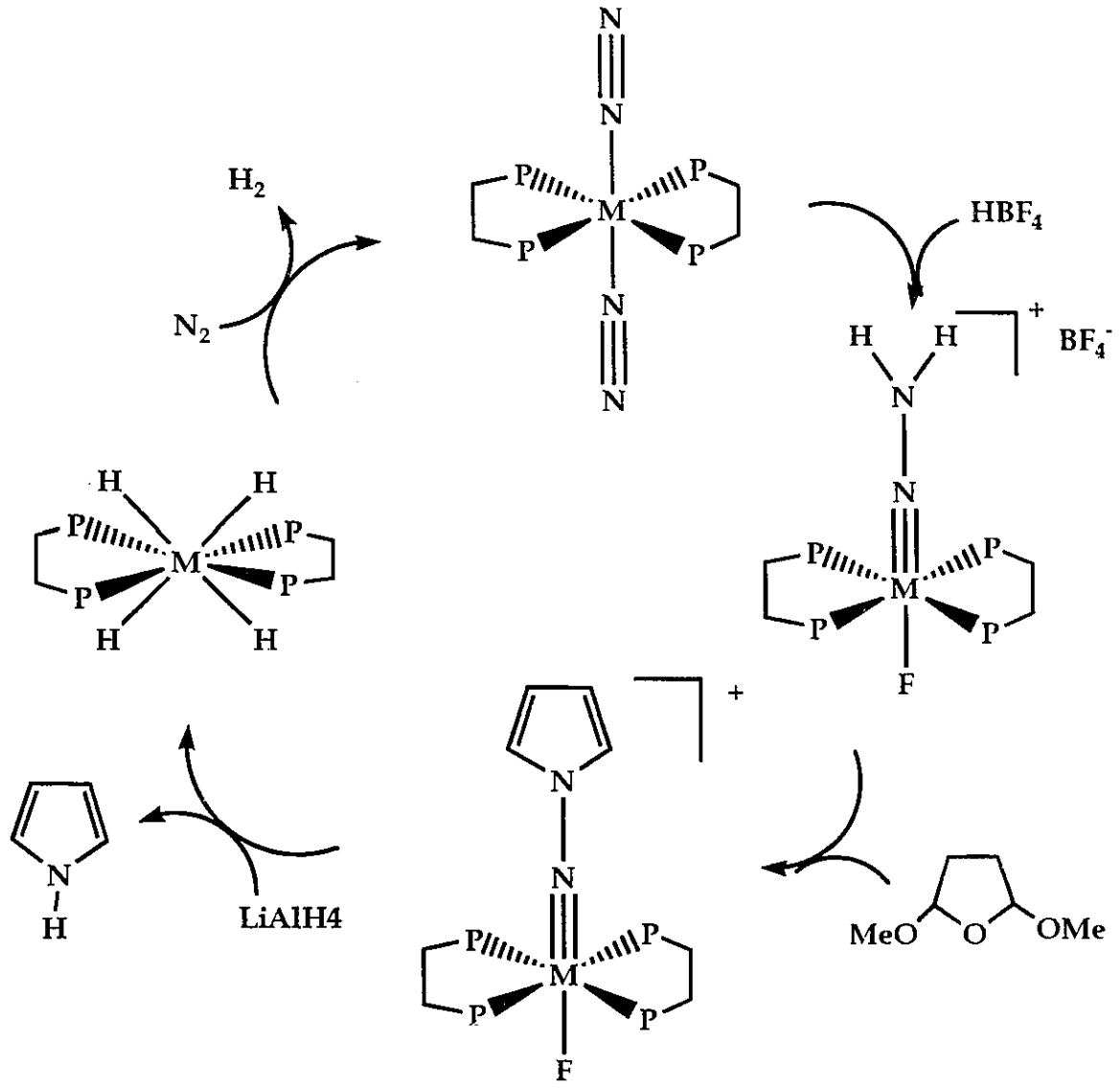
The ability of transition metal complexes to activate molecular nitrogen and to induce its reduction under mild conditions opens the way to various transformations of dinitrogen. Of particular interest is, of course, the metal-promoted incorporation of dinitrogen into organic compounds. Since the insertion of unsaturated molecules into the M-C bond is well known in various catalytic transformations, insertion of dinitrogen into the M-C bond of organometallic derivatives was also attempted. In the case of Cp_2TiPh_2, the product obtained after hydrolysis contained aniline along with ammonia[15]. Even though this result is

extremely promising, unfortunately, it does not provide any information about the nature of intermediate species. Similar types of transformations were attempted on well defined dinitrogen complexes but still the existence of these nitrogenous complexes is limited to Mo and W complexes[16].



Scheme 1.5

The most spectacular achievement in this field was provided by the preparation of amines *via* alkylation of dinitrogen complexes, followed by reduction with $LiAlH_4$. The formation of pyrrolidine was observed during the reactions of Mo and W complexes, *trans*-$[MBr\{NN(CH_2)_3CH_2\}(dppe)_2]Br$[17] (**Scheme 1.5**) with $LiAlH_4$ followed by hydrolysis in MeOH and then HBr. Similarly, the *trans*-$[WBr\{NN(CH_3)_2\}(dppe)_2]Br$ gave Me_2NH[18] under similar conditions. In the reaction of $WF(NNCH{=}CHCH{=}CH)(dppe)_2][BF_4]$ with $LiAlH_4$, pyrrole[19] was isolated after hydrolysis, together with $[MH_4(dppe)_2]$ which eventually was converted back to the initial dinitrogen complex, thus completing the cycle (**Scheme 1.6**).



Scheme 1.6

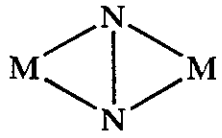
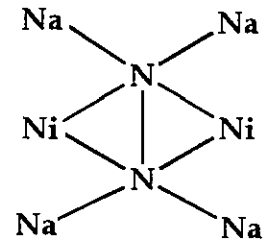
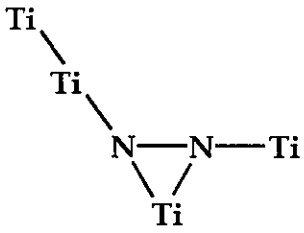
N-aminopiperidine[20] was also prepared following a similar procedure in which a dinitrogen complex was recovered during the controlled electrolysis of *trans*-[MoBr{NN(CH$_2$)$_4$CH$_2$}(dppe)$_2$]Br under N_2. Piperidine[21] was obtained *via* electroreduction of this hydrazido complex or by the reaction with t-BuLi. The synthesis of i-PrNH$_2$[22] and n-BuNH$_2$[12a] have also been reported using Mo and W complexes upon reactions with $LiAlH_4$ or $NaBH_4$. The synthesis of organonitrogen

compounds by reactions with simple organic substrates through C-N bond formation at coordinated N_2 is an important step and the target of current research in the development of the chemistry of dinitrogen.

Bonding Modes of Dinitrogen:

The type of bonding of dinitrogen to a transition metal determines its activation or further transformation. Therefore it is not surprising that considerable effort was made to understand the factors which determine the type of bonding. In principle, dinitrogen can bind to a metal in a variety of ways. **Scheme 1.7** gives a schematic representation of the possible modes.

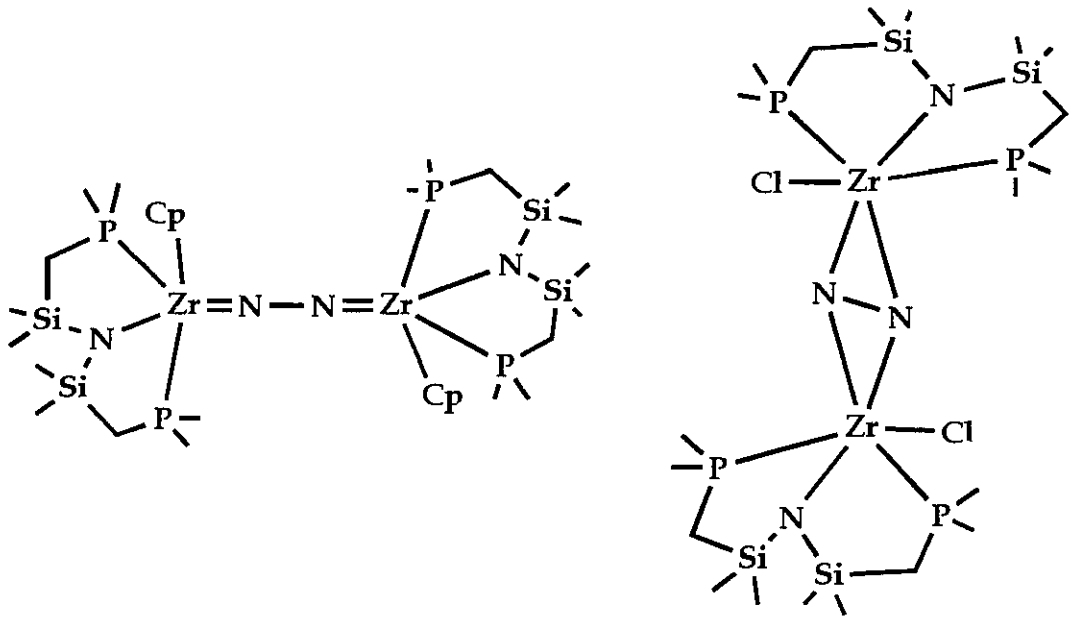
A large number of complexes has been reported containing either terminal or bridging end-on dinitrogen[23] while the side-on bonding mode remains relatively rare[24]. From the theoretical point of view, the side-on type of coordination implies a significant donation of charge from the metal to the π^* orbitals of dinitrogen, thus resulting in a significant reduction of the N-N bond order. In addition, this latter type of bonding, facilitates bond dissociation based on the low calculated N-N overlap population, and increases the net negative charge on each of the nitrogen atoms necessary for protonation. Recently, two closely-related dinuclear zirconium-dinitrogen complexes[26], but with dinitrogen bonded in two different bonding modes, have been synthesized. (**Scheme 1.8**) Complex $\{[(iPr_2PCH_2SiMe_2)_2N]Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2)$ has a N_2 ligand bridging the two Zr atoms with a linear end-on

Bonding Mode	Ref
M—N≡N	11, 12a
M—N=N—M	25a, b
	24a
	24b
	25c

Scheme 1.7

geometry and a N-N bond distance of 1.301Å showing considerable reduction of N_2. Complex $\{[(iPr_2PCH_2SiMe_2)_2N]ZrCl\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ contains side-on bonded N_2, bridging both metal atoms, and exhibits the longest ever found N-N bond distance [N-N = 1.548Å], even longer than the N-N bond of hydrazine.

Molecular orbital calculations show that in the end-on bridged dinitrogen complex, the cyclopentadienyl ligand overlaps with the Zr *d* orbital which, therefore, can not form the δ-molecular orbital with N_2 necessary for the



Scheme 1.8

stabilization of the side-on mode. It was thus proposed that the end-on bonding mode is just the result of the impossibility of forming a M-N_2 δ-bond. While the presence of suitable *d* orbitals , which can give a δ overlap with the π^* orbital of the dinitrogen, is the factor determining the coordination mode, the presence of *d* electrons is commonly regarded as a prerequisite for dinitrogen fixation.

In accordance with this, no dinitrogen complex was ever reported for a d^0 transition metal or main group element. Only recently, a unique example of side-on coordination of dinitrogen to a Li^+ countercation of a Zr(III) complex was described. In the complex $[Cp_2ZrPPh]_2[Li(THF)_3]_2(\mu\text{-}N_2)_2]$[27], the N-N bond distance (1.06Å) is comparable to the N-N bond distance in the complex $[Cp^*_2Sm]_2(\mu\text{-}N_2)$[28] (1.09Å) and is even shorter than in free N_2 (1.10Å). This suggests that no reduction has taken

place in spite of the side-on bonding of N_2. By contrast, the Zr complexes discussed by Fryzuk with a similar side-on bonding mode of the dinitrogen moiety {[(i-$Pr_2PCH_2SiMe_2)_2N]ZrCl\}_2(\mu$-$N_2)$, has a remarkably long N-N bond distance (1.55Å) which implies a complete reduction of N_2 to the hydrazido tetraanion. The fixation of dinitrogen by a Li^+ cation certainly marks a milestone in this chemistry and is opening new perspectives for dinitrogen activation.

Chemistry of Titanium and Vanadium:

Early transition metals have been successfully used for promoting a very large number of organic transformations such as insertion[29], reductive coupling[30], hydroamination[31], cyclization[32] and hydrosilation reactions[33]. In particular, reductive coupling and insertion reactions are commonly performed by a considerable number of transition metals to form C-C bonds through either catalytic or stoichiometric reactions[34]. While the insertion reactions are the most versatile chemical pathways for polymerization processes[34a, 35], reductive couplings are targets of continuous studies for regio- and stereo-selective metal-promoted organic synthesis[30a, 36]. This latter class of reactions has been documented for the large majority of unsaturated organic compounds such as dienes[37], olefins[30c, 38], acetylenes[39], isocyanides[40], nitriles[41] and carbon monoxide[42]. Formation of ammonia was observed in the reaction of dinitrogen gas with a mixture of transition metal salt and organo-magnesium, -lithium or -aluminum moieties followed by hydrolysis[43]. This result shows that there is the possibility of readily converting

dinitrogen into nitrogenous compounds in the presence of transition metal organometallic species.

Among early transition metals, vanadium and titanium occupy a special place due to several unique features which make these elements promising substrates with which to study dinitrogen activation.

(i) Catalytic activation of dinitrogen was reported to be promoted by *in situ* generated V(II) and Ti(II) systems in protic medium[44-46].

(ii) The high reactivity of V and Ti carbonyls, which have played an important role in the development of modern transition metal chemistry[47], indicated that these species possess very high reducing power. This is, of course, a prerequisite for N_2 fixation.

(iii) Only little information is available for Ti(II) and Ti(III) or V(II) complexes, the most significant part of this chemistry having been developed in the sole direction of cyclopentadienyl system and derivatives[48, 49].

(iv) These metals have been proved to play an important role in both organic synthesis and catalysis. Especially of particular interest, is the ability of Ti(II) complexes to activate small molecules like CO[47f, 50], CO_2[51], N_2[45, 49f, 52] and H_2[38a].

(v) Vanadium is an important component of some metalloenzymes[7, 53] and tunicates and therefore, the development of vanadium chemistry will be beneficial for understanding the mechanisms of action in the living systems.

The high reactivity of low-valent early transition metals and their strong reducing power[54] is the key to understand the ability of these species to react with exceptionally stable molecules, such as dinitrogen. Lately, there has been a considerable growth of interest for the synthesis of V(II) complexes to explore its chemistry and in particular the reactivity of these species with N_2. The d^3 electronic configuration of V(II) was regarded as particularly promising since a dinuclear V(II) system potentially has the ability to transfer the 6 electrons necessary for the cleavage of the N-N triple bond. Conversely, the d^2 or d^1 electronic configuration of Ti(II), V(III) and Ti(III) respectively may be regarded as promising for potential reduction of N_2 to the reactive intermediates such as hydrazido anions. The first example of metal promoted incorporation of dinitrogen into an organic substrate was described by Volpin who found that aromatic organolithium reagents react at room temperature with dinitrogen in the presence of titanium compounds (Cp_2TiCl_2) to yield, after hydrolysis, aromatic amines and NH_3.

Altogether, these features indicated to us that the chemistry of these complexes may be productive and interesting as far as N_2 is concerned. By contrast, the characterization of the coordination chemistry of vanadium and titanium,

especially, in +2 oxidation state, particularly for nonorganometallic complexes, has lagged well behind that of the most of the other first- row elements[55]. Therefore, our project had to start from the synthesis of suitable starting complexes containing the metal in the final desired oxidation state. These species should form the final product *via* simple, mild-condition ligand exchange reactions.

Dinitrogen complexes of Titanium and Vanadium:

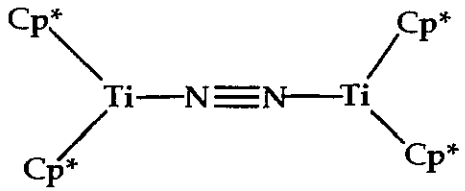
Since the first report of the ability of titanocene to form an isolable dinitrogen complex[56], this area has been extensively studied. The proposed end-on coordination of dinitrogen to titanium has been demonstrated by isolation and crystallographic characterization of several titanium dinitrogen complexes[49]. In case of vanadium, the dinitrogen complexes have attracted considerable attention because of the V-containing nitrogenases[53]. However, the first structurally characterized vanadium dinitrogen complex[57] was reported only in 1989, even though, the N_2 fixing ability of V(II) species was already well established much earlier. Another mononuclear vanadium dinitrogen complex with terminal end-on N_2 ligand was the negative valent $[Na(THF)][V(N_2)_2(dmpe)_2]$[58]. It is well known that the formation and the structures of dinitrogen complexes are very sensitive to the nature of the ligands and typical ancillary ligands successfully used for the stabilization of dinitrogen complexes with other metals were organophosphines[59], alkyls/aryls and cyclopentadienyl groups. However, the chemistry of Ti and V with these ligands is confined to only a few examples, in spite of the fact that more

diversified type of ligands can be used to isolate stable dinitrogen complexes. These include biologically relevant ligands like porphyrins[60], porphyrinogens and pyrazolylborates[61], sulfur containing ligands like thioethers[62], and sterically congested ligands such as amides or amidinates.

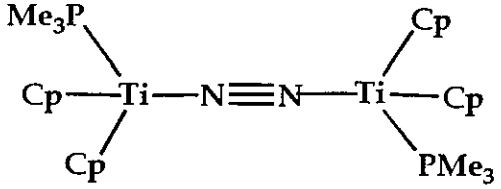
Cyclopentadienyl ligands:

The ability of titanium complexes of cyclopentadienyl and related ligands to give dinitrogen fixation is the result of the enhanced carbenoid behaviour of divalent titanium as well as of the strength of divalent titanium as a powerful reducing agent. In contrast to the catalytic transformation of N_2 promoted by in situ generated V(II) aryloxide, there is no report of dinitrogen complex of V(II) or V(III) using Cp or Cp* as the supporting ligand. Even on titanium, most of the complexes were characterized on the basis of microanalytical data. Since the isolation of the first dinitrogen complex on titanium, a few dinitrogen complexes having titanium in different oxidation states with different bonding modes (**Scheme 1.9**) of dinitrogen have been isolated and reported e.g. $[Cp^*_2Ti]_2N_2$[25a, 49c, 49e], $[Cp_2Ti(PMe_3)]_2(\mu\text{-}N_2)$[25b], $[Cp_2Ti(p\text{-}CH_3\text{-}C_6H_4)]_2(\mu\text{-}N_2)$[49b], $[Ti(Oi\text{-}Pr)_2N_2]_x$. A unique example of dinitrogen activation was reported by Pez[25c] in 1982 who isolated and characterized the Ti cluster $(\mu^3\text{-}N_2)[(\eta^5\text{:}\eta^5\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2Ti_2][\eta^1\text{:}\eta^5C_5H_4)\ (C_5H_5)_3Ti_2]$ during the reaction of $[\mu\text{-}(\eta^1\text{:}\eta^5\text{-}C_5H_4)](\eta\text{-}C_5H_5)_3Ti_2$ with dinitrogen.

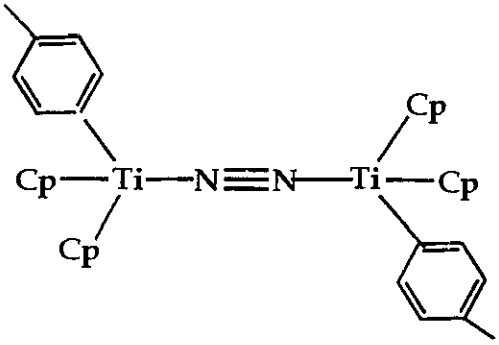
Ref



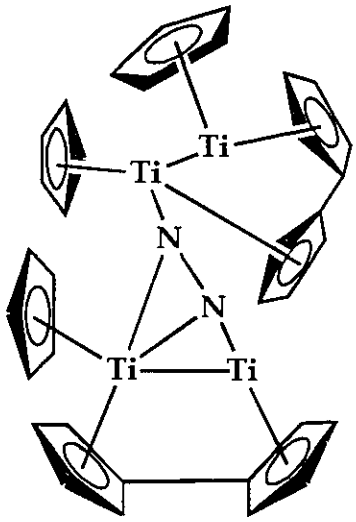
25a, 49c, 49e



25b



49b

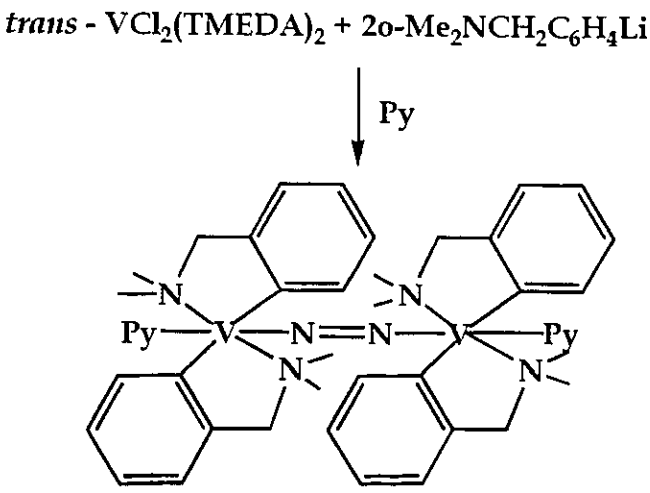


25c

Scheme 1.9

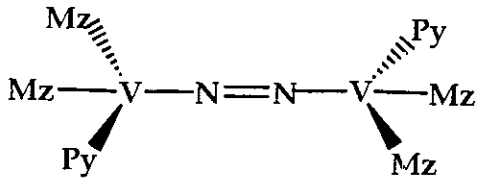
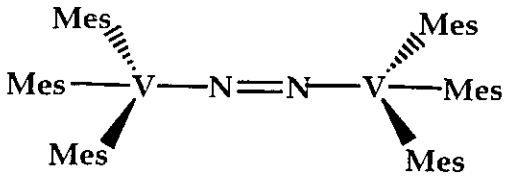
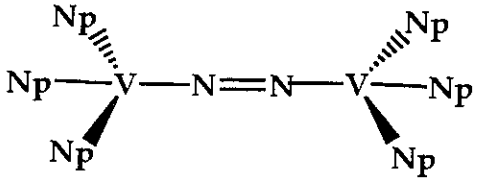
Alkyls / Aryls :

Transition metal alkyl/aryl complexes constitute a very important class of



Scheme 1.10

compounds because of the pivotal role played by these species in both synthesis and catalysis[63]. Dinitrogen complexes using alkyl / aryl ligands are unknown for titanium in +2 oxidation state. However, in the case of vanadium in +2 and +3 oxidation states, the carbon - donor based ligands have promoted the coordination of dinitrogen. As mentioned above, the very first dinitrogen complex[57] on vanadium $[(Me_2NCH_2Ph)_2VPy]_2(\mu - N_2)$ was isolated and characterized in 1989 **(Scheme 1.10)** and was obtained by reacting *trans* - $VCl_2(TMEDA)_2$ with $Li(o\text{-}CH_2NMe_2)Ph$ in the presence of pyridine. The formation of this complex proved the high reactivity of divalent vanadium towards dinitrogen. Following this, other organometallic dinitrogen complexes of V(II)[64] and V(III)[65] were obtained **(Scheme 1.11)**. The coordination of dinitrogen to V(III) is quite interesting due to the occurrence of this oxidation state in some metalloenzymes and tunicates[66]. In addition, the studies on V-nitrogenases predict the involvement of medium-valent vanadium as the active

Complexes	Ref
	57
	64
	65

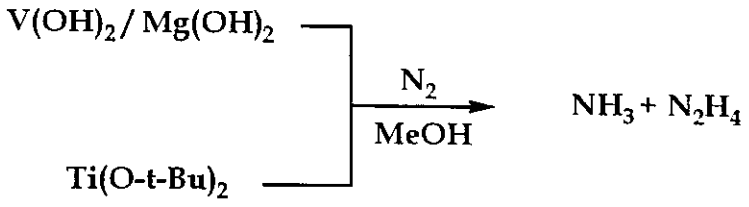
Scheme 1.11

species responsible for the activation of dinitrogen in biological systems. Although di- and tri-valent vanadium organometallic complexes have been proved to be able to interact with dinitrogen, yet the reversibility of dinitrogen coordination, the high reactivity and thermal unstability render these complexes unsuitable for further activation studies.

Alkoxides / Aryloxides :

Interest in the chemistry of low- and medium-valent transition metal alkoxides

has been steadily increasing in recent years[67].



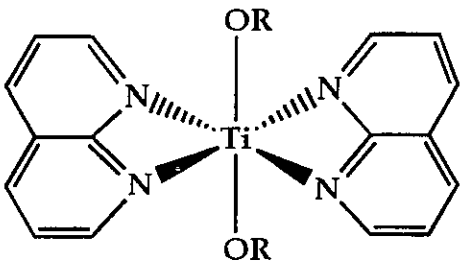
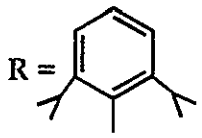
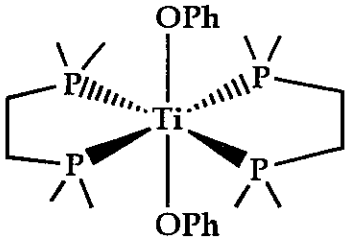
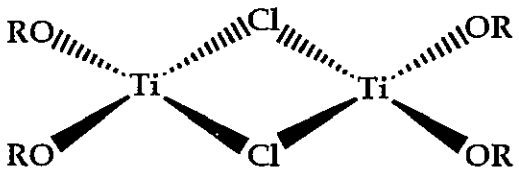
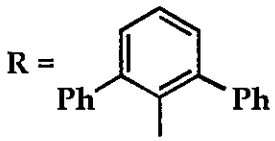
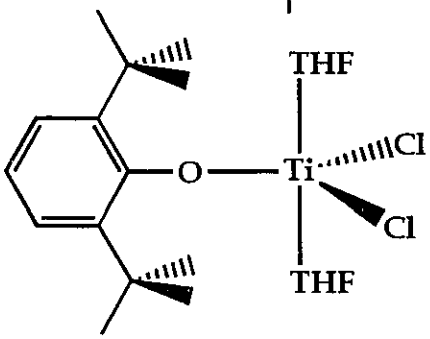
In situ generated divalent vanadium and titanium complexes with oxygen-containing ligands (catecholate, hydroxide)[44-46] while in protic media are known to catalytically convert dinitrogen into ammonia and hydrazine. In an attempt to model these transformations, another complex of V(II), using bulky 3,5-di-tert-butylcatechol as a ligand, was used to reduce dinitrogen. The reaction also evolved H_2 from the solvent (methanol) and formed a V(II)/V(III) mixed valence complex[44c]. The presence of MeOH was necessary to provide hydrogen ions even though, in the end, it paralyzes the catalytic cycle by oxidizing V(II) to V(III).

In agreement with the findings of Van Tamelen, Schrauzer and Shilov[44-46], the

$$2V(II) + 2CH_3OH \longrightarrow 2V(III) + H_2 + 2CH_3O^-$$

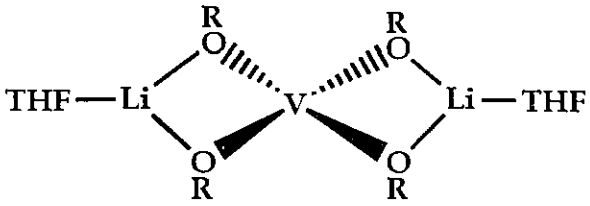
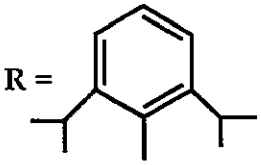
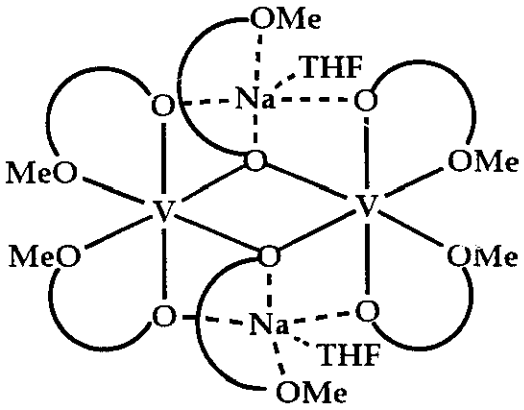
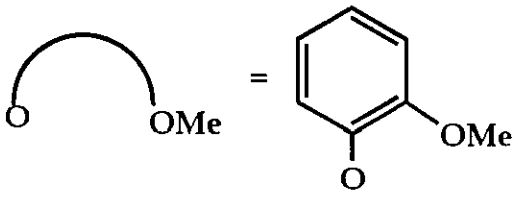
$$6V(II) + N_2 + 6CH_3OH \longrightarrow 6V(III) + 2NH_3 + 6CH_3O^-$$

ligands with oxygen based donor atom seem to be the most promising for the vanadium and titanium promoted activation of dinitrogen. Other interesting characteristics of these ligands are: (i) the electronic configuration of the oxygen

Ti Aryloxides	Ref
 	68
	69
 	70
	71

Scheme 1.12

donor atom which allows different molecular complexities by adopting

V Aryloxides	Ref
	72a
	
	72b
	

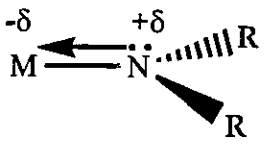
Scheme 1.13

different bonding modes, (ii) the unlimited choice of organic substituents which allows to adjust the steric hindrance, (iii) the possibility of introducing optical activity by using optically active alkoxides / aryloxides. It should be mentioned that, in contrast to these promising features, the only two Ti(II) aryloxides obtained by using *dipy*[68]and *dmpe*[69] as supporting ligands, and one dimeric Ti(III) aryloxide

halide[70] showed no interaction with dinitrogen (**Scheme 1.12**). Similar was the case with vanadium, where the only two anionic V(II) aryloxides[72] reported in the literature, were found unreactive with N_2 (**Scheme 1.13**).

Amides :

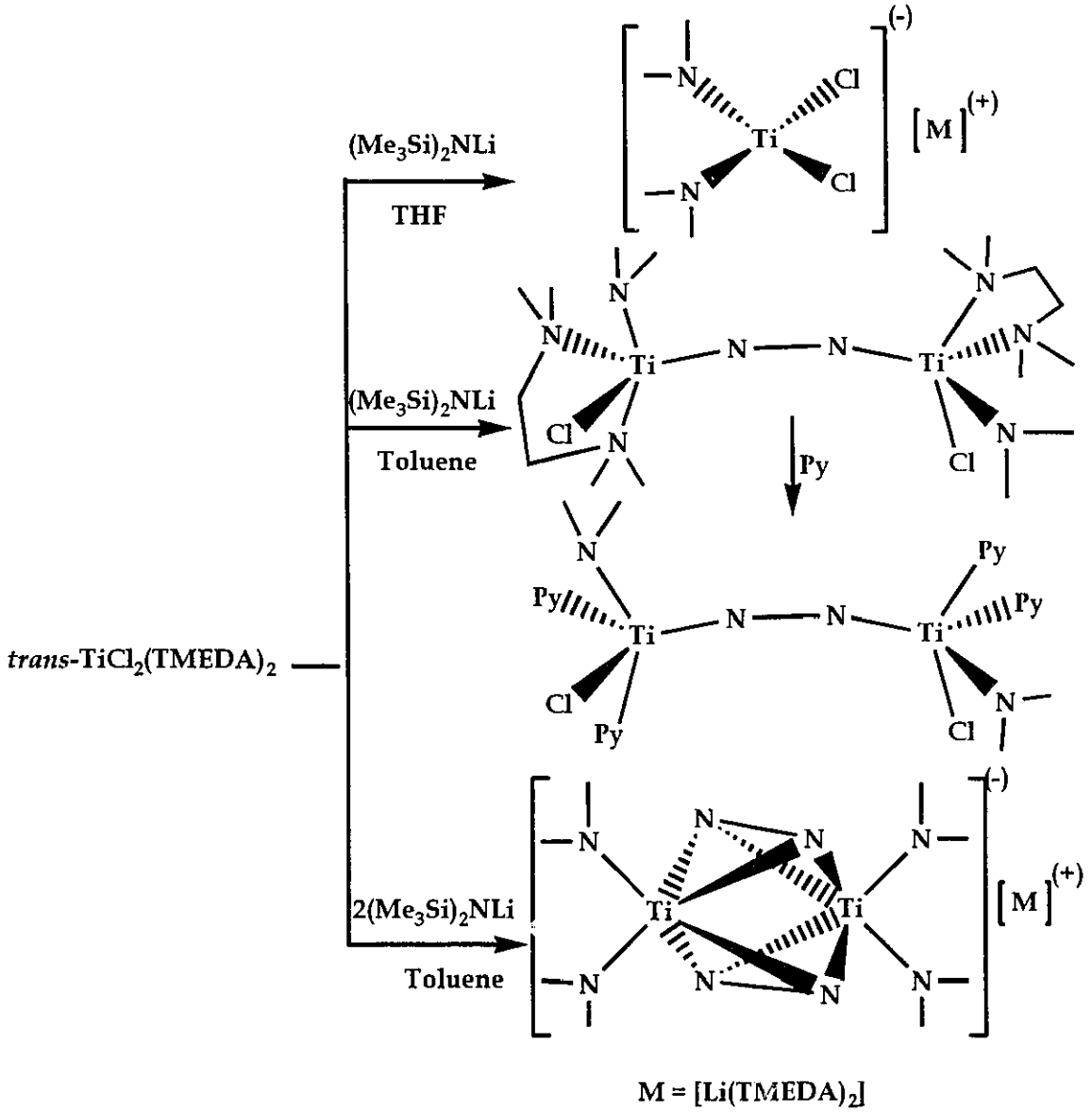
The employment of ligands with nitrogen based donor atoms for the preparation of low- and medium- valent titanium and vanadium complexes was advised by some unique characteristics of these ligands. (i) The electronic flexibility of nitrogen atom allows the overlap of nitrogen lone pair with an appropriate empty *d* orbital of the metal atom, thus giving partial π-bond character to the M-N bond[73]. (ii) The ability to act as a bridging ligand between two or more metal centers may promote formation of polynuclear species. The electron deficiency of the early transition metal atoms and the consequent tendency to achieve a partial saturation



by sharing the amido ligands may be regarded as the driving force behind this bonding mode. (iii) The steric bulk may be varied by selecting the appropriate organic substituents on the nitrogen atom. (iv) The strong reducing power stabilizes a wide range of oxidation states.

Transmetallation reactions carried out with Li amides and metal halides are one

of the most convenient routes for the preparation of transition metal amides, even though other synthetic strategies are available. In the case of titanium, the reaction of *trans*- $TiCl_2(TMEDA)_2$ with $(Me_3Si)_2NLi$[74] was dependent upon the nature of the

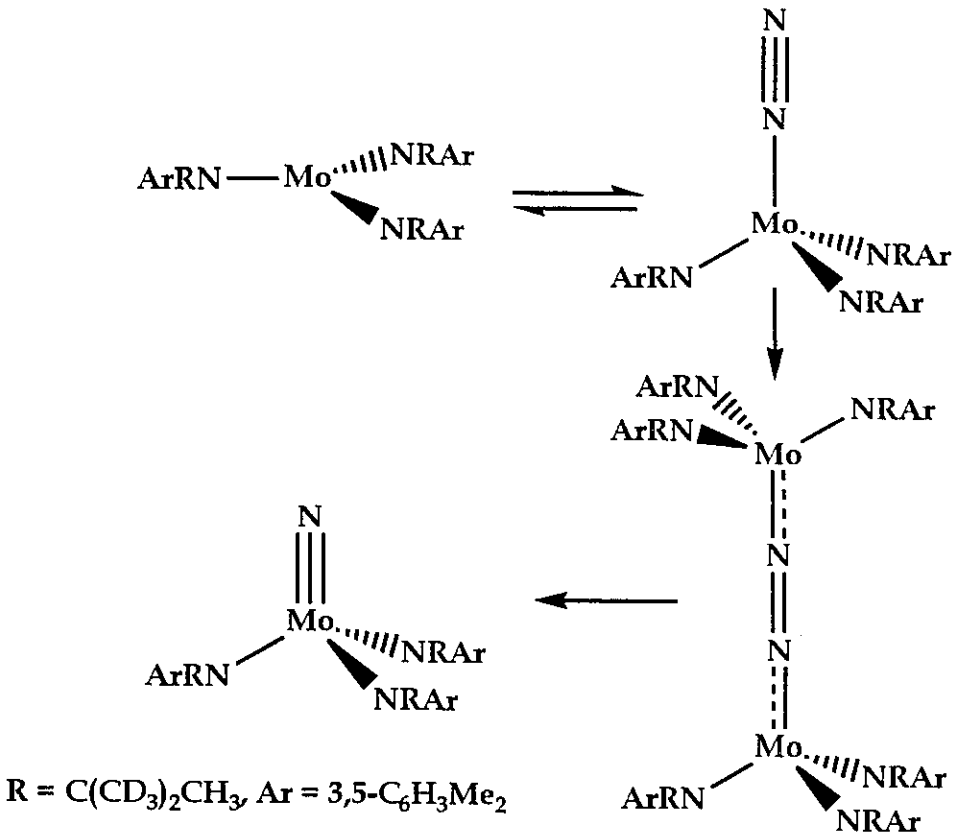


Scheme 1.14

solvent and stoichiometry of the reaction. Two novel dinitrogen Ti(II) and mixed

valence Ti(I) / Ti(II) amido complexes were obtained *via* chlorine replacement at *trans*- $TiCl_2(TMEDA)_2$. The reaction in toluene, in 1:1 molar ratio formed an end-on bonded quite robust dinitrogen complex (**Scheme 1.14**) $\{[(Me_3Si)_2N]TiCl(TMEDA)\}_2(\mu\text{-}N_2)$, which, once formed, did not lose N_2 on treatment with polar solvents like Py. However, when the reaction was carried out in THF, the reaction led instead to disproportionation, forming the anionic Ti(III) amide $[(Me_3Si)_2N]_2TiCl_2[(TMEDA)_2Li]$. When a 1:2 molar ratio was used in combination with hydrocarbon solvents, an unprecedented complex $[\{[(Me_3Si)_2N]_2Ti\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)_2][(TMEDA)_2Li]$ with two side-on bonded dinitrogen molecules was obtained. This complex was also thermally stable, thus underlining the irreversible nature of dinitrogen coordination. The completely different bonding mode (end-on versus side-on) is intriguing and was attributed to the different steric bulk of two complexes.

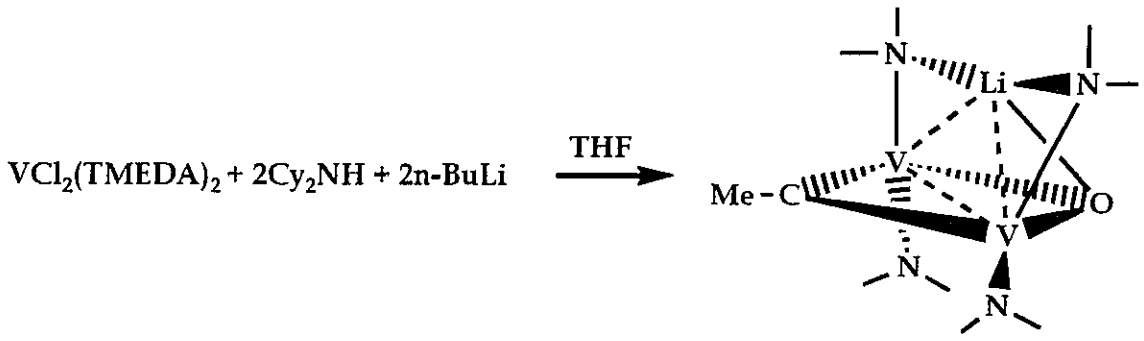
As discussed earlier, the reduction of N_2 to form two nitride moieties requires six electrons. Therefore, the dinitrogen complex of a dinuclear d^3 V(II) moiety should be the ideal system, since each of the two d^3 V(II) atoms can easily undergo a 3 electron reduction to d^0 V(V) centers. This was recently observed in the case of a d^3 Mo(III)complex, which upon reaction with N_2, gave preliminary formation of an end-on dinitrogen complex which further evolved into a terminal Mo-N species[75]. The formation of a dinuclear end-on dinitrogen complex by reaction of $Mo(NRAr)_3$ complex with N_2 was followed by N-N cleavage and subsequent formation of a



Scheme 1.15

nitrido complex $NMo(NRAr)_3$ [R = $-C(CD_3)_2CH_3$, Ar = $3,5-C_6H_3Me_2$](**Scheme 1.15**).

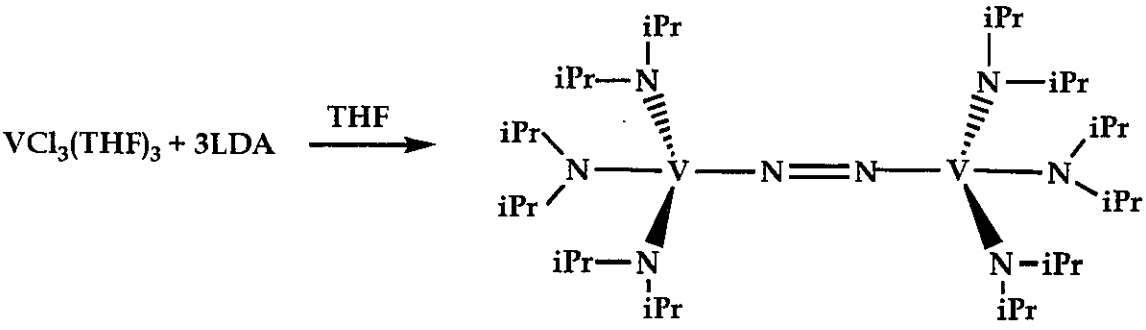
This observation encouraged further attempts to synthesize low- or medium-valent amides of vanadium , which, however, displayed a remarkably different behavior. For example, the reaction of *trans*-$VCl_2(TMEDA)_2$ with Cy_2NLi, prepared *in situ* from Cy_2NH and n-BuLi in THF, formed an unprecedented complex $[(Cy_2N)_2V]_2Li(\mu^3\text{-}O)(\mu^2,\eta^1\text{:}\eta^1\text{-}CMe)$[76] (**Scheme 1.16**). The μ^3-O and $\mu^2,\eta^1\text{:}\eta^1$-CMe moieties are probably obtained *via* fragmentation of the THF solvent. Similar reaction with Ph_2NNa afforded a triangular ionic cluster



Scheme 1.16

$[V_3Cl_5(TMEDA)_3][(Ph_2N)_4V]$ through a complicated disproportionation reaction.

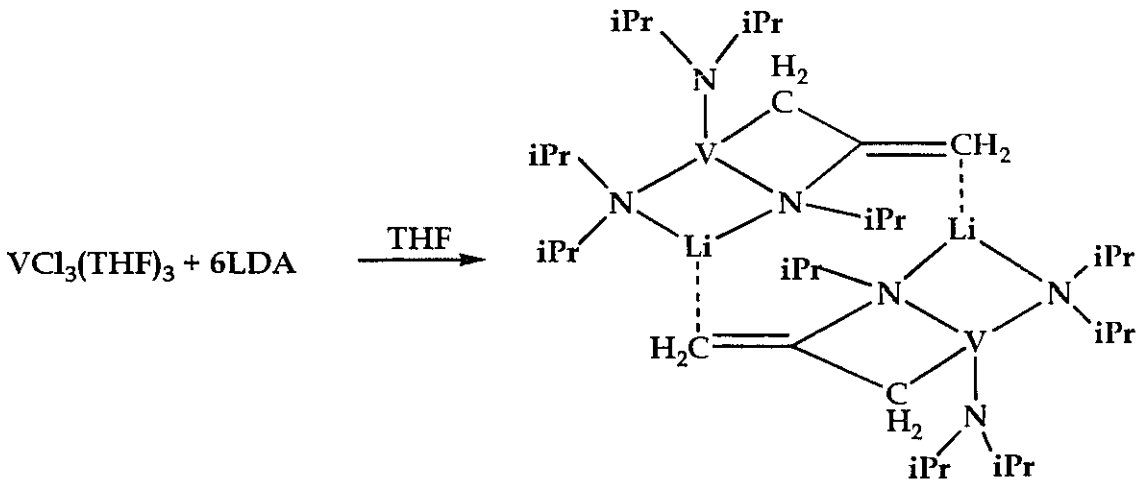
Rather unexpected results were obtained from the reaction of V(III) dinitrogen complexes with amides as supporting ligands. Similar to the case of closely related d^2 titanium systems it was possible to isolate very robust dinitrogen complexes. As expected, the reaction of $VCl_3(THF)_3$ with $(i\text{-}Pr)_2NLi$ provided end-on bonded dinitrogen complex $\{[(i\text{-}Pr)_2N]_3V\}_2(N_2)$[77] whose cyclic voltammograms did not show any reduction or oxidation in a wide range of potentials (**Scheme 1.17**). In addition these complexes were unreactive towards several reagents (PR_3, Py, CO, RNC, RCN, azide, diazo). This result contrasts with the nature of the dinitrogen *organometallic*



Scheme 1.17

complexes of vanadium in the +2 and +3 oxidation states where dinitrogen is always liberated upon treatment with Lewis base. This result suggests that the d^2 electronic configuration, in combination with N-donor based ligands, can provide exceptionally stable dinitrogen complexes.

The reaction of $VCl_3(THF)_3$ with LDA gave a surprisingly different result when 1:6 molar ratio was used. Rather than forming the dinitrogen complex, a dimeric $\{[(i\text{-}Pr)_2N]_2V[\mu\text{-}CH_2C(=CH_2)N(i\text{-}Pr)]Li\}_2$[77] was formed. The metallacycle was

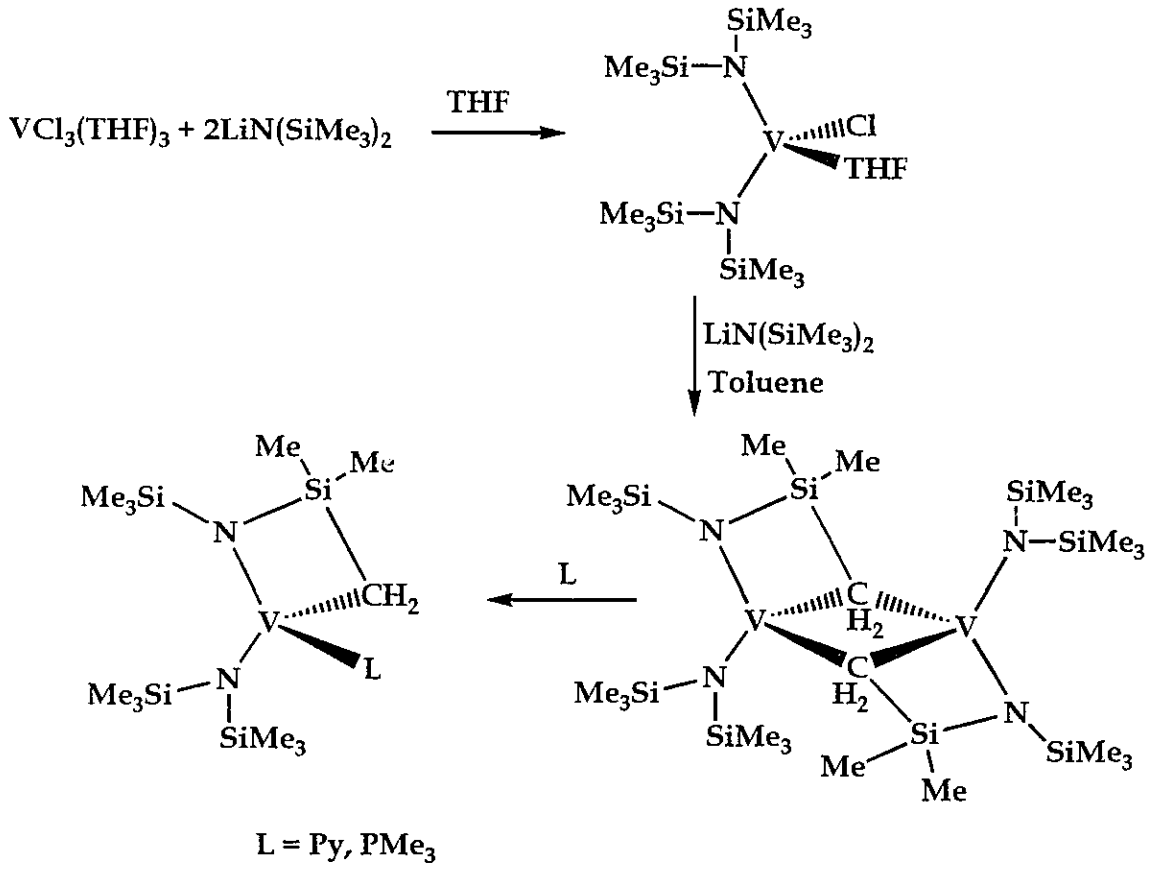


Scheme 1.18

formed by one amido group which chelates the vanadium atom by using both the nitrogen and one deprotonated methyl group, thus forming a four-membered vanadacyclobutane ring (**Scheme 1.18**). The second carbon atom and the methylene carbon of same isopropyl group engaged in the formation of metallacycle have also been dehydrogenated to form an exocyclic $C=CH_2$ double bond. These observations

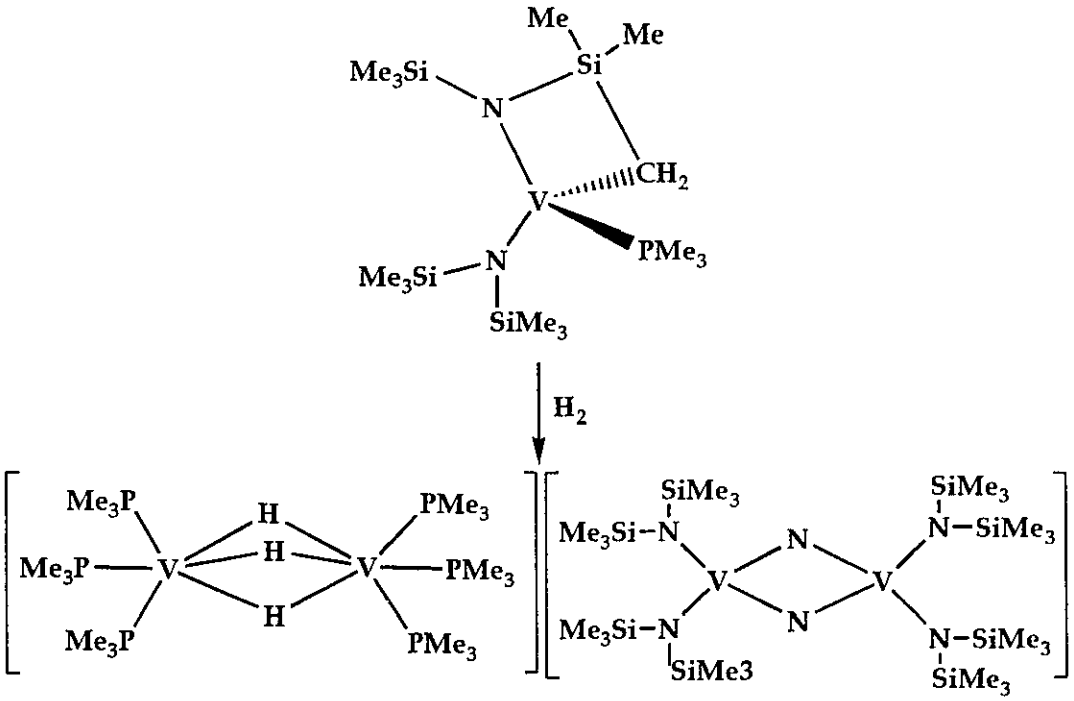
showed that organic amides are able to transfer H_2 from the alkylamide to a substrate and to form in the process metallacyclobutane rings and olefinic functions. Even though the fate of the hydrogen atoms is unclear, the possibility that H_2 might be transferred directly from the ligand side chain to several substrates opens interesting perspectives in terms of dinitrogen reduction.

The reaction of $VCl_3(THF)_3$ with the bulkier dialkylamide, $(Me_3Si)_2NLi$ did not form any dinitrogen complex or even the previously reported $V[N(Me_3Si)_2]_3$[78]. Instead it formed $[(Me_3Si)_2NV(\mu\text{-}CH_2SiMe_2N(SiMe_3)]_2$[79] *via* C-H σ-bond metathesis



Scheme 1.19

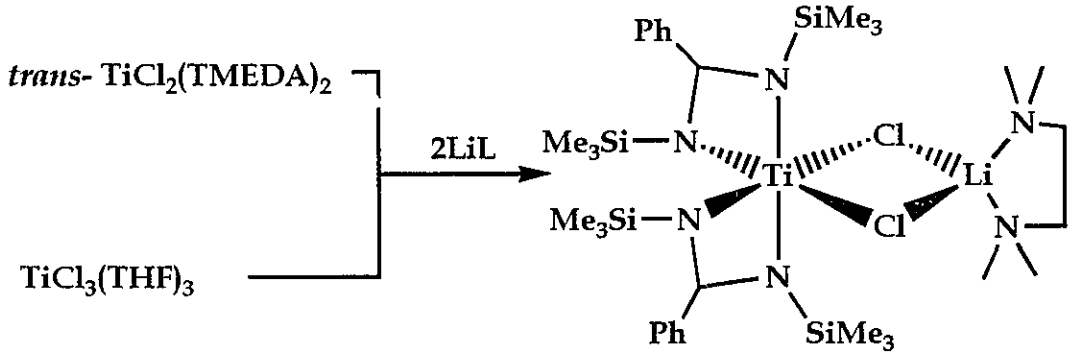
reaction. The formation of the metallacycle *via* deprotonation of a silyl group is probably promoted by the third equivalent of $LiN(SiMe_3)_2$ which acted as a base rather than a nucleophile (**Scheme 1.19**). This dimer can be cleaved by Py or PMe_3 forming very reactive $[(Me_3Si)_2N]V[CH_2SiMe_2N(SiMe_3)]L$[80] (L = Py or PMe_3) where the vanadaazacyclobutane ring was preserved. In the case of the phosphine derivative, the complex was hydrogenated under pressure and at room temperature forming an unusual mixed valence ionic complex[81] $\{[(PMe_3)_3V]_2(\mu\text{-}H)_3\}^+/\{([(Me_3Si)_2N]_2V)_2(\mu\text{-}N_2)\}^-$ (**Scheme 1.20**). The presence of hydrides was supported by the formation of three equivalents of H_2 during a degradation experiment with seven equivalents of HCl. The two nitrides are identified by the formation of NH_3 during hydrolysis. The hydride moiety is formed by the



Scheme 1.20

hydrogenolysis of the V-CH_2 bond followed by homolytic cleavage of the V-N bond since large amounts of $(Me_3Si)_2NH$ were identified in the GC-MS of the reaction mixture. Since this complex could only be formed when the reaction was carried out under N_2, this indirectly proves that the dinitrogen is the source of nitrides. Also the absence of methane and silanes in the reaction mixture confirms that the bridging nitrides do not arise from the hydrogenolysis of the N-Si bond.

Amidinate ligands, which are closely related to the amides have been also used to stabilize low-valent vanadium. Promising features of these ligands are the unique ability of these chelating ligands to stabilize the low oxidation states of early transition metals[82] and lanthanides[83]. Furthermore, the chelating nature of the



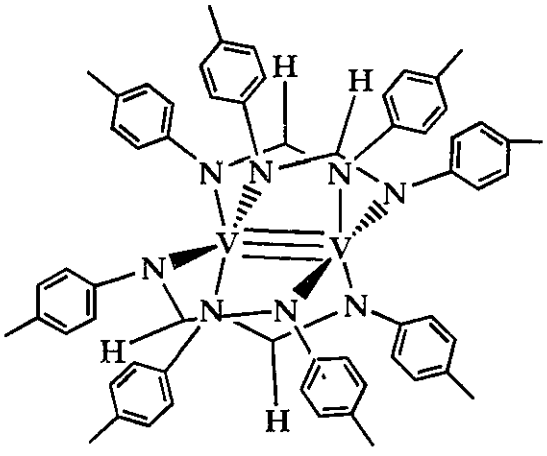
LiL = $PhC[(Me_3Si)N]_2Li(TMEDA)$

Scheme 1.21

ligand might engage the transition metal into partial dissociation equilibria which, by making available additional coordination sites, may be important for catalytic performances of coordinated dinitrogen. However, different from the case of the

amides, attempts to synthesize Ti(II) and Ti(III) amidinate complexes gave only disproportionation (**Scheme 1.21**) and formation of Ti(III) complexes with no sign of dinitrogen fixation[82c].

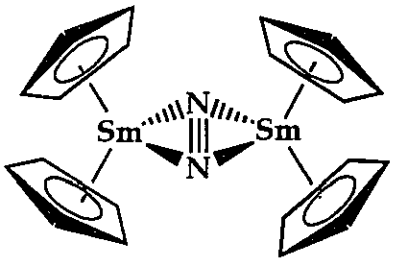
Even in the case of vanadium, the results were not encouraging. No dinitrogen fixation was observed in the two cases of vanadium amidinate reported in the literature. The reaction of V(II) with [(tolyl)NC(H)N(tolyl)]Li gave instead the dinuclear $[\{(tolyl)NC(H)N(tolyl)\}_2V]_2$[84] with the shortest ever reported V-V distance (1.968Å). The molecule consists of a V2 unit bridged by four formamidinate groups placed *trans* with respect to each other, with each pair of *trans*-positioned ligands defining two perpendicular planes. Utilization of VCl_2Py_4 starting material yielded the monomeric and octahedral $(amidinate)_2V(Py)_2$[85].



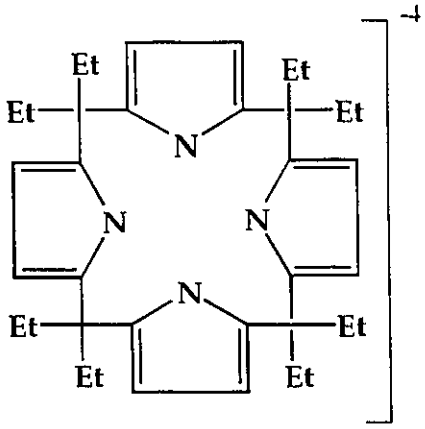
Dinitrogen complexes of Samarium

The first and the only dinitrogen complex reported on a f-element metal is on

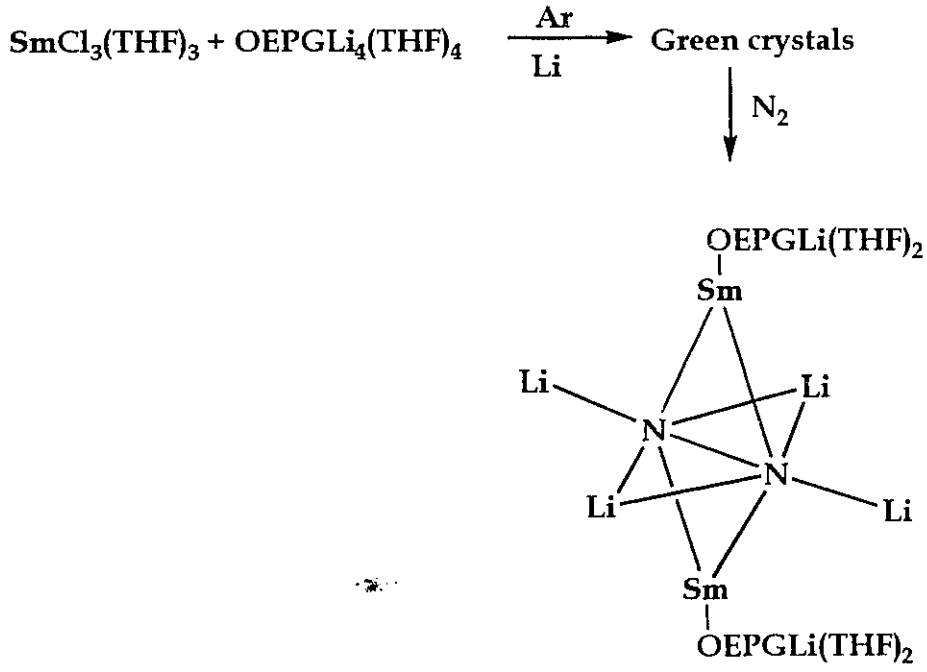
samarium. Samarocene dinitrogen complex $[Cp^*_2Sm]_2(\mu\text{-}N_2)$[28] described by Evans in 1988, was also the first complex with planar, side-on bonded dinitrogen ligand between the two metal atoms. As mentioned earlier, the N-N bond distance in this complex [1.088Å] is strikingly short, and in contrast to the side-on bonding mode, is even shorter than in gaseous N_2. This suggests minimal N_2 reduction. The coordinated dinitrogen in this complex is labile and is easily eliminated with formation of samarocene. This is achieved *via* simple treatment of the complex with toluene. Recent results have shown that anionic chelating amide, such as the porphyrinogen tetraanions $OEPGLi_4$ (OEPG = octaethylporphyrinogen)[86] provides a



versatile tool to stabilize the lower oxidation states of early transition metals or lanthanides and to provide a rather unusual chemical reactivity. In particular, in the case of samarium, the reaction of $OEPGLi_4$ with $SmCl_3(THF)_3$ gave a yellow crystalline complex, which, upon reduction, yielded a dinuclear side-on bonded dinitrogen complex $[(THF)_2Li(OEPG)Sm]_2(N_2Li_4)$[87]. This dimeric complex has two $(THF)_2Li(OEPG)Sm$ units bridged by a planar N_2Li_4 moiety (**Scheme 1.22**). The molecule of N_2 is encapsulated in the Sm_2Li_4 octahedron and is coaxial with one Li-

OEPG = 

Li diagonal. The N_2Li_4 core is formed by one N_2 unit with two side-on lithium atoms and the two other coplanar and coaxial with the N-N vector. The Sm atoms



Scheme 1.22

are symmetrically placed side-on with respect to the N_2 moiety above and below the N_2Li_4 plane. The very long N-N distance in this species [1.525Å], indicated a

significant extent of reduction of dinitrogen, which of course, given the side-on bonding mode, is in striking contrast to the cyclopentadienyl dinitrogen complex reported by Evans. The stoichiometry of this compound indicates that N_2 has undergone a 4 electron reduction. Given that Sm(II) can transfer only one electron, the structure of the complex indicated that the reaction has probably followed a multistep pathway likely proceeding through the formation of a polynuclear intermediate. A possible reason for this striking difference between these two sole Sm(II) N_2 complexes might reside in the presence of the alkali cation which could assist an efficient electron transfer from samarium to the dinitrogen molecule. These observations have prompted the efforts to prepare Sm(II) complex of the same ligand in the absence of alkali cation.

The reaction of *in situ* generated $[\{(Me_3Si)_2N\}_2Sm(TMEDA)]$ with OEPG formed a Sm(II) complex $[(OEPGSm_2)(Et_2O)_2]$[88] *via* transamination reaction. The complex has a $Sm_2(Et_2O)_2$ unit which is almost linear and which is surrounded by the macrocyclic ligand. The complex does not contain dinitrogen thus indicating that indeed Li cations play a crucial role in this system, in assisting and promoting the coordination of dinitrogen.

$$[\{(Me_3Si)_2N\}_2Sm(TMEDA)] \xrightarrow[-(Me_3Si)_2NH]{0.5\ OEPGH_4} [OEPG(Sm\text{-}OEt_2)_2]$$

These observations suggested to us that Sm(II) is an ideal substrate with which

to study the factors which promote dinitrogen activation.With this respect, nitrogen-based donor atoms are particularly promising due to their ability to stabilize low-valent transition metals, to promote polynuclear aggregation, and to enhance the chemical reactivity.

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CHAPTER II

Monomeric, Dimeric and Linear Trimeric Titanium (III) Aryloxides Without a Ti-Ti Bond. The Effect of Bulky Substituents in the Ligand on the Molecular Structure.

II. 1 : Introduction

The interest in the chemistry of low-valent titanium alkoxides has been stimulated by their ability to facilitate catalytic dinitrogen activation/fixation[1], as well as the enormous reducing capability of these species with a variety of organic substrates[2]. The versatility of alkoxides as supporting ligands can be attributed to: i) the unlimited choice of organic substituents, which allows fine tuning of the steric hindrance around the transition metal, ii) the electronic flexibility of the oxygen donor atom which permits the molecule to adopt different geometries *via* several bonding modes, and iii) the possibility of introducing optical activity. Some other notable reactions which have been performed with *in situ* generated low-valent titanium aryloxides include i) reductive couplings,[3] ii) oxidative additions,[4] iii) formation of imide,[5] and iv) ethylene coordination[6].

In spite of these very attractive features, the chemistry of low-valent titanium alkoxides has not been thoroughly investigated[7]. Only two examples of monomeric Ti(II) aryloxides with strongly stabilizing ligands (*dmpe*[8] or *dipy*[9]), one dimeric

Ti(III) alkoxo-halide containing a short Ti-Ti nonbonding distance[10] and one monomeric aryloxide dihalide comp[illegible][11] have been reported to date. The other two tricoordinated homoleptic derivatives which have been reported, have not been structurally characterized[12]. The possibility of using alkoxides as supporting ligands to stabilize important functionalities such as hydrides and alkyls, remains unexplored.

The reason for such a paucity in the literature about titanium alkoxides probably lies in the lack of readily accessible starting materials which contain the metal in a low oxidation state. The recent preparation of *trans*-$TiCl_2(TMEDA)_2$[14] is expected to provide an easy entry into the chemistry of low-valent and mixed-valence titanium derivatives since ligand replacement reactions which occur under mild reaction conditions can be utilized.

Our interest in the identification of the role of the aryloxide ligands was stimulated by their ability to : (i) act as bridges between two or more metal centers, (ii) determine the magnetic properties of the metals[13] in different oxidation states (iii) determine the nuclearity of the complex, (iv) influence the intermetallic distance, and (v) catalytically transfer N_2 into NH_3 or hydrazine. In order to investigate these roles further, we attempted to synthesize and characterize some trivalent titanium aryloxides obtained from the ligand replacement reactions of Ti(II) and Ti(III) halides.

II. 2 : Experimental Section

All operations were performed under inert (N_2 or Ar) atmosphere using standard Schlenk techniques, or in a nitrogen-filled drybox (Vacuum Atmosphere). *Trans*-$TiCl_2(TMEDA)_2$ and $TiCl_3(THF)_3$ were prepared according to published procedures[14]. TMEDA was refluxed over molten potassium and distilled under N_2; pyridine was refluxed over CaH_2 and distilled under nitrogen. Phenols (Aldrich) were purified by sublimation. NaH suspension in mineral oil was washed with hexane, dried and stored under nitrogen in sealed ampoules. Infrared spectra were recorded on a Perkin-Elmer 393 instrument from Nujol mulls prepared in a dry-box. Elemental analyses were carried out at the Microanalytical Department of the Chemistry Department at the Rijksuniversiteit Groningen and at the Galbraith Laboratories. Samples for magnetic susceptibility measurements were weighed out inside a dry-box equipped with an analytical balance and sealed in pre-calibrated tubes. Measurements were carried out at room temperature using a Gouy balance (Johnson Matthey). Magnetic moments were calculated following standard methods[15], and data were corrected for underlying diamagnetism[16].

Preparation of $Ti_3(PhO)_9(TMEDA)_2$ (2.1):

Method A : The addition of NaH (0.45 g, 18.8 mmol) to a phenol solution (1.7 g, 18.1 mmol) in THF (75 ml) was stirred and refluxed for about 30 minutes. The solution was filtered to remove excess NaH and the filtrate was cooled to -90°C. *Trans*-$TiCl_2(TMEDA)_2$ (3.1 g, 10.5 mmol) was added, and the color of the reaction

mixture slowly changed to red. The mixture was stirred continuously while warming to room temperature over a period of about 3 hours. The resulting solution was evaporated to dryness *in vacuo* and the residual red solid was suspended in toluene (75 ml). This suspension was filtered to remove NaCl and the filtrate was then concentrated to a small volume (20 ml). Light green crystals of **2.1** (1.7 g, 1.4 mmol, 40 %) separated out from the resulting solution upon cooling overnight at -30°C.

Method B : A solution of phenol (1.5 g, 15 mmol) in THF (75 ml) was stirred and refluxed with NaH (0.41 g, 17.1 mmol). The solution was filtered at room temperature, the resulting clear solution was cooled and added to a solution of $TiCl_3(THF)_3$ (1.85 g, 5 mmol) in THF (50 ml) containing a small amount of TMEDA (2 ml). The color changed instantly from blue to orange red. The mixture was stirred for about two hours and then evaporated to dryness. The residual solid was suspended in toluene and NaCl was filtered out. The filtrate was concentrated to small volume and light green crystals of **2.1** (0.7 g, 0.5 mmol, 30 %) separated out at -30°C.

Elemental Analysis for $C_{66}H_{77}O_9N_4Ti_3$: Calcd (obsvd): C 65.30 (65.27); **H** 6.39 (6.28); **N** 4.62 (4.17); **Ti** 11.83 (11.07).

Magnetic Moment: $\mu_{eff.} = 1.69\ \mu_B$.

Infrared Spectrum (Nujol mull, cm^{-1}): 1585(sh), 1485(sh), 1475(sh), 1380(sh), 1350(m), 1295(br), 1280(w), 1230(w), 1170(m), 1160(m), 1145(s), 1120(s), 1070(br), 1020(sh), 960(m), 910(sh), 875(m), 845(br), 800(m), 755(sh), 740(sh), 690(sh), 680(sh), 650(sh), 630(sh), 615(m), 590(sh), 555(s), 530(s), 515(s), 490(m).

Preparation of $Ti(OPh)_3(Py)(TMEDA)$ (2.1a):

Method A : A solution of phenol (4.4 g, 46.8 mmol) in THF (70 ml) was stirred and refluxed with NaH (1.25 g, 52 mmol) for 30 min. Excess NaH was filtered off and the resulting clear solution was added to a solution of $TiCl_3(THF)_3$ (5.78 g, 15.5 mmol) containing a small amount of TMEDA (2 ml). The light green color of the reaction mixture changed to deep red on addition of pyridine (1.2 ml). The solution was evaporated to dryness *in vacuo* and the residual solid was dissolved in toluene (50 ml). Dark red crystals of **2.1a** (3.5 g, 6.2 mmol, 40%) separated out at -30°C.

Method B: A light green solution of $Ti_3(PhO)_9(TMEDA)_2$ **(2.1)** (2.0 g,1.6 mmol) in THF (60 ml) was boiled with small amount of pyridine. The color changed to deep red. The solution was concentrated *in vacuo* and dark red crystals of **2.1a** (1.2 g, 2.1 mmol, 44%) were obtained from toluene at low temperature.

Elemental Analysis for $C_{29}H_{36}N_3O_3Ti$: Calcd (Obsvd): C 66.67 (66.27); H 6.94 (6.75); N 8.04 (7.94); Ti 9.16 (8.99).

Magnetic Moment: $\mu_{eff} = 1.72\ \mu_B$

Infrared Spectrum (Nujol mull, cm^{-1}): 1590(sh), 1490(br), 1450(sh), 1380(sh), 1355(s), 1315(s), 1285(m), 1215(m), 1170(sh), 1155(s), 1120(s), 1070(sh), 1045(sh), 1025(sh), 1010(s), 1000(sh), 955(sh), 930(s), 905(s), 875(sh), 800(sh), 755(sh), 690(sh), 650(m), 630(sh), 610(sh), 520(m), 500(m), 475(s), 450(sh).

Preparation of $[Ti(OR)Cl(TMEDA)]_2(\mu\text{-}OR)_2$ [R =3,5-(t-Bu)$_2$C$_6$H$_3$] (2.2):

A THF (60 ml) solution of 3,5-(t-Bu)$_2$PhOH (4.5 g, 21.8 mmol) was stirred and refluxed with NaH (0.6 g, 25.0 mmol) until no further consumption of NaH was observed. This mixture was filtered to remove any excess NaH and then cooled to -90°C. The addition of *trans*-$TiCl_2(TMEDA)_2$ (3.7 g, 12.5 mmol) caused the color to change very slowly to deep orange. The mixture was stirred and allowed to warm slowly to ambient temperature (3 hours). The resulting deep orange-brown solution was evaporated to dryness *in vacuo* and the residual red solid suspended in toluene (75 mL). The suspension was filtered to remove NaCl and the filtrate was concentrated to a small volume (20 mL). Light-pink crystals of **2.2** (2.9 g, 2.5 mmol, 40%) separated upon slow concentration of the solution.

Method B : A toluene solution (70 ml) of 3,5-(t-Bu)$_2$PhOH (2.75 g, 13.3 mmol) was stirred and refluxed with NaH (0.60 g, 25 mmol) overnight. Excess NaH was filtered out and the clear solution was cooled to room temperature. This solution

was transferred by cannula into a solution of $TiCl_3(THF)_3$ (2.47 g, 6.6 mmol) in toluene (50 ml) containing TMEDA (2.0 ml) at -20°C . The mixture was stirred and warmed slowly to room temperature. The color became deep orange-brown and NaCl precipitated out of solution. After removing NaCl by filtration, the resulting solution was concentrated to about 30 ml and light pink crystals of **2.2** (1.1 g, 0.9 mmol, 27 %) separated overnight at -30°C .

Elemental Analysis for $C_{68}H_{116}O_4N_4Cl_2Ti_2$: Calcd (Obsvd): C 66.93 (66.37); H 9.58 (9.38); N 4.59 (4.51); **Ti** 8.16 (8.01).

Magnetic Moment: $\mu_{eff} = 0.75\ \mu_B$

Infrared Spectrum (Nujol mull, cm^{-1}): 1580(m), 1465(m), 1375(sh), 1315(sh), 1230(sh), 1200(s), 1150(br), 1110(m), 1020(sh), 1000(sh), 980(sh), 950(s), 930(s), 900(s), 870(m), 850(m), 815(m), 790(sh), 760(s), 720(sh), 700(sh), 685(s), 660(sh).

Preparation of $[Ti(OR)_2(TMEDA)Cl_2][Na(TMEDA)_2(THF)]$ [R =3,5-$(t\text{-}Bu)_2C_6H_3$] (2.3a):

The addition of NaH (0.5 g, 20 mmol) to a THF solution (75 mL) of freshly sublimed 3,5-$(t\text{-}Bu)_2C_6H_3OH$ (3.2 g, 15 mmol) was refluxed and stirred for about 30 min. The excess NaH was removed by filtration and the resulting clear solution was mixed with a solution of $TiCl_3(THF)_3$ (2.8 g, 7.7 mmol) in THF (50 mL) containing TMEDA (4 mL). The resultant orange solution was evaporated to dryness and the

residual solid resuspended in toluene (50 mL). The mixture was filtered to remove NaCl, concentrated to a small volume (30 mL) and layered with hexane (30 mL). Orange-red crystals of **2.3a** (2.6 g, 2.8 mmol, 37%) separated out upon standing overnight at -30°C.

Elemental Analysis for $C_{50}H_{98}O_3N_6Cl_2TiNa$: Calcd (Obsvd): C 61.71 (61.37); H 10.15 (10.08); N 8.64 (8.51); Ti 4.92 (4.51).

Magnetic Moment: $\mu_{eff} = 1.79\ \mu_B$.

Preparation of $[Ti(OR)_2(TMEDA)Cl_2][TMEDA\text{-}H]$ [R =3,5-(t-Bu)$_2$C$_6$H$_3$] (2.3b):

A solution of $TiCl_3(THF)_3$ (2.93 g, 7.9 mmol) in THF (80 mL) was treated with TMEDA (4.8 ml, 31.8 mmol) followed by addition of 3,5-(t-Bu)$_2$PhOH (3.26 g, 15.8 mmol). The reaction mixture was boiled and stirred for about two hours, after which time the pale yellow ammonium salt started to precipitate out. The orange-yellow suspension was evaporated *in vacuo* and the residual yellow solid resuspended in toluene (80 mL). The suspension was filtered and concentrated to a small volume (40 mL). Bright-yellow crystals of **2.3b** (1.2 g, 1.5 mmol, yield 14%) separated upon cooling to -30°C.

Elemental Analysis for $C_{40}H_{75}O_2N_4Cl_2Ti$: Calcd (obsvd): C 60.44 (60.29); H 9.51 (9.66); N 7.05 (6.92); Ti 6.02 (5.99).

Magnetic Moment: $\mu_{eff} = 1.93\ \mu_B$.

Infrared Spectrum (Nujol mull, cm^{-1}): 1580(sh), 1450(sh), 1375(m), 1360(s), 1320(sh), 1235(sh), 1200(s), 1120(sh), 1065(s), 1025(sh), 1000(sh), 980(m), 930(s), 900(s), 870(sh), 850(sh), 820(sh), 800(sh), 770(m), 730(sh), 710(sh), 690(sh), 660(sh).

Preparation of $Ti[N(SiMe_3)_2]_3$ (2.4):

A green suspension of $TiCl_3(THF)_3$ (15.0 g, 40 mmol) in toluene (300 mL) was treated with $(Me_3Si)_2NLi$ (20.3 g, 120 mmol) at room temperature. The reaction mixture was stirred for about 4 hours and then boiled for five minutes. The color changed from light green to deep bluish purple and white LiCl began to precipitate out. The suspension was filtered whilst boiling and the volume of the solution reduced to 40 ml. Purple crystals of **2.4** (14.8 g, 29 mmol, 73%) separated from the purple solution upon standing two days at room temperature.

Elemental Analysis for $C_{18}H_{54}Si_6N_3Ti$: Calcd (Obsvd): C 40.87 (40.02); H 10.29 (10.11); N 7.94 (7.33); Ti 9.05 (8.87).

Magnetic Moment: $\mu_{eff} = 1.74\ \mu_B$

Infrared Spectrum (Nujol mull, cm^{-1}): 1650(br), 1460(m), 1380(sh), 1250(sh), 1020(s), 900(m), 790(s), 700(sh), 670(sh).

Preparation of $[Ti(2,6\text{-}Me_2C_6H_3O)_3]_2$ (2.5):

A toluene (70 ml) solution of $[(Me_3Si)_2N]_3Ti$ **(2.4)** (5.0 g, 9.4 mmol) was stirred and refluxed with freshly sublimed 2,6-Me_2PhOH (3.5 g, 28.6 mmol) for two hours. The color of the solution changed from deep blue violet to dark green-blue. The solution was concentrated to a small volume (30 ml) and then layered with hexane. Green-blue crystals of **2.5** were obtained upon standing overnight at room temperature (3.7 g, 4.5 mmol, 96%).

Elemental Analysis for $C_{48}H_{54}O_6Ti_2$: Calcd (Obsvd): C 70.08 (69.99); H 6.62 (6.55); Ti 11.64 (11.11).

Magnetic Moment: $\mu_{eff} = 0.64\ \mu_B$

Infrared Spectrum (Nujol mull, cm^{-1}): 1600(sh), 1470(m), 1430(s), 1385(sh), 1275(sh), 1240(s), 1225(sh), 1200(s), 1100(m), 1030(s), 900(m), 890(s), 850(m), 770(sh), 740(sh), 725(m), 700(m), 610(sh).

Preparation of $Ti[2,6\text{-}(i\text{-}Pr)_2C_6H_3O]_4$ (2.6):

The addition of 2,6-$(i\text{-}Pr)_2C_6H_3OH$ (3.0 g, 17 mmol) to a purple solution of **2.4** (3.0 g, 5.7 mmol) in toluene (50 mL) whilst stirring at room temperature yielded a deep orange colored solution over a period of about two hours. After concentration to small volume (30 mL) and subsequent layering with hexane (50 mL), bright

yellow air-stable crystals of **2.6** (1.9 g, 2.5 mmol, 45%) were obtained upon standing two days at room temperature.

Elemental Analysis for $C_{48}H_{68}O_4Ti$: Calcd (Obsvd): C 76.16 (75.99); H 9.06 (8.86); Ti 6.33 (6.00).

Magnetic Moment: Diamagnetic.

Infrared Spectrum (Nujol mull, cm^{-1}): 1650(br), 1460(sh), 1435(sh), 1385(m), 1360(s), 1320(sh), 1250(sh), 1190(sh), 1100(sh), 1045(m), 915(br), 880(s), 810(s), 795(m), 750(sh), 740(sh), 720(sh), 615(m).

Preparation of $Ti[2,6\text{-}(i\text{-}Pr)_2C_6H_3O]_4[(TMEDA)_2Li].C_7H_8$(2.7):

A THF (150 ml) solution of $2,6\text{-}(i\text{-}Pr)_2C_6H_3OH$ (8 ml, 43.2 mmol) was cooled to -80°C and MeLi (31 ml, 1.4 M solution in ether) was added dropwise. The solution was allowed to warm to room temperature. After cooling it again to -80°C, a solution of TMEDA (4.0 ml, 26.5 mmol) and $TiCl_3(THF)_3$ (4.0 g, 10.8 mmol) was added to the mixture. The resulting emerald-green slurry was stirred and allowed to warm to room temperature after which time it was stirred for further two hours. The solvent was evaporated *in vacuo* and the residual solid redissolved in toluene (100 mL). LiCl was removed by filtration and the filtrate was concentrated to small volume. Orange crystals of **2.7** (7.5 g, 6.9 mmol, 64%) separated from the resulting

blue-green solution upon standing at -30°C overnight.

Elemental Analysis for $C_{67}H_{108}O_4N_4TiLi$: Calcd (Obsvd): C 73.93 (73.69); H 10.00 (9.86); N 5.15 (5.01); Ti 4.40 (4.17).

Magnetic Moment: μ_{eff}= 1.67 μ_B

Preparation of $[Ti(OR)_2Cl(TMEDA)]$ [R= 2-$(OCH_3)C_6H_4$] (2.8):

A solution of 2-$(OCH_3)C_6H_4OH$ (3.0 ml, 27.3 mmol) in THF (80 ml) was stirred and refluxed with NaH (1.0 g, 41 mmol) for 30 minutes. The solution was cooled to room temperature and excess NaH removed by filtration. The addition of a solution of $TiCl_3(THF)_3$ (3.37 g, 9.1 mmol) in THF (75 ml), containing TMEDA (2.75 ml, 18.2 mmol) caused the solution to turn orange-yellow. The mixture was stirred for two hours at room temperature and then the solvent was evaporated *in vacuo*. The orange residue was resuspended in toluene (75 ml), the suspension was filtered and the clear solution was layered with hexane (50 ml). Bright yellow crystals of **2.8** (1.2 g, 2.6 mmol, 29 %) separated from the mixture after two days.

Elemental Analysis for $C_{20}H_{30}O_4N_2ClTi$: Calcd (Obsvd): C 53.88 (53.56); H 6.78 (6.54); N 6.28 (6.05); Ti 10.74 (10.58).

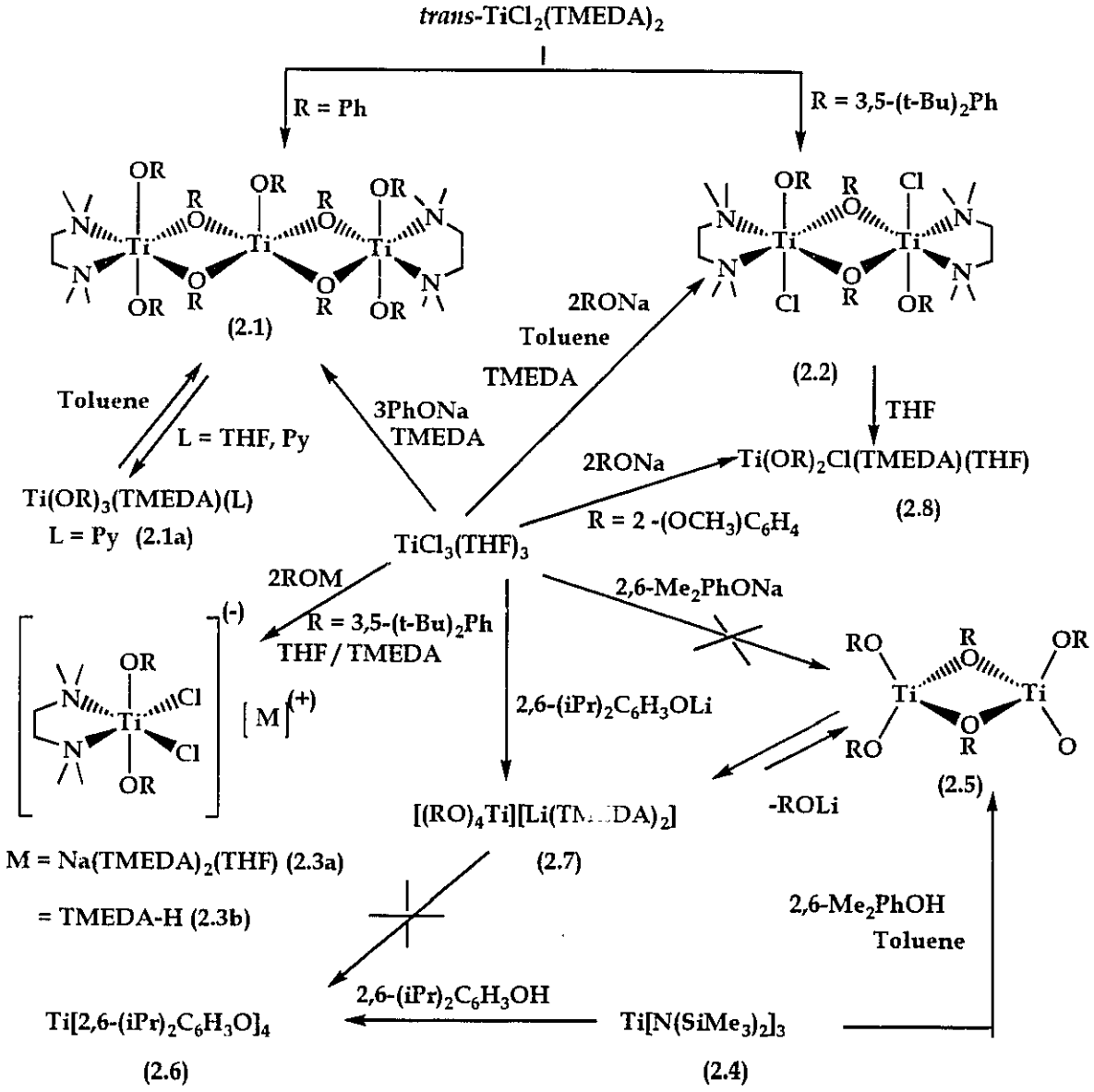
Magnetic Moment: $\mu_{eff.}$ = 1.73 μ_B.

Infrared Spectrum (Nujol mull, cm^{-1}): 1650(br), 1570(m), 1480(sh), 1450(sh), 1370(m), 1325(sh), 1275(sh), 1250(sh), 1220(sh), 1200(s), 1175(s), 1165(s), 1100(sh), 1015(sh), 945(sh), 920(s), 900(s), 880(sh), 840(sh), 790(sh), 760(sh), 745(sh), 735(sh), 610(sh).

II. 3 : Results And Discussion

As illustrated in **Scheme 2.1**, the reactions of $TiCl_3(THF)_3$ were carried out with different sodium or lithium aryloxides/alkoxides in THF and toluene at room temperature. The resulting solutions were evaporated *in vacuo* and very air-sensitive crystalline samples were obtained by crystallization of the residual solids from either toluene or a mixture of toluene-hexane. The nuclearity of these complexes seems to be dependent on both the substituents in the aromatic ring and the utilization of coordinating solvents. The presence of coordinating solvents tends to break the high nuclearity complexes up into monomers. This is illustrated by the reaction of the green linear trimeric $Ti_3(PhO)_9(TMEDA)_2$ **(2.1)** with THF, which resulted in a bright yellow monomeric complex $Ti(PhO)_3(TMEDA)(THF)$. This reaction was reversible and the green trimer **2.1** was obtained by boiling the yellow complex in toluene. Pyridine, another coordinating solvent also cleaved the trimer giving monomeric $Ti(PhO)_3(TMEDA)(Py)$ **(2.1a)**, which was obtained as purple red crystals from toluene. This reaction was irreversible and the trimer could not be retrieved by removing pyridine. Complex **2.1**, which was prepared as light green, air-sensitive crystals could also be prepared from *trans*-$TiCl_2(TMEDA)_2$ and its

structure was determined by X-ray crystallographic studies. Repeated attempts to grow crystals of pyridine complex **2.1a** suitable for X-ray structure determination remained unsuccessful. Consequently, the complex was characterized on the basis of microanalytical data.



Scheme 2.1

In the case of the substituted phenoxide $[(3,5\text{-t-Bu})_2C_6H_3O]^-$, the coordinating solvent has even stronger effect on the nuclearity of the complex. The ionic, paramagnetic monomer $[Ti(OR)_2Cl_2(TMEDA)]^-[Na(THF)(TMEDA)_2]^+$ **(2.3a)** was isolated as bright yellow crystals if the reaction was done in THF whereas light pink very air-sensitive crystals of dimeric $\{[Ti(TMEDA)Cl]_2(\mu\text{-}OR)_2\}$ **(2.2)** were obtained when the reaction was done in toluene. The dinuclear framework of complex **2.2** could also be cleaved in THF giving very fine colorless needles of $Ti(OR)_2Cl(TMEDA)(THF)$ but the reaction is irreversible in this case. Another monomeric, ionic and paramagnetic species $[Ti(OR)_2Cl_2(TMEDA)]^-[(TMEDA)H]_{0.5}$ **(2.3b)** was isolated in good yield from the reaction with neat phenol $[(3,5\text{-t-Bu})_2 C_6H_3OH]$ in the presence of excess TMEDA, which acts as a base to saltify the phenol. Complex **2.2** was also prepared starting from *trans*-$TiCl_2(TMEDA)_2$. Here, the dimer was obtained even when the reaction was done in THF. A slight increase in steric hindrance by substitution of two t-Bu groups in the *meta* position of the phenol resulted in a change in the nuclearity of the complex from trinuclear to dinuclear.

In accordance with the dependence of the nuclearity of these Ti(III) aryloxides on steric hindrance, treatment of $Ti[N(SiMe)_2]_3$ **(2.4)** with $(2,6\text{-}Me_2C_6H_3OH)$ led to the formation of the homoleptic, dinuclear complex $[Ti(2,6\text{-}Me_2C_6H_3O)_2(\mu\text{-}2,6\text{-}Me_2C_6H_3O)]$ **(2.5)** as blue-green, very air-sensitive crystals. However, complex **2.5** could not be prepared from the reaction of $TiCl_3(THF)_3$ with

the corresponding sodium phenoxide since only ill-defined products were obtained. In contrast, increasing the steric hindrance further i.e. reacting 2,6-(i-Pr)$_2$C$_6$H$_3$OH with **2.4** gave exclusively the homoleptic and mononuclear Ti(IV) derivative, Ti[2,6-(i-Pr)$_2$C$_6$H$_3$O]$_4$ **(2.6)**. The oxidation state of titanium in the starting material could not be preserved even by adding a dilute solution of phenol to a solution of **2.4** or by carrying out the reaction at low temperature. However the reaction of TiCl$_3$(THF)$_3$ with 2,6-(i-Pr)$_2$C$_6$H$_3$OLi gave orange, very air-sensitive crystals of a paramagnetic and monomeric Ti(III) complex [Ti{2,6-(i-Pr)$_2$C$_6$H$_3$O}$_4$][Li(TMEDA)$_2$].toluene **(2.7)**. The intense blue-green color formed by the orange crystals of **2.7** in a solution of toluene suggests the existence of a reversible dissociation equilibrium of ROLi and the formation of a dinuclear species similar to **2.5**. Using bidentate aryloxides such as guaiacol [2-(OCH$_3$)C$_6$H$_4$OH] to bridge two Ti atoms did not result in the formation of the dimeric complex, but only the monomeric [Ti(GuO)$_2$Cl(TMEDA)] **(2.8)**, with one guaiacolate molecule behaving as a monodentate ligand was formed. Attempts to reduce this complex using Na sand or NaBH$_4$ yielded only intractable products which were difficult to characterize.

A marked dependence of the magnetic moments on the nuclearity can be observed among these complexes. Complexes **2.3a**, **2.3b**, **2.7** and **2.8** ($\mu_{eff.}$= 1.79, 1.93, 1.67 and 1.73 μ_B per Ti atom, respectively) have the magnetic moments as expected for d^1 Ti(III) monomeric species. Conversely, the magnetic moments of complexes

2.2 and **2.5** ($\mu_{eff.}$= 0.75 and 0.64 μ_B per Ti atom, respectively) are considerably lower than expected. This is probably a result of either antiferromagnetic through space or super-exchange coupling in the dimetallic cores. The magnetic moment of complex **2.1** ($\mu_{eff.}$= 1.69 μ_B per molecule) is in agreement with one unpaired electron per trimetallic unit, suggesting that the trimetallic array is capable of performing very efficient magnetic coupling.

II. 4 : X-Ray Crystallography

Data were collected at temperatures in the range 23 to -160°C using the ω-2θ scan technique to a maximum 2θ value of 50.0° , for suitable air-sensitive crystals mounted on glass fibres. Cell constants and orientation matrices were obtained from the least-squares refinement of 25 carefully centered high-angle reflections. Redundant reflections were removed from the data set. The intensities of three representative reflections were measured after every 150 reflections to monitor crystal and instrument stability. Data were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were located in the difference Fourier maps and refined isotropically in the case of favourable observation/paremeter ratio. The final cycle of full-matrix least-squares refinement was based on the number of observed reflections with [I > 2.5σ (I)]. Neutral atomic scattering factors were taken from Cromer and Waber. Anomalous dispersion effects were included in Fcalc. All calculations were performed using the

TEXSAN package on a Digital VAX station. Selected bond distances and angles are given in **Appendix A.**

The structures of the complexes **2.1**, **2.2**, **2.3b**, **2.4**, **2.5**, **2.7** and **2.8** were determined by X-ray analysis. The linear trimeric structure of **2.1** is composed of two terminal $Ti(PhO)_4(TMEDA)$ octahedral fragments and one central square-pyramidal $Ti(PhO)_5$ fragment **(Fig. 2.1)**. The distorted octahedral coordination geometry of the two terminal titanium atoms [O1-Ti2-O2 = 72.8(3)°, O3-Ti2-O4 = 170.1(4)°, O3-Ti2-N1 = 88.7(1)°, N1-Ti2-O2 = 104.6(1)°, N1-Ti2-N2 = 78.5(2)°] is defined by two terminal and two bridging aryloxide oxygen atoms and by the two nitrogen atoms from one TMEDA molecule. The Ti-O bond distances formed by the two differently bonded alkoxides (terminal and bridging) are slightly different [Ti2-O3 = 1.902(8)Å, Ti2-O1 = 2.089(7)Å]. The central titanium atom is five-coordinate and its coordination geometry can be described as square-pyramidal (or distorted trigonal bipyramidal) [O1-Ti1-O1a = 154.8(3)°, O2-Ti1-O2a = 129.3(3)°, O1-Ti1-O5 = 102.6(2)°, O2-Ti1-O5 = 115.3(2)°]. Four bridging oxygens comprise the basal plane while a fifth alkoxide occupies the apical site. The Ti-O distances formed by the bridging alkoxide groups [Ti1-O1 = 2.067(7)Å, Ti1-O2 = 2.030(7)Å] compare well with those of the terminal units. Conversely, the apical alkoxide forms a considerably shorter Ti-O distance [Ti1-O5 = 1.802(11)Å] suggesting the possibility of Ti-O multiple bonding. The Ti_2O_2 core is folded along the intermetallic vector [Ti1-O1-Ti2-O2 = 15.5(1)°] and forms a Ti..Ti distance [Ti1-Ti2 = 3.264(2)Å] which is

not likely to be in agreement with the presence of a direct Ti-Ti bond.

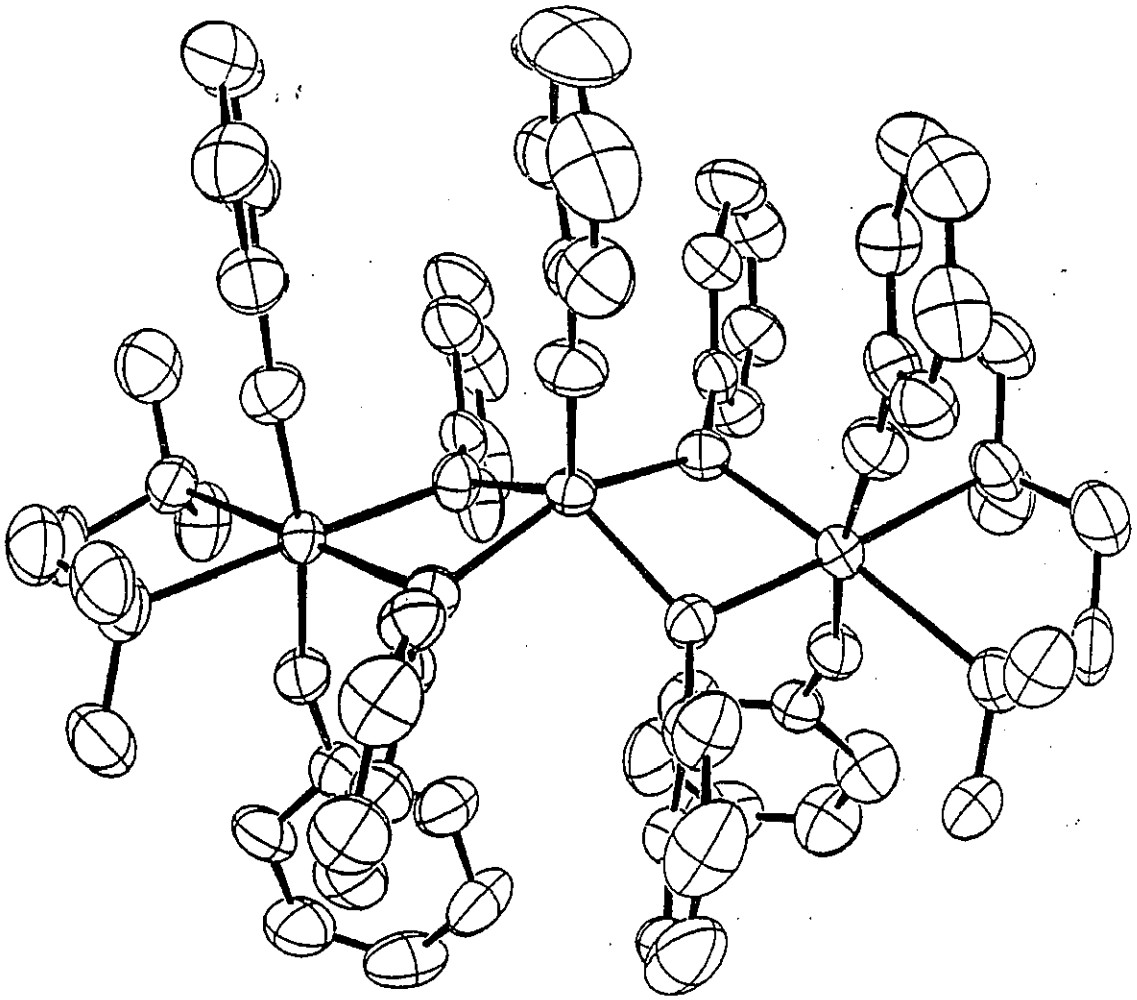


Fig. 2.1. X-Ray Structure of 2.1, $Ti_3(PhO)_9(TMEDA)_2$

Selected Bond Distances (Å) and Bond Angles (deg): Ti1-O1 = 2.067(7), Ti1-O2 = 2.030(7), Ti1-O5 = 1.802(11), Ti1...Ti2 = 3.264(2), Ti2-O3 = 1.902(8), Ti2-O1 = 2.089(7), Ti2-Ti1-Ti2a = 151.92(6), N1-Ti2-N2 = 78.6(2), O1-Ti2-O2 = 72.8(3), O3-Ti2-O4 = 170.1(4), O3-Ti2-N1 = 88.7(1), N1-Ti2-O2 = 104.6(1), O1-Ti1-O1a = 154.8(3), O2-Ti1-O2a = 129.3(3), O1-Ti1-O5 = 102.6(2), O2-Ti1-O5 = 115.3(2).

Complex **2.2** is dinuclear and possesses a typical edge-sharing bioctahedral geometry. In spite of the fact that poor scattering power prevented convergence to satisfactory R values, the chemical connectivity could be observed. The two coordination octahedra centered on each titanium atom are defined by one terminal aryloxide oxygen atom and one chlorine atom placed on the apical positions, while two nitrogen atoms of the chelating TMEDA and two bridging aryloxide oxygen

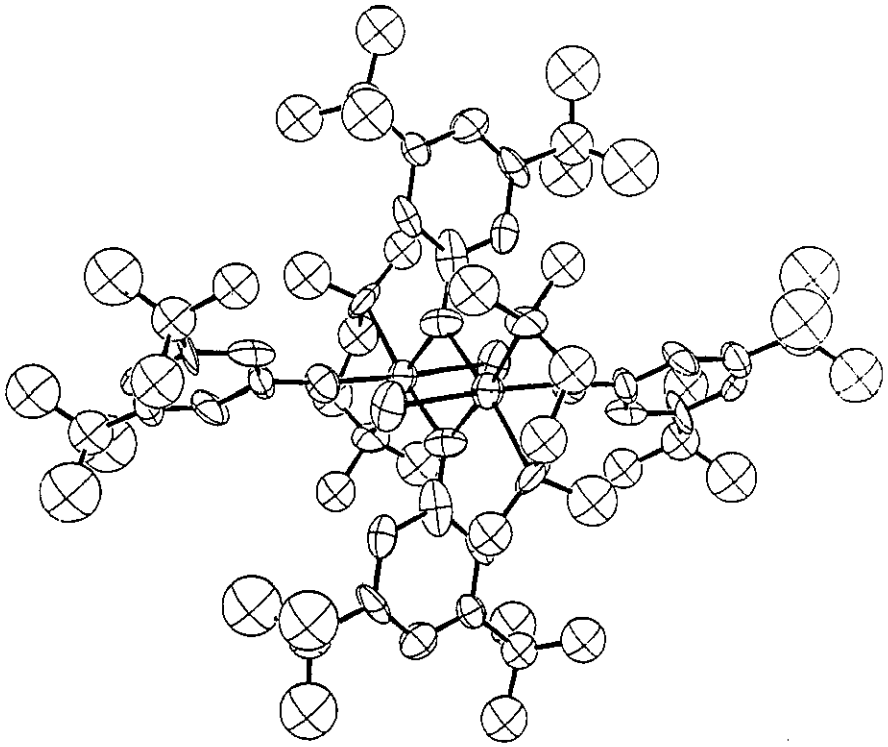


Fig. 2.2. X-Ray Structure of 2.2, Ti{3,5-(t-Bu)$_2$C$_6$H$_3$O}Cl(TMEDA)]$_2$ [μ-(3,5-tBu)$_2$C$_6$H$_3$O]$_2$

Selected Bond Distances (Å) and Bond Angles (deg): Ti1-O1 = 1.853(14), Ti1-O2 = 2.067(15), Ti1-O2a = 2.073(14), Ti1-Cl1 = 2.435(7), Ti1...Ti2 = 3.296(18), Ti1-O2-Ti2 =

105.5(6), O1-Ti1-Cl1 = 167.8(5), O2a-Ti1-Cl1 = 92.0(4), O2-Ti1-Cl1 = 90.0(5), O2-Ti1-O2a = 74.5(6), O1-Ti1-O2 = 98.7(6), O1-Ti1-O2a = 98.5(6).

atoms form the equatorial plane **(Fig. 2.2)**. The geometry of the $Ti_2(OR)_2$ core is normal with Ti-O [Ti1-O1 = 1.853(14)Å] and Ti-Ti [Ti1-Ti1a = 3.296(18)Å] distances as expected. In analogy to complex **2.1**, the intermetalllic distance suggests the absence of a direct Ti-Ti bonding interaction

Complex **2.3b** is mononuclear and composed of an anion and a cation **(Fig. 2.3)**. The anionic moiety is composed of a titanium atom with octahedral geometry defined by two aryloxide groups, placed *trans* to each other [O1-Ti1-O2 = 176.2(2)°], two nitrogen atoms of one TMEDA molecule [N1-Ti1-N2 = 79.99(2)°] and two chlorine atoms in *cis* positions [Cl1-Ti1-Cl2 = 96.09(8)°]. The Ti-O [Ti1-O1 = 1.899(4)Å] and Ti-Cl [Ti1-Cl1 = 2.492(2)Å] distances are normal. The cation consists of one molecule of TMEDA protonated at one of the two nitrogen atoms forming a hydrogen bridge with one of the two chlorine atoms of the cationic fragment.

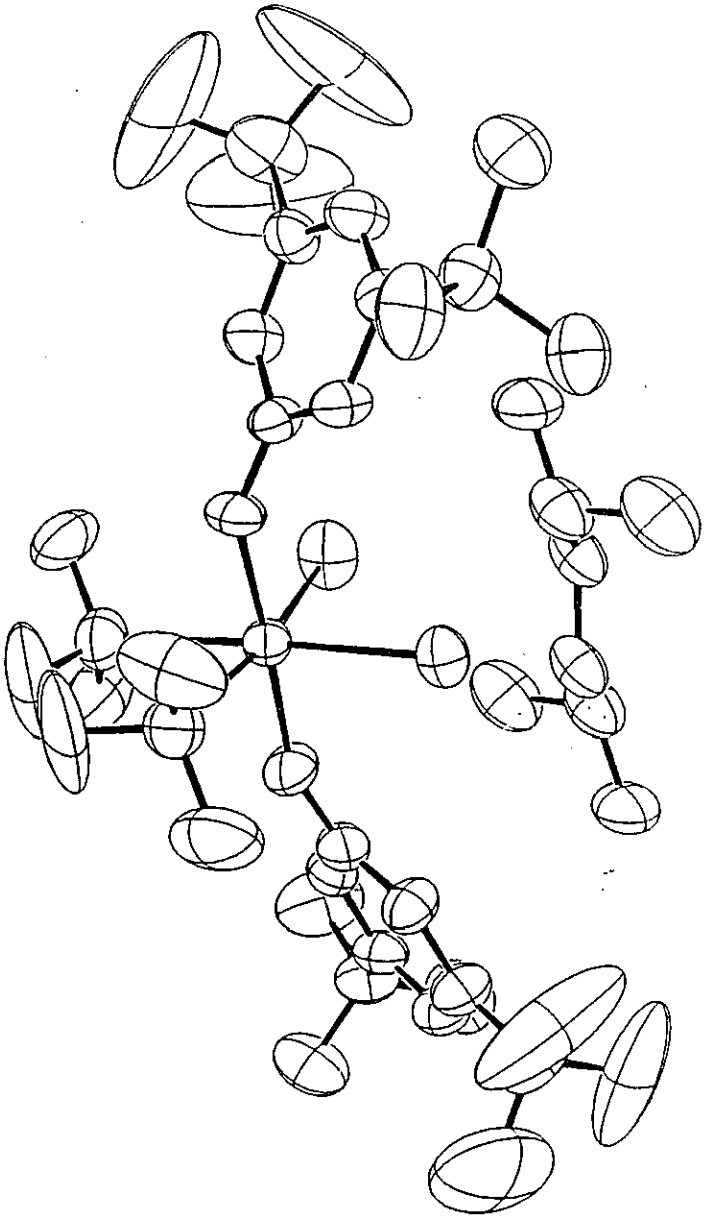


Fig. 2.3. X-Ray Structure of 2.3b, $Ti\{3,5\text{-}(t\text{-}Bu)_2C_6H_3O\}_2(TMEDA)Cl_2][TMEDA\text{-}H]$

Selected Bond Distances (Å) and Bond Angles (deg): Ti1-O1 = 1.899(4), Ti1-Cl1 = 2.492(2), Ti1-N1 = 2.288(6), Cl1...N3 = 3.080(6), O1-Ti1-O2 = 176.2(2), N1-Ti1-N2 = 79.99(2), Cl1-Ti1-Cl2 = 96.09(8), Cl1-Ti1-N1 = 172.6(2), Cl1-Ti1-O1 = 90.3(2).

Complex 2.4 is mononuclear (**Fig. 2.4**) and the geometry around the Ti atom is triangular [N-Ti-N1 = 119.89(9)°, Ti-N = 1.945(8)Å]. Each Si atom has roughly

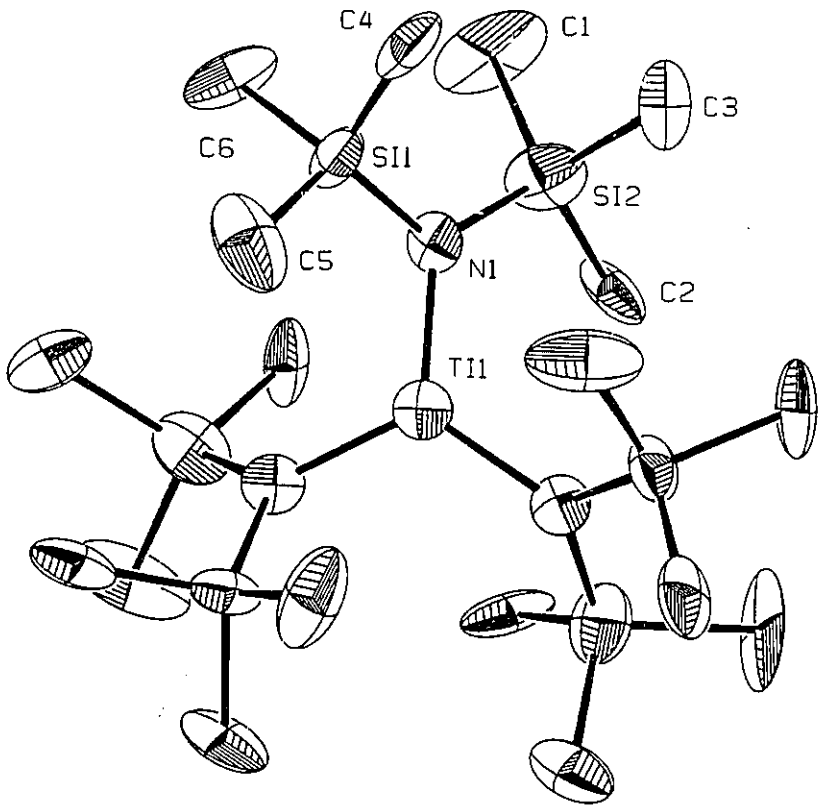


Fig. 2.4. X-Ray Structure of 2.4, $Ti[N(SiMe_3)_2]_3$

Selected Bond Distances (Å) and Bond Angles (deg): Ti1-N1 = 1.945(8), N1-Si1 = 1.69(2), N1-Si2 = 1.82(2), Si1-C4 = 1.86(3), Si1-C5 = 1.83(3), Si1-C6 = 1.80(2), Si2-C1 = 1.89(3), Si2-C2 = 1.89(2), Si2-C3 = 2.01(3), N1-Ti1-N2 = 119.89(9), N1-Si1-C4/5 = 111(1), Ti1-N1-Si1 = 122(1), Ti1-N1-Si2 = 118(1), Si1-N1-Si2 = 120.2(5).

tetrahedral coordination with three C and one N in the coordination sphere

[C4-Si1-C5 = 104.6(9)°, C4-Si1-C6 = 105(1)°, C5-Si1-C6 = 103(1)°, N1-Si1-C4 = 111(1)°, N1-Si1-C5 = 111(1)°] and the N atom has also trigonal planar geometry [Ti1-N1-Si1 = 122(1)°, Ti1-N1-Si2 = 118(1)°, Si1-N1-Si2 = 120.2(5)°].

The homoleptic dinuclear complex **2.5** possesses a characteristic edge-sharing di-tetrahedral geometry. The two identical and slightly distorted coordination

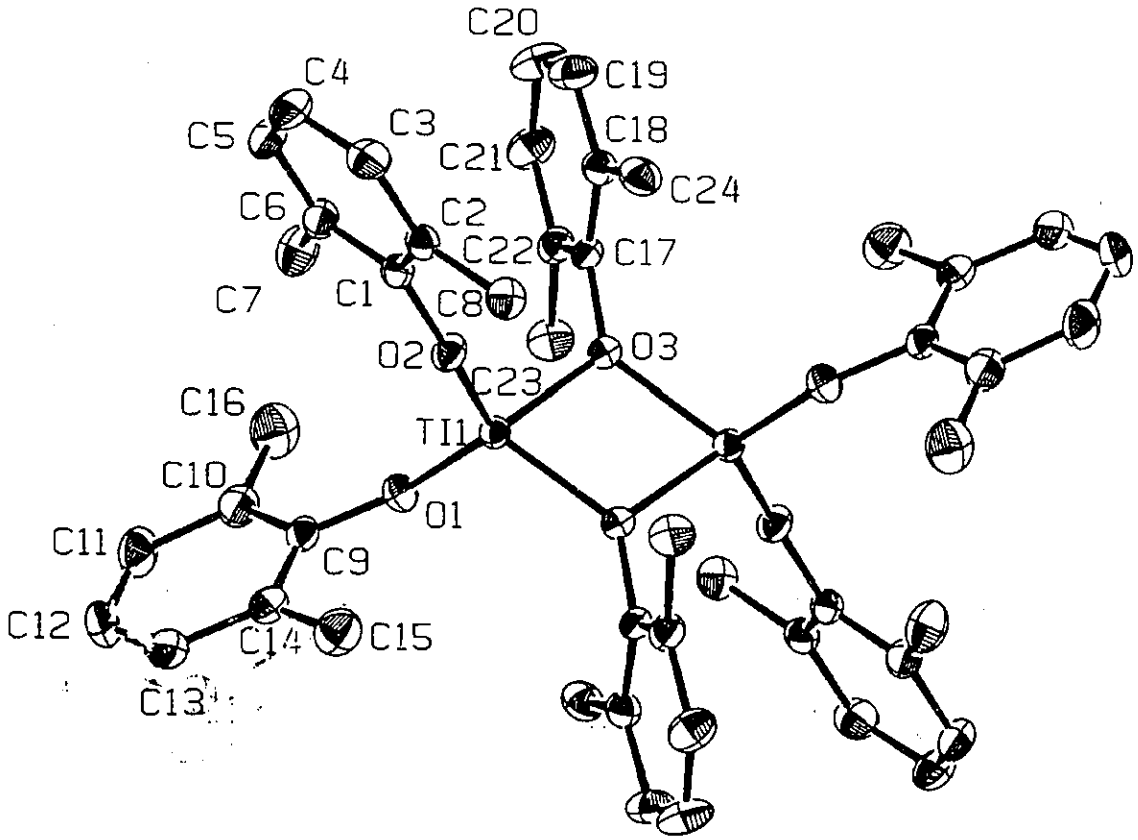


Fig. 2.5. X-Ray Structure of 2.5, $[Ti(2,6\text{-}Me_2C_6H_3O)_3]_2$

Selected Bond Distances (Å) and Bond Angles (deg): Ti1-Ti1a = 3.085(2), Ti1-O1 = 1.830(2), Ti1-O3 = 2.009(2), O1-Ti1-O2 = 119.26(9), O1-Ti1-O3 = 113.88(9), O2-Ti1-O3

= 108.32(8), O3-Ti1-O3a = 79.45(8), Ti1-O1-C9 = 146.1(2), Ti1-O2-C1 = 154.6(2), Ti1-O3-Ti1a = 100.55(8)

tetrahedra centered on each titanium atom [O1-Ti1-O2 = 119.26(9)°, O1-Ti1-O3 = 113.88(9)°, O2-Ti1-O3 = 108.32(8)°] are defined by two terminal and two bridging aryloxide oxygen atoms **(Fig. 2.5)**. The Ti-O distances formed by the two inequivalent oxygen atoms are different [Ti1-O1 = 1.830(2)Å, Ti1-O3 = 2.009(2)Å] suggesting some extent of Ti-O multiple bonding with the terminal aryloxide groups. Consistently, the angles subtended at the oxygen atoms {Ti1-O1-C9 = 146.1(2)°, Ti1-O2-C1 = 154.6(2)°] deviate significantly from the value expected for an sp^2 oxygen atom. The $Ti_2(OR)_2$ core is perfectly planar with the two bridging oxygen atoms in a trigonal planar coordination geometry [Ti1-O3-Ti1a = 100.55(8)°, O3-Ti1-O3a = 79.45(8)°]. The Ti..Ti distance [Ti1-Ti1a = 3.085(2)Å] compares well with those of complexes **2.1** and **2.2**.

Complex **2.7** is mononuclear and is composed of two different ionic moieties **(Fig. 2.6)**. The anionic part is formed by a titanium atom with distorted tetrahedral geometry defined by four aryloxide groups [O1-Ti1-O2 = 105.07(25)°, O2-Ti1-O4 = 102.63(24)°, O4-Ti1-O3 = 101.9(3)°, O1-Ti1-O3 = 104.5(3)°]. The Ti-O distances [Ti1-Oavg. = 1.9 Å] are quite normal. The cation consists of two TMEDA molecules surrounding a Li atom.

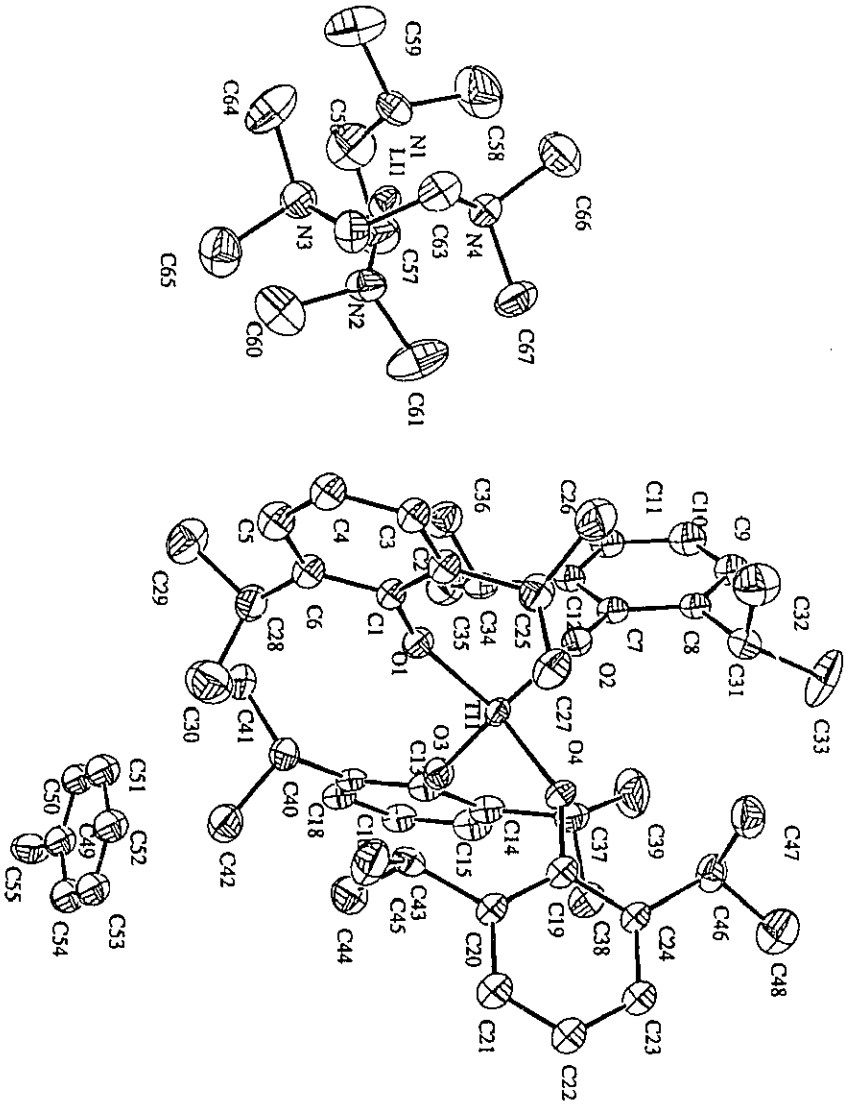


Fig. 2.6. X-Ray Structure of 2.7, Ti[2,6-(i-Pr)$_2$C$_6$H$_3$O]$_4$[Li(TMEDA)$_2$]

Selected Bond Distances (Å) and Bond Angles (deg): Ti1-O1 = 1.917(6), Ti1-O2 = 1.900(6), Ti1-O3 = 1.905(6), Ti1-O4 = 1.909(5), O1-C1 = 1.349(8), O2-C7 = 1.354(7), O3-C13 = 1.352(7), O4-C19 = 1.365(7), O1-Ti1-O4 = 125.3(3), O2-Ti1-O3 = 118.75(25), Ti1-O1-C1 = 151.5(5), Ti1-O2-C7 = 148.4(5), Ti1-O3-C13 = 145.2(4), Ti1-O4-C19 = 146.5(5).

Complex **2.8** is mononuclear and is composed of an octahedrally coordinated Ti atom [Cl1-Ti1-O2 = 94.7°, Cl1-Ti1-O3 = 92.9°, Cl1-Ti1-N2 = 94.2°, Cl1-Ti1-N1 = 174.8°, Cl1-Ti1-O1 = 92.3°] with the coordination sphere **(Fig. 2.7)** defined by two

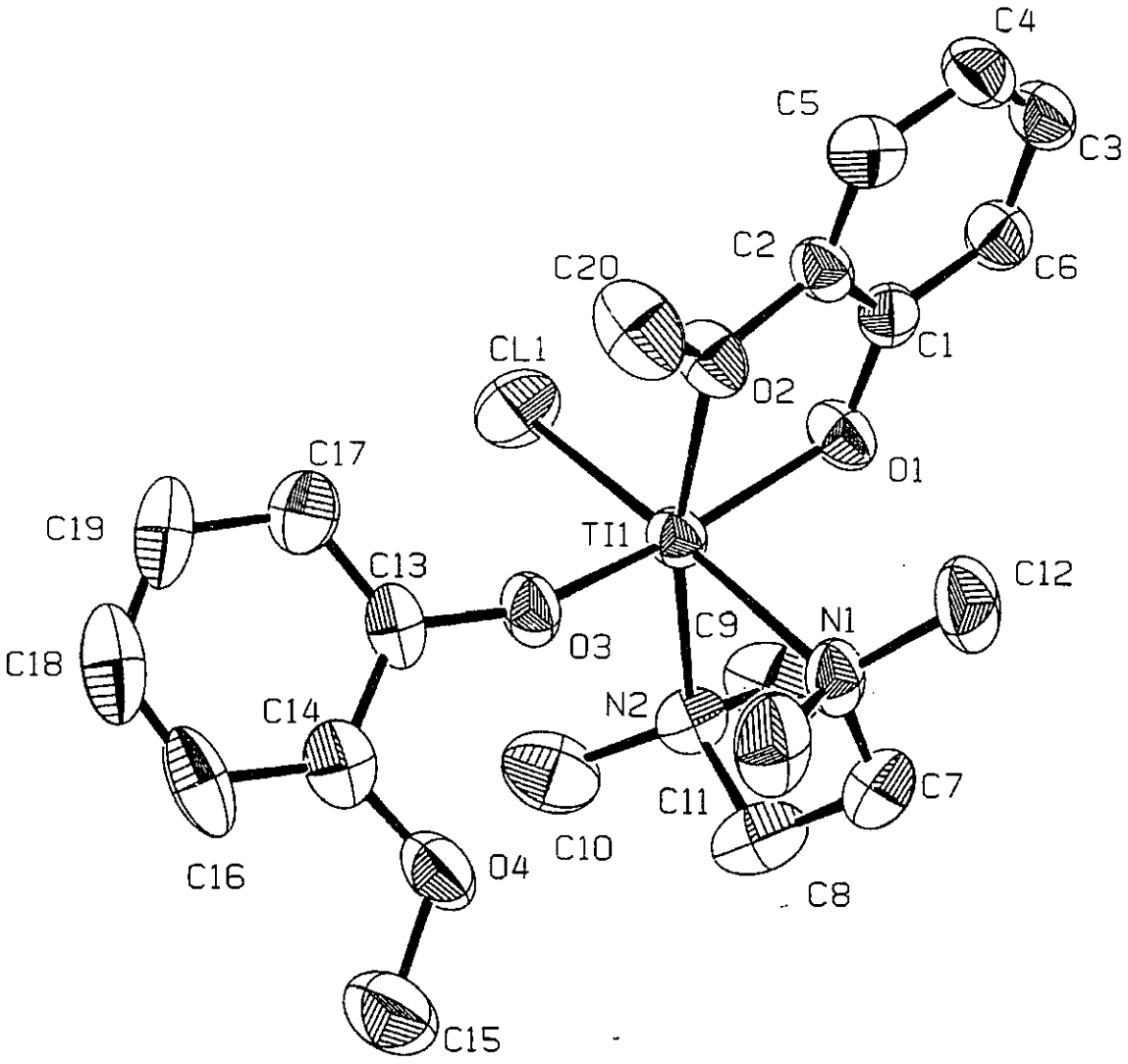


Fig. 2.7. X-Ray Structure of 2.8, [Ti{2-(OCH$_3$)C$_6$H$_4$O}$_2$Cl(TMEDA)]

Selected Bond Distances (Å) and Bond Angles (deg): Ti1-Cl1 = 2.402(2), Ti1-O1 =

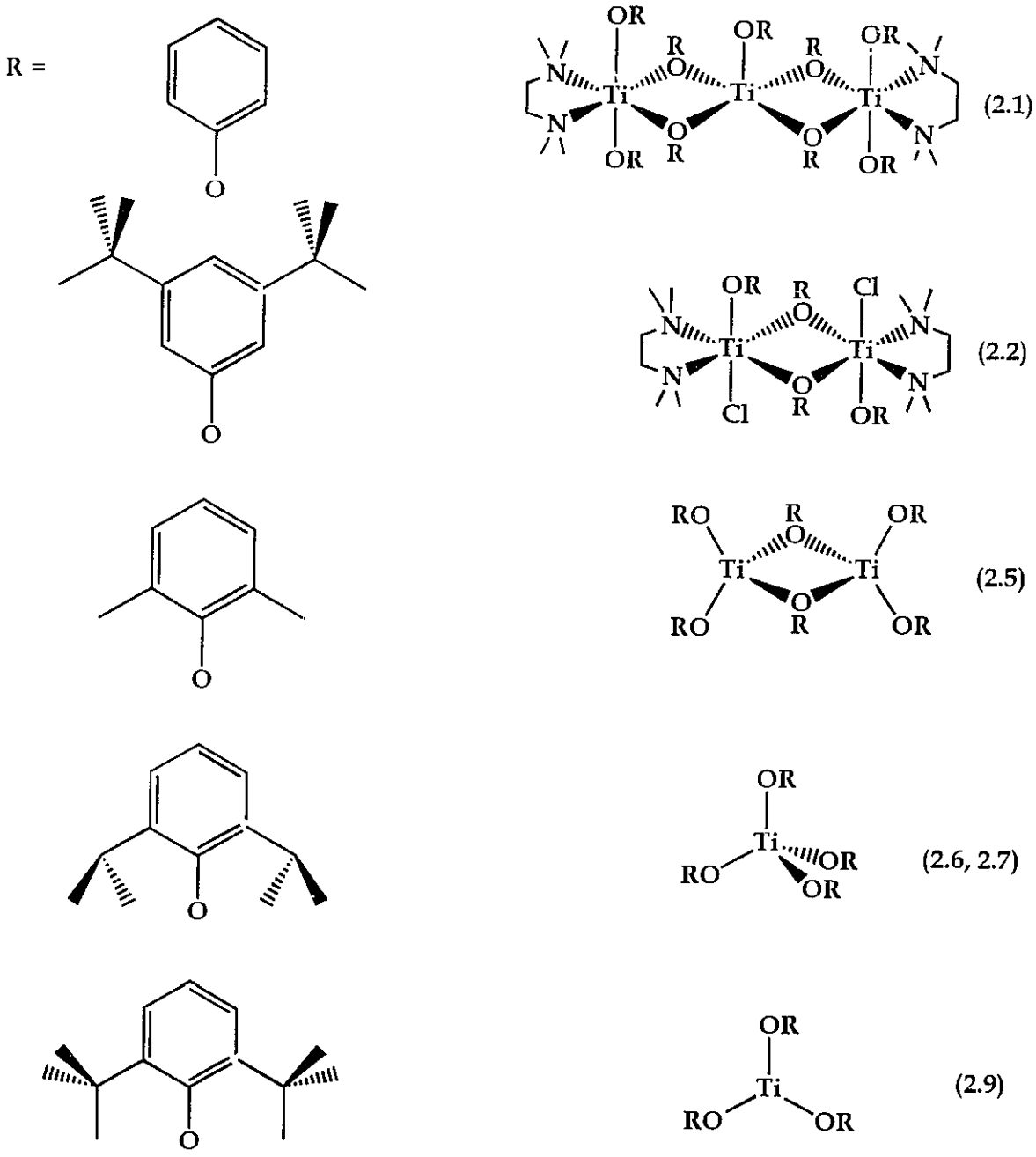
1.955(3), Ti1-O2 = 2.255(4), Ti1-O3 = 1.870(3), O1-Ti1-O2 = 74.2(1), O1-Ti1-O3 = 164.7(2), O1-Ti1-N1 = 87.2(1), O1-Ti1-N2 = 97.1(2), O2-Ti1-O3 = 91.1(1), O2-Ti1-N1 = 90.2(2), O2-Ti1-N2 = 167.8(2), O3-Ti1-N1 = 88.8(2), O3-Ti1-N2 = 96.8(2), N1-Ti1-N2 = 80.7(2).

guaiacolate units, one molecule of TMEDA and one Cl atom in an axial position. The Ti-N bond distances formed by equatorially and axially bound N atoms of TMEDA molecule are slightly different [Ti1-N1 = 2.316 Å, Ti1-N2 = 2.211 Å]. The Ti-O bond distance is shorter in the mononucleating guaiacolate unit [Ti1-O3 = 1.870 Å] compared to a binucleating guaiacolate [Ti1-O2 = 2.255 Å, Ti1-O1 = 1.955 Å]. The Ti1-O2 bond distance is large compared to Ti1-O1 due to steric hindrance caused by a $-CH_3$ group on O2.

II. 5 : Conclusion

The results presented above are listed in **Scheme 2.2** which shows the role played by sterically bulky substituents in the aryloxide for predicting the geometry and the nuclearity of Ti(III) complexes. The crystal structures of complexes **2.1**, **2.2**, **2.5**, **2.6**, **2.7** and **2.9** show the decrease of nuclearity as well as metal coordination number, along with an increase in the steric bulk around the aromatic ring of aryloxide.

However, a consistent trend within the series of reactions is not observed since



Scheme 2.2

different synthetic pathways have been used for the preparation of the complexes. Steric bulk also has the ability to stabilise the trivalent oxidation state. The unusual trigonal planar geometry around Ti in complex **2.9**[12b] is probably due to two bulky

ortho tert-butyl groups on the aryloxide ligand which prevent the oxygen atoms from bridging and hence the complex is mononuclear. Also, the steric bulk of the ligand prevents the aggregation of four aryloxides around Ti thus stabilising the trivalent oxidation state. In the case of complex **2.6**, reducing the steric hindrance slightly by using 2,6-$(iPr)_2C_6H_3OH$, the steric bulk of the ligand is not sufficient to stabilise the Ti(III) aryloxide by protecting it from further oxidation and is not small enough for dimerisation as in complex **2.5**. The possible explanation for its oxidation to Ti(IV) is that a neutral, coordinatively unsaturated Ti(III) complex, $Ti(OR)_3$, is formed in the reaction of **2.4** with phenol which then reacts further with unreacted phenol to form the final Ti(IV) complex *via* the evolution of H_2 (**Eq. 2.1**)

$$Ti(NR_2)_3 \xrightarrow{ROH} Ti(OR)_3 \xrightarrow{ROH} Ti(OR)_4 + H_2$$

Equation 2.1

However, this does not explain the formation of complexes **2.1** and **2.2** starting from *trans*-$TiCl_2(TMEDA)_2$. The oxidation of Ti(II) and Ti(III) aryloxides can be ascribed either to disproportionation or to the same type of oxidation observed during failed attempts to prepare V(II) aryloxides using V(II) starting materials.[17]. Although no evidence has been found for the presence of co-products in the reaction mixtures, the occurrence of oxidative deoxygenation pathways similar to those observed in the chemistry of chromium (II)[18] and yttrium aryloxides[19] cannot be ruled out.

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CHAPTER III

Synthesis, Characterization and Reactivity of Titanium (III) and (IV) Alkyls using Organic Dialkylamides as the Supporting Ligands.

III.1 : Introduction

Transition metal alkyl complexes (L_nM-R) constitute a very important class of compounds because of the pivotal role played by these species in both synthesis and catalysis.[1] In particular group IV organometallic derivatives have been the target of intense study since the initial discovery by Ziegler and Natta[2] that mixtures of $TiCl_3$ and aluminium alkyls act as catalysts for stereoselective olefin polymerization. As a result, interest in the synthesis, characterization and reactivity of group IV organometallic species[3] has grown steadily and titanium alkyls are today well established[4] and widely employed in a number of important industrial processes e.g. olefin cationic polymerization[5], insertion reactions[6], hydrogenation[7] and metal-promoted organic synthesis[8]. A synthetically useful characteristic of titanium alkyls is their ability to act as precursors for the preparation of alkylidene[9] derivatives *via* C-H σ - bond metathesis reactions. These families of tetravalent titanium complexes have also proven their potential use in applications like ROMP[10], metathesis and polymerization[11]. In this respect, sterically demanding alkyl groups lacking β - hydrogens (Bz, Np, Nf) seem to be particularly versatile. In fact, by preventing β - H elimination reactions, it is possible to obtain an unusual

high stability[12], and thus favor α - H abstraction during C-H σ - bond metathesis with consequent cyclometallation or alkylidene formation[13].

In spite of the potential offered by Ti alkyl systems, their chemistry has been extensively studied in the sole direction of using cyclopentadienyl rings and related systems as supporting ligands[4]. Titanium alkyls containing other supporting ligands remain rare, mainly generated *in situ*, and are poorly characterized. Only a very few, containing bulky phenoxides as ancillary ligands[9a,14] have been fully characterized, including crystallography.

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 of several transition elements. Such stability can be ascribed to both the reducing ability of these anions and the possibility of M-N π - bond formation which obviously improves the stability of electron rich complexes *via* an increased electronic delocalization. In addition, these ligands may function as bridging ligands, thus promoting multinuclear aggregation through bridging interactions of the nitrogen donor atom. Recently, we have described the preparation and characterization of novel titanium methyl and methylidene complexes[9a] stabilized by bulky organic amides. In this chapter, we further describe the synthesis, characterization and thermal stability of other mono- and dinuclear Ti(III) and Ti(IV) alkyls along with a preliminary discussion of the factors influencing their ability.

III.2 : Experimental Part

All operations were performed under an inert atmosphere of a nitrogen filled drybox or by using standard Schlenk-type glassware and a nitrogen-vacuum line. $TiCl_3$ and $TiCl_4$ were used as received (Aldrich) and transformed into the corresponding THF adducts following literature procedures[15,16]. Cy_2NH, $i\text{-}Pr_2NH$, $(Me_3Si)_2NH$ and TMEDA were distilled prior to use over Na and K metals. The corresponding lithium salts (R_2NLi) were prepared by treating the hexane solutions of the amines with stoichiometric amounts of n-BuLi. NpLi, NfLi and $LiCH_2SiMe_3$ were obtained by reacting the corresponding chlorides by treatment with metallic lithium. The complexes $[(Cy_2N)_2Ti(\mu\text{-}Cl)_2Li(TMEDA)]$ **(3.1)**[9a], $[\{(Me_3Si)_2N\}_2TiCl_2][Li(TMEDA)_2]$ **(3.3)**[17] $(Cy_2N)_2Ti(\mu\text{-}Me)_2Li(TMEDA)]$ **(3.4b)**[9a] and $[(Cy_2N)_2TiCl_2]$ **(3.5)**[9a] were synthesized according to published procedures. C_6D_6 was dried over Na/K alloy, vacuum transferred into an ampoule and stored under nitrogen. NMR spectra were recorded on a Varian Gemini 200 and on a Bruker AMX-500 spectrometer using vacuum sealed NMR tubes, samples being prepared inside a dry-box. Infrared spectra were recorded on a Mattson 3000 FTIR instrument from Nujol mulls prepared inside the dry-box. Samples for magnetic susceptibility measurements were prepared inside the dry-box and the measurements were carried out at room temperature using a Gouy balance (Johnson Matthey). Magnetic moments were calculated by following standard methods[18] and corrections for underlying diamagnetism were applied to the data[19]. Elemental analyses were

carried out using Perkin Elmer Series II CHN/O 2400-analyzer.

Preparation of $[(i\text{-}Pr_2N)_2TiCl_2][Li(TMEDA)_2]$ (3.2):

A solution of $i\text{-}Pr_2NLi$ (3.8 g, 35.5 mmol) in THF (50 ml) was added to a stirred suspension of $TiCl_3.(THF)_3$ (6.5 g , 17.6 mmol) in THF (150 ml) at -10°C, followed by 2 equivalents of TMEDA (5.0 ml, 33 mmol). The reaction was instantaneous and the resulting green solution was warmed to room temperature. After stirring for an additional 30 min. the solvent was evaporated *in vacuo* and the residue was dissolved in hexane (150 ml). The LiCl was removed by filtration and the resulting solution was allowed to stand overnight at -30°C, upon which forest green crystals of **3.2** (4.2 g, 7.5 mmol, 43%) separated.

Elemental Analysis for $C_{24}H_{60}N_6TiLiCl_2$: Calcd (obsvd): C 51.61 (51.56), H 10.83 (10.04), N 15.05 (14.64).

Magnetic Moment: μ_{eff}= 1.8 μ_B.

Infrared Spectrum (Nujol mull, cm^{-1}): 1461(s), 1376(m), 1292(w), 1261(w), 1168(m), 1101(m), 1035(w), 931(m), 811(m), 792(w), 723(w), 605(w), 493(m).

Preparation of $[(Cy_2N)_2Ti(\mu\text{-}CH_2Ph)_2Li(TMEDA)]$(3.4a):

A solution of **3.1** (1.0 g, 1.7 mmol) in diethylether (80 ml) was treated with BzLi(TMEDA) (0.75 g, 3.5 mmol). The color of the solution changed immediately to

reddish-brown and stirring was continued for about 30 minutes. The white precipitate was eliminated by filtration and the resulting solution allowed to stand at room temperature for two hours, upon which purple microcrystalline **3.4a** (0.4 g, 0.56 mmol, 33%) separated.

Elemental Analysis for $C_{44}H_{74}N_4TiLi$: Calcd (obsvd): C 74.03 (73.85); H 10.45 (10.41); N 7.85 (7.79).

Magnetic Moment: μ_{eff}= 1.88 μ_B.

Infrared Spectrum (Nujol mull, cm^{-1}): 3056(w), 1585(m), 1288(m), 1261(m), 1213(m), 1157(m), 1143(m), 1110(s), 1097(s), 1031(s), 950(s), 898(s), 854(m), 800(s), 738(s), 681(s), 561(m), 533(m).

Preparation of $(Cy_2N)_2Ti(CH_2Ph)_2$ (3.6):

Solid $PhCH_2Li$.TMEDA (1.7 g, 8.2 mmol) was added to an orange suspension of $(Cy_2N)_2TiCl_2$ **(3.5)** (1.9 g, 4.0 mmol) in hexane (150 ml) yielding a dark orange solution over a period of 2 days. After removal of LiCl.TMEDA, the solvent was evaporated *in vacuo* to yield an orange oil.

Elemental Analysis for $C_{38}H_{58}N_2Ti$: Calcd (obsvd): C 77.26 (77.01); H 9.90 (9.76), N 4.74 (4.64).

^{1}H NMR [C_6D_6, 200 MHz, δ(ppm)]: 7.25-6.85 (m, 5H, Ph), 3.7-3.52 (m, 2H, Cy), 2.7 (s, 2H, Bz), 1.88-0.82 (m, 20H, Cy).

^{13}C NMR [C_6D_6, 50 MHz, δ(ppm)]: 150.7 (C, Ph), 129.2, 127.6, 122.8 (CH, Ph), 80.9 (CH_2, Bz), 58.8 (CH, Cy), 36.8, 27.7, 26.6 (CH_2, Cy).

Preparation of $(Cy_2N)_2Ti(CH_2CMe_3)_2$ (3.7):

Method A: The addition of NpLi (Np = CH_2CMe_3, 0.8 g, 10.2 mmol) to an orange suspension of $(Cy_2N)_2TiCl_2$ **(3.5)** (2.6 g, 5.4 mmol) in diethyl ether (150 ml) at -10°C turned the color greenish-yellow. An insoluble light yellow-green solid was collected and recrystallized from hexane to give yellow crystals of **3.7** after standing overnight at room temperature (1.6 g, 2.9 mmol, 54%).

Method B: NpLi (0.4 g, 5.13 mmol) was added to a stirred emerald green solution of $[(Cy_2N)_2Ti(\mu\text{-}Cl)_2Li(TMEDA)]$ **(3.1)** (1.5 g, 2.5 mmol) in diethylether (60 ml) at -10°C. The color turned brownish-orange and the stirring was continued for about 3 hours at room temperature. The insoluble colorless material which had separated was filtered off and the resulting clear solution gave yellow microcrystalline **3.7** (0.5 g, 0.91 mmol, 36%) upon standing overnight at -30°C.

Elemental Analysis for $C_{34}H_{66}N_2Ti$: Calcd (Obsvd): C 74.14 (74.57); H 12.08 (12.27); N 5.09 (5.11).

Infrared Spectrum (Nujol mull, cm^{-1}): 1455(s), 1366(s), 1252(m), 1225(m), 1158(m), 1142(m), 1107(sh), 1091(sh), 1025(sh), 978(m), 944(sh), 887(sh), 842(sh), 803(sh), 778(sh), 750(sh), 696(sh), 680(m),589(m), 579(m), 546(w), 506(sh), 488(sh), 453(m).

^{1}H NMR [C_6D_6, 500 MHz, δ(ppm)]: 3.75-3.69 (m, 2H, Cy), 2.02-1.11 (m, 20H, Cy), 1.65 (s, 2H, Np), 1.3 (s, 9H, Np).

^{13}C NMR [C_6D_6, 125 MHz, δ(ppm)]: 98.7 (CH_2, Np), 58.2 (CH, Cy), 36.9 (C, Np), 34.8 (CH_3, Np), 36.3, 27.1, 26.2 (CH_2, Cy).

Preparation of $(Cy_2N)_2Ti(CH_2CMe_2Ph)_2$ (3.8):

Method A: Solid $LiCH_2CMe_2Ph$ (1.35 g, 9.6 mmol) was added to a stirred solution of $(Cy_2N)_2TiCl_2$ **(3.5)** (2.3 g, 4.8 mmol) in diethyl ether (50 ml) at room temperature. The color became yellow instantaneously. After a few hours, , the solvent was evaporated *in vacuo* and the residual solid was redissolved in hexane (40 ml). Removal of LiCl followed by overnight standing at -30°C afforded greenish-yellow crystals of **3.8** (1.7 g, 2.5 mmol, 52%).

Method B: NfLi (0.52 g, 3.7 mmol) was added to a solution of **3.1** (1.16 g, 1.9 mmol) in diethyl ether (100 ml) at room temperature along with stirring. The stirring was continued for further two hours and the color of the solution changed

to yellow-brown. After filtering off the LiCl, the concentrated solution of ether was layered with hexane (30 ml). Green-yellow crystalline solid **3.8** (0.75 g, 1.1 mmol, 58%) separated at -30°C overnight.

Elemental Analysis for $C_{44}H_{70}N_2Ti$: Calcd (Obsvd): C 78.30 (77.88); H 10.45 (10.46); N 4.15 (4.02).

Infrared Spectrum (Nujol mull, cm^{-1}): 1600(w), 1494(sh) 1454(bd), 1376(m), 1249(m), 1188(w), 1172(w), 1157(m), 1093(m), 1081(sh), 1029(m), 1020(m), 975(w), 944(sh), 887(sh), 842(sh), 806(m), 779(m), 761(sh), 698(sh), 582(w), 551(m).

^{1}H NMR [C_6D_6, 500 MHz, δ(ppm)]: 7.52-7.5 (m, 2H, Ph), 7.28-7.24 (m, 2H, Ph), 7.1-7.07 (m, 1H, Ph), 3.7-3.65 (m, 2H, Cy), 1.93-0.83 (m, 20H, Cy), 1.78 (s, 2H, CH_2, Nf), 1.54 (s, 6H, CH_3, Nf).

^{13}C NMR [C_6D_6, 125 MHz, δ(ppm)]: 153.7 (C, Ph, Nf), 127.8, 126.0, 125.3 (CH, Ph, Nf), 97.5 (CH_2, Nf), 58.5 (CH, Cy), 43.6 (C, Nf), 34.3 (CH_3, Nf), 36.4, 27.0, 26.1 (CH_2, Cy).

Preparation of $(Cy_2N)_2Ti(CH_2SiMe_3)_2$ (3.9):

Method A: Addition of $LiCH_2SiMe_3$ (0.85 g, 10.5 mmol) to a stirred orange suspension of $(Cy_2N)_2TiCl_2$ **(3.5)** (2.5 g, 5.2 mmol) in THF (60 ml) at room temperature slowly turned the color brown . The stirring was continued overnight

after which LiCl was removed by filtration. The filtrate was cooled and yellow microcrystals of **3.9** separated upon standing overnight (1.6 g, 2.7 mmol, 53%) at -30°C.

Method B: Addition of $LiCH_2SiMe_3$ (0.4 g, 5.2 mmol) to an emerald green solution of $(Cy_2N)_2Ti(\mu\text{-}Cl)_2Li(TMEDA)$ **(3.1)** (1.6 g, 2.6 mmol) in hexane (40 ml) at -10°C turned the color to brown. The solution was slowly warmed to room temperature and the stirring was continued at room temperature for about 24 hours. The resulting solution was filtered which yielded bright yellow, microcrystalline **3.9** (0.9 g, 1.5 mmol, 58%) upon standing overnight at -30°C.

Elemental Analysis for $C_{32}H_{66}N_2Si_2Ti$: Calcd (Obsvd): C 65.93 (65.76); H 11.41 (11.48); N 4.81 (4.62).

Infrared Spectrum (Nujol mull, cm^{-1}) : 1452(s), 1376(s), 1344(in), 1245(s), 1159(m), 1143(w), 1103(s), 1068(w), 1027(s), 980(m), 952(s), 897(s), 836(s), 779(w), 747(m), 718(s), 682(m), 614(m), 591(m), 580(m), 510(m), 493 (m), 427(m).

^1H NMR [C_6D_6, 200 MHz, δ(ppm)]: 3.5 (m, 2H, Cy), 2.1-1.1 (bd m, 20H, Cy), 1.3 (s, 2H, CH_2), 0.3 (s, 9H, $SiMe_3$).

^{13}C NMR [C_6D_6, 125 MHz, δ(ppm)]: 69.7 (CH_2, CH_2SiMe_3), 58.2 (CH, Cy), 37.1,

27.8, 26.3 (CH_2, Cy), 5.0 (CH_3, $SiMe_3$).

Preparation of $(Cy_2N)_2Ti(CH_2CMe_2C_6H_4)$ (3.10):

A solution of $(Cy_2N)_2Ti(CH_2CMe_2Ph)_2$ **(3.8)** (1.8 g, 2.7 mmol) in hexane (70 ml) was heated at 60°C for five minutes. The resulting clear yellow solution yielded yellow crystals of **3.10** (1.2 g, 2.2 mmol, 81%) upon standing at -30°C for two days.

Elemental Analysis for $C_{34}H_{56}N_2Ti$: Calcd (Obsvd): C 75.52 (75.38); H 10.44 (10.61); N 5.18 (5.17).

Infrared Spectrum (Nujol mull, cm^{-1}): 1567(w), 1421(w), 1392(w), 1376(w), 1365(w), 1348(w), 1251(m), 1230(w), 1162(m), 1143(m), 1118(br), 1089(w), 1066(w), 1031(br), 981(m), 966(br), 890(s), 840(sh), 806(sh), 781(sh), 761(sh), 723(m), 709(sh), 686(w), 603(s), 590(m), 586(m), 503(sh), 488(sh), 453(sh).

^1H NMR [C_6D_6, 500 MHz, δ(ppm)]: 7.27-7.16 (m, 2H, Ph), 7.12-7.0 (m, 2H, Ph), 3.85-3.79 (m, 4H, CH, Cy), 2.02 (s, 2H, CH_2, Nf), 1.69 (s, 6H, CH_3, Nf), 1.99-0.87 (m, 40H, CH_2, Cy).

^{13}C NMR [C_6D_6, 125 MHz, δ(ppm)]: 193.5, 160.5 (C, Ph, Nf), 131.0, 128.6, 124.9, 123.8 (CH, Ph, Nf), 57.3 (CH, Cy), 41.8 (C, Nf), 37.0 (CH_2, Nf), 36.9 (CH_3, Nf), 27.1, 26.9, 26.1 (CH_2, Cy).

Preparation of $[(i\text{-}Pr_2N)_2TiPh_2][Li(TMEDA)_2]$ (3.11):

The addition of $PhLi.(Et_2O)_{1.5}$ (1.6 g, 8.2 mmol) to a forest green solution of $[(i\text{-}Pr_2N)_2TiCl_2][Li(TMEDA)_2]$ **(3.2)** (2.4 g, 4.3 mmol) in Et_2O turned the color cherry red. The reaction mixture was stirred at room temperature for about 2 hours and then filtered to remove LiCl. Dark red crystals of **3.11** (1.7 g, 2.6 mmol, 60%) were obtained from the resulting solution upon standing overnight at room temperature.

Elemental Analysis for $C_{36}H_{70}N_6TiLi$: Calcd (Obsvd): C 67.37 (66.69); H 10.99 (10.75); N 13.09 (12.78).

Magnetic Moment: $\mu_{eff.} = 1.77\ \mu_B$.

Infrared Spectrum (Nujol mull, cm^{-1}): 1610(w), 1549(s), 1457(s), 1407(m), 1381(s), 1346(s), 1287(s), 1245(m), 1228(m), 1169(s), 1126(m), 1099(s), 1068(s), 1043(m), 1029(s), 1009(s), 978(s), 946(s), 921(s), 848(s), 806(s), 788(s), 714(m), 705(s), 633(w).

Preparation of $[\{(Me_3Si)_2N\}_2Ti(CH_2Ph)_2][Li(TMEDA)_2]$ (3.12):

TMEDA (4.0 ml) was added to a solution of $[\{(Me_3Si)_2N)_2TiCl_2][Li(TMEDA)_2]$ **(3.3)** (1.9 g, 2.8 mmol) in toluene (40 ml) at room temperature followed by the addition of t-BuLi (3.3 ml of 1.7 M, 5.6 mmol) at -78°C. The reaction was instantaneous and orange crystals of **3.12** (1.9 g, 2.4 mmol, 86%) separated from the

resultant solution upon standing overnight at room temperature.

Elemental Analysis for $C_{38}H_{82}N_6Si_4TiLi$: Calcd (Obsvd): C 57.75 (57.45); H 10.46 (10.12); N 10.63 (10.52).

Magnetic Moment: $\mu_{eff.} = 1.73\ \mu_B$.

Infrared Spectrum (Nujol mull, cm^{-1}): 1589(s), 1470(br), 1376(m), 1357(m), 1288(sh), 1249(br), 1209(m), 1182(m), 1159(m), 1128(sh), 1097(sh), 1068(sh), 1029(sh), 1014(sh), 970-775(br), 746(br), 698(m), 665(m), 624(m), 588(w), 559(m), 512(m), 493(w), 439(w).

Preparation of $[\{(Me_3Si)_2N\}_2Ti(CH_2Ph)_2]$ (3.13):

A solution of $[\{(Me_3Si)_2N\}_2Ti(CH_2Ph)_2][Li(TMEDA)_2]$ (**3.12**) (1.7 g, 2.1 mmol) in toluene (60 ml) was cooled to -10°C and treated with diphenyl fulvene (0.5 g, 2.2 mmol). The color immediately turned dark red and the stirring was continued for 2 hours at room temperature. After removal of the solvent, the residual solid was recrystallized in Et_2O and the resulting solution allowed to stand at -30°C overnight, upon which red cubes of **3.13** (0.7 g, 1.3 mmol, 62%) separated.

Elemental Analysis for $C_{26}H_{50}Si_4N_2Ti$: Calcd (Obsvd): C 56.68 (56.06); H 9.15 (8.88); N 5.08 (4.76).

Infrared Spectrum (Nujol mull, cm^{-1}): 1596(sh), 1488(m), 1465(br), 1376(m), 1249(s, br), 1207(m), 1027(w), 1012(w), 993(w), 871-671(br), 619(w), 561(m), 507(m), 428(m).

^1H NMR [C_6D_6, 200 MHz, δ(ppm)]: 7.4-7.35 (m, 5H, Ph, Bz), 3.33 (s, 2H, CH_2, Bz), 0.49 (s, 18H, Me_3Si).

^{13}C NMR [C_6D_6, 50 MHz, δ(ppm)]: 148.7 (C, Ph, Bz), 128.3, 127.1, 123.5 (CH, Ph, Bz), 99.9 (CH_2, Bz), 5.9 (Me, $SiMe_3$).

Preparation of $[(Cy_2N)_2TiCl]_2O$ (3.14):

The addition of styrene oxide to a green toluene solution of $[(Cy_2N)Ti(\mu\text{-}Cl)_2Li(TMEDA)]$ **(3.1)** (2.4 g, 4.0 mmol) at room temperature with stirring changed the color immediately to orange. The solution was filtered to remove LiCl.TMEDA and allowed to stand at -30°C overnight upon which orange crystals of **3.14** separated (1.1 g, 2.4 mmol, 60%).

Elemental Analysis for $C_{48}H_{88}N_4Ti_2Cl_2O$: Calcd (Obsvd): C 63.78 (62.38); H 9.81 (9.70); N 6.20 (5.93).

Infrared Spectrum (Nujol mull, cm^{-1}): 1452(s, br), 1376(sh), 1344(w), 1251(w), 1159(m), 1143(w), 1105(s), 1079(m), 1027(br), 981(m), 960(sh), 892(s), 842(s), 808(w),

786(w), 746(sh), 709(w), 590(w), 572(m), 511(m), 491(w), 449(m).

^{1}H NMR [C_6D_6, 200 MHz, δ(ppm)]: 3.85 (m, 1H, Cy), 2.3-1.1 (bd m, 10H, Cy).

^{13}C NMR [C_6D_6, 50 MHz, δ(ppm)]: 60.3 (CH, Cy), 35.7, 26.7, 25.9 (CH_2, Cy).

Preparation of $(Cy_2N)_2TiMe]_2O$ (3.15):

MeLi (1.5 ml, 2.0 mmol of 1.4M solution in diethylether) was added to a THF (80 ml) suspension of **3.14** (0.9 g, 1.0 mmol) at -70°C while stirring. The stirring was continued for 24 hours and the solvent was removed *in vacuo*. The residual solid was recrystallized from toluene (25ml) and yellow microcrystalline solid (80 mg, 0.09 mmol, 9%) was obtained upon cooling for two days at -30°C.

Elemental Analysis for $C_{50}H_{94}N_4Ti_2O$: Calcd (Obsvd): C 69.58 (68.87); H 10.98 (10.36); N 6.49 (5.98).

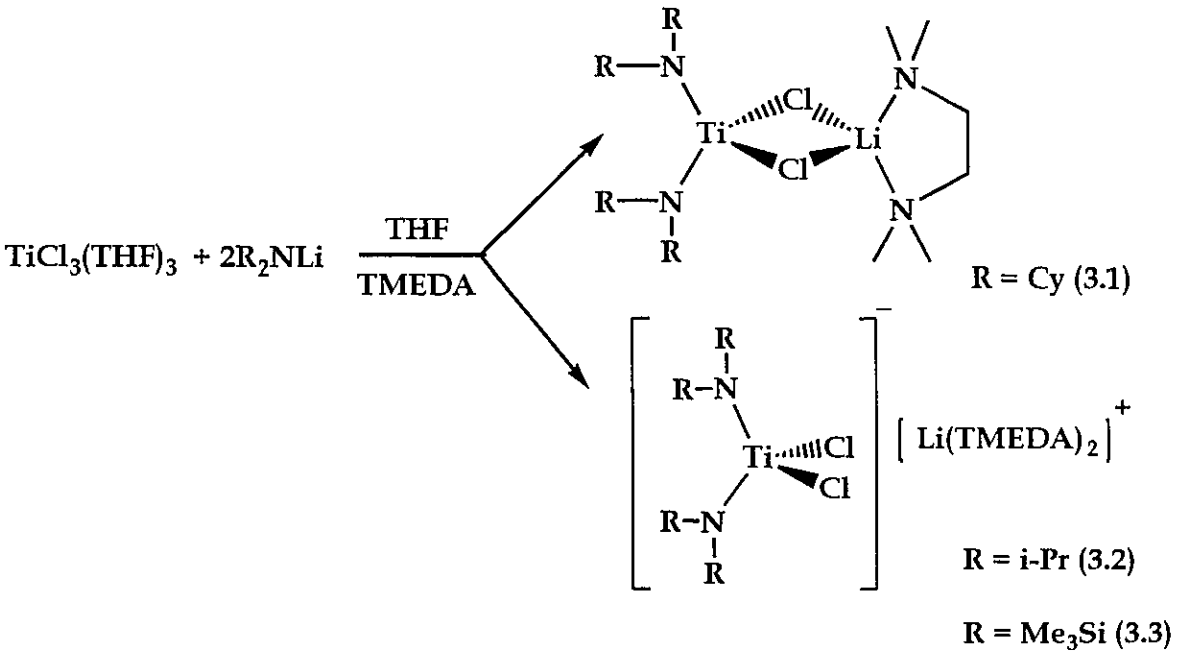
Infrared Spectrum (Nujol mull, cm^{-1}): 1450(sh), 1376(s), 1344(m), 1267(w), 1249(m), 1159(m), 1143(m), 1112(sh), 1087(sh), 1029(br), 981(m), 968(sh), 890(sh), 842(sh), 771(br), 707(m), 588(m), 576(w), 530(w), 501(br).

^{1}H NMR [C_6D_6, 500 MHz, δ(ppm)]: 3.66 (m, 4H, Cy), 2.1-1.13 (bd m, 40H, Cy), 0.94 (s, 3H, Me).

^{13}C NMR [C_6D_6, **125 MHz, δ(ppm)]:** 58.1 (CH, Cy), 38.4 (CH_3, Me), 36.4, 26.9, 26.8 (CH_2, Cy).

III.3 : Results and Discussion

As illustrated in **Scheme 3.1**, the reaction of $TiCl_3(THF)_3$ with two equivalents of R_2NLi (R = Cy, i-Pr, Me_3Si) in THF, and in the presence of TMEDA yielded the corresponding bisamide titanium halides which were isolated as very air-sensitive green crystals. Depending upon the nature of the dialkylamide organic substituent,



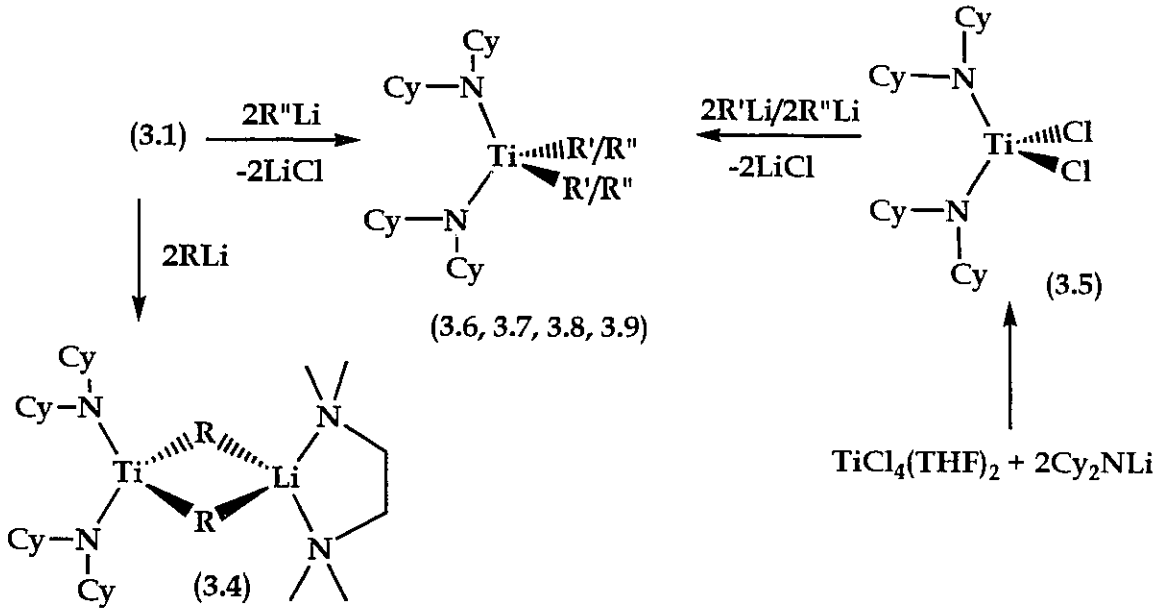
Scheme 3.1

heterodinuclear [R = Cy **(3.1)**] or ionic [R = i-Pr **(3.2)**; R = Me_3Si **(3.3)**] complexes were isolated. Combustion analysis data were in agreement with the proposed formulations while X-ray fluorescence data gave the expected 1:2 Ti:Cl ratio for all

the complexes.

Complexes $[(Cy_2N)_2Ti(\mu\text{-}Cl)_2Li(TMEDA)]$ **(3.1)**[9a], $[(i\text{-}Pr_2N)_2TiCl_2][Li(TMEDA)_2]$ **(3.2)**[21] and $[\{(Me_3Si)_2N\}_2TiCl_2][Li(TMEDA)_2]$ **(3.3)**[17] are paramagnetic, with magnetic moments (μ_{eff} = 1.7-1.8 μ_B) as expected for the d^1 electronic configuration of Ti(III) and display uninformative NMR spectra. In addition, the molecular structures of complexes **(3.1)**[21] and **(3.3)**[17] were elucidated by X-ray crystal structures. Alkylation of **(3.1)** carried out with alkyllithium reagents gave the corresponding tri- and tetravalent alkyl complexes depending on the nature of the alkylating agent employed. The reaction of **(3.1)** with BzLi(TMEDA) and MeLi gave simple chloride substitution forming the trivalent $[(Cy_2N)_2TiR_2Li(TMEDA)]$ [R = Bz **(3.4a)**, Me **(3.4b)**] where both the oxidation state and the heterodinuclear frame were preserved[9a]. Conversely, in the case of bulkier alkylating agents, air-sensitive tetravalent neutral complexes, formulated as $(R_2N)_2TiR''_2$ [R'' = CH_2CMe_3 **(3.7)**, CH_2CMe_2Ph **(3.8)**, CH_2SiMe_3 **(3.9)**] were formed **(Scheme 3.2)**. The formulae were inferred from combustion analysis data. X-ray fluorescence data and qualitative analytical tests for both Li and Cl were also in agreement with the proposed formulation. Complexes **3.6, 3.7, 3.8** and **3.9** were conveniently synthesized in higher yield (50-55%) by using the tetravalent complex $(Cy_2N)_2TiCl_2$ **(3.5)** as the starting material. All the complexes were yellow in color and have been isolated in crystalline form. The common feature in the ^1H NMR spectra of all these complexes is the presence of the multiplet in the range 2.1-1.0 ppm attributed to the methylene

protons of the cyclohexyl rings, and a multiplet in the range 3.5-4.0 ppm due to the *ipso* protons of the cyclohexyl rings. Complex $(Cy_2N)_2Ti(CH_2Ph)_2$ **(3.6)** shows a sharp singlet at 2.7 ppm for the methylene protons of benzyl along with a multiplet in the aromatic region for the phenyl ring protons. $^{13}C\{^1H\}$ and HMQC spectra were also



R = Bz (3.4a), Me (3.4b)

R'/R" = CH_2CMe_3 (3.7), CH_2CMe_2Ph (3.8), CH_2SiMe_3 (3.9)

R' = CH_2Ph (3.6),

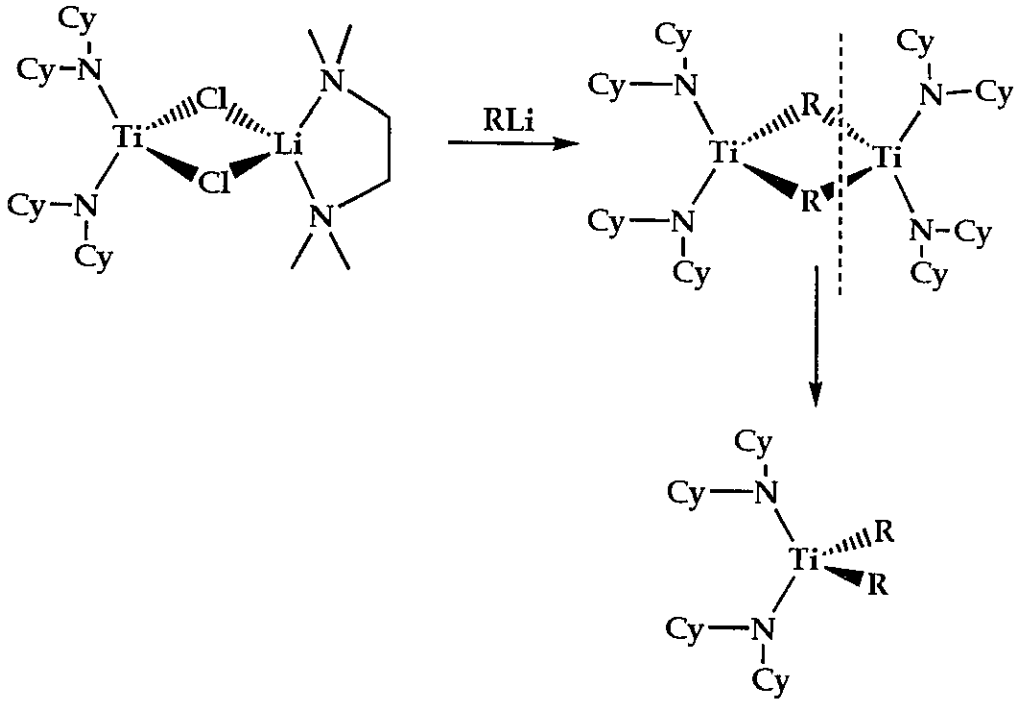
Scheme 3.2

consistent with this formulation showing the appropriate coupling. The ^1H NMR spectrum of complex $(Cy_2N)_2Ti(CH_2CMe_3)_2$ **(3.7)** showed a sharp singlet at 1.65 ppm for the methylene protons in the alkyl group and another singlet at 1.3 ppm for the methyl protons of the neopentyl group in the ratio 2:9.

Complex $(Cy_2N)_2Ti(CH_2CMe_2Ph)_2$ **(3.8)** showed three multiplets in the aromatic region (7.52-7.07 ppm) assigned to the phenyl groups. In addition, two singlets at 1.78 ppm for the methylene protons and at 1.54 ppm for the methyl protons of the neophyl substituent were found in the correct ratio 1:3. The fact that only one methyne proton resonance was determined in the spectra of all these complexes indicates that the cyclohexyl rings are equivalent. Two singlets at 1.3 ppm for the methylene protons and at 0.3 ppm for the Me_3Si protons respectively in the ratio 2:9 are present in the NMR spectrum of complex $(Cy_2N)_2Ti(CH_2SiMe_3)_2$ **(3.9)**. The methylene groups of the alkyl directly connected to the titanium atom display chemical shifts at fields (1.3 - 2.7 ppm) which are considerably lower than those of the cyclopentadienyl analogues. This trend, which becomes even more pronounced in the ^{13}C-NMR spectra, indicates that the amide groups significantly modify the nature of the Ti-C bond by introducing a higher degree of covalency.

In order to explain the oxidation of Ti(III) alkyl to Ti(IV) corresponding derivatives, we tentatively suggest that the initially formed intermediate $(Cy_2N)_2TiR'$ species cannot be sufficiently stabilized by the formation of ionic species $[(Cy_2N)_2TiR'_2Li(TMEDA)]$ such as in the case of complexes **3.1, 3.2, 3.3** and **3.4**. This is also suggested by the fact that the result of the reaction was not modified by a different stoichiometric ratio or by the use of excess of alkylating agent. Therefore, we speculate that the coordinatively unsaturated $(Cy_2N)_2TiR'$ moiety probably forms a dinuclear complex where the two metal centers are bridged *via*

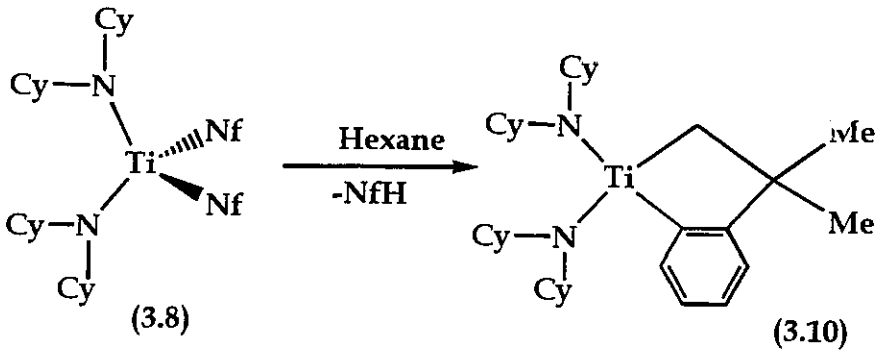
either amide or alkyl. Subsequent disproportionation of this dimer **(Scheme 3.3)** forms both tetravalent and divalent species through a mechanism analogous to that previously described for **3.4b** or Zr(III) dimers. However, different from the case of Zr, attempts to isolate the corresponding Ti(II) species formed as a result of such a disproportionation remained unsuccessful in the present work.



Scheme 3.3

This new class of Ti(IV) alkyl complexes display a moderate thermal stability in the solid state. However, these complexes were found to be rather unstable in solution, where all these derivatives showed a tendency to slowly decompose, even at room temperature. Complex **3.7** completely decomposed at room temperature in about 4-5 days forming neopentane together with some intractable materials. However, complex **3.8** yielded the cyclometallated species

$(Cy_2N)_2Ti(CH_2CMe_2C_6H_4)$ **(3.10)** upon standing **(Scheme 3.4)** at room temperature for a period of 5-6 weeks. As expected, the reaction was greatly accelerated when a hexane solution of **3.8** was heated for a few minutes at 60°C. The ^1H NMR spectrum



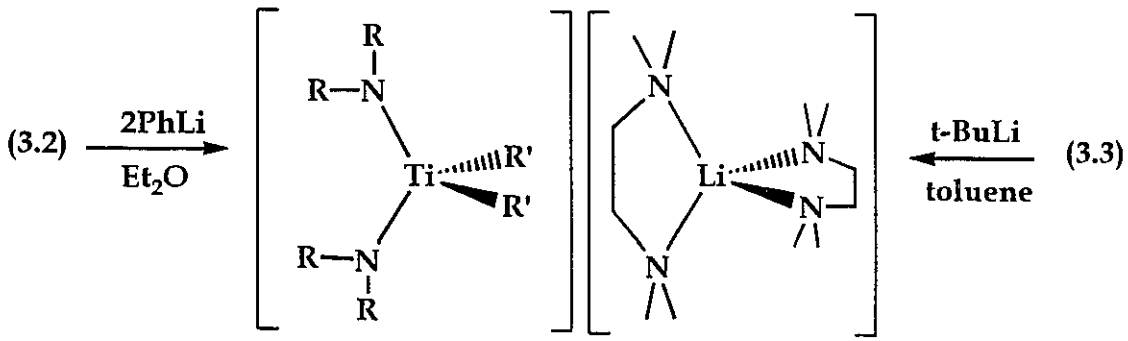
NfH = CMe_3Ph

Scheme 3.4

of this complex showed singlets attributed to methylene and methyne protons being considerably shifted to lower fields. For example the methylene protons were found at 2.02 ppm while the methyl protons of neophyl were located at 1.69 ppm. The aromatic signals were also significantly modified with respect to those of complex **3.8**. The integration of the spectrum showed loss of one neophyl ligand. Accordingly, during the thermolysis in a sealed NMR tube, one equivalent of $(CH_3)_3C(Ph)$ was formed thus indicating that deprotonation of the remaining neophyl molecule occurred probably *via* metallation of the aromatic ring and consequent formation of a metallacycle.

The reaction of the isopropyl halide derivative **3.2** with a number of

alkyllithium agents yielded intractable materials. Only in the case of PhLi was a clean reaction obtained, allowing the isolation of a new complex $[(i\text{-}Pr_2N)_2TiPh_2][Li(TMEDA)_2]$ **(3.11)** in crystalline form **(Scheme 3.5)**. The magnetic moment (μ_{eff} = 1.77 μ_B), calculated on the basis of the formulation provided by analytical data and X-ray crystal structure[21] was in agreement with a d^1 electronic configuration of a Ti(III) metal center.



R = i-Pr, R' = Ph (3.11)

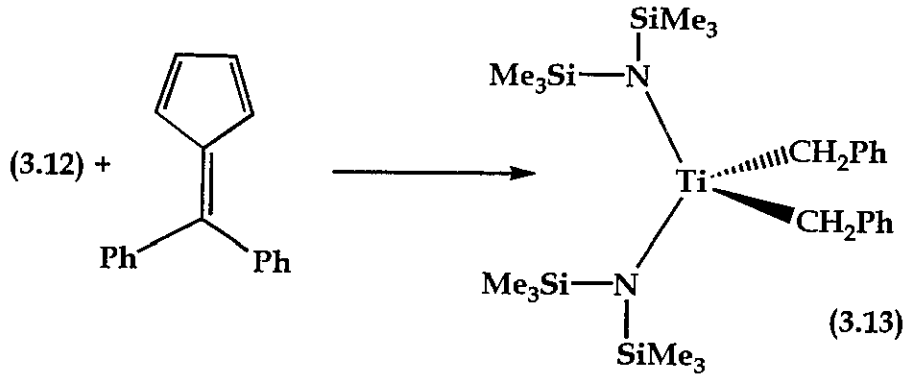
R = Me_3Si, R' = CH_2Ph (3.12)

Scheme 3.5

Anionic Ti(III) dibenzyl complex **(3.12)** was obtained in the case of the silylated amide derivative **3.3**. Golden yellow crystals of $[\{(Me_3Si)_2N\}_2Ti(Bz)_2]^-$ **(3.12)** were obtained by treating **3.3** with t-BuLi in toluene. A mixture of isobutene and isobutane was found in both the gaseous mixture and the mother liquor. The origin of the benzyl groups in complex **3.12** might be attributed to the formation of $PhCH_2Li$ generated *in situ* by the fast reaction of t-BuLi with toluene, and subsequent reaction with the Ti substrate. However, the possibility that **3.12** might

originate from reaction with toluene of the *in situ* generated $\{[(Me_3Si)_2N]_2Ti(t\text{-}Bu)_2\}^-[Li(TMEDA)_2]^+$ cannot be excluded. Reaction of **3.12** with t-BuLi in either hexane or ether gave only intractable materials.

Similar to the other Ti(III) and Ti(IV) alkyls reported in this chapter, complex **3.12** was also found to be thermally labile as solution, in both toluene and THF in



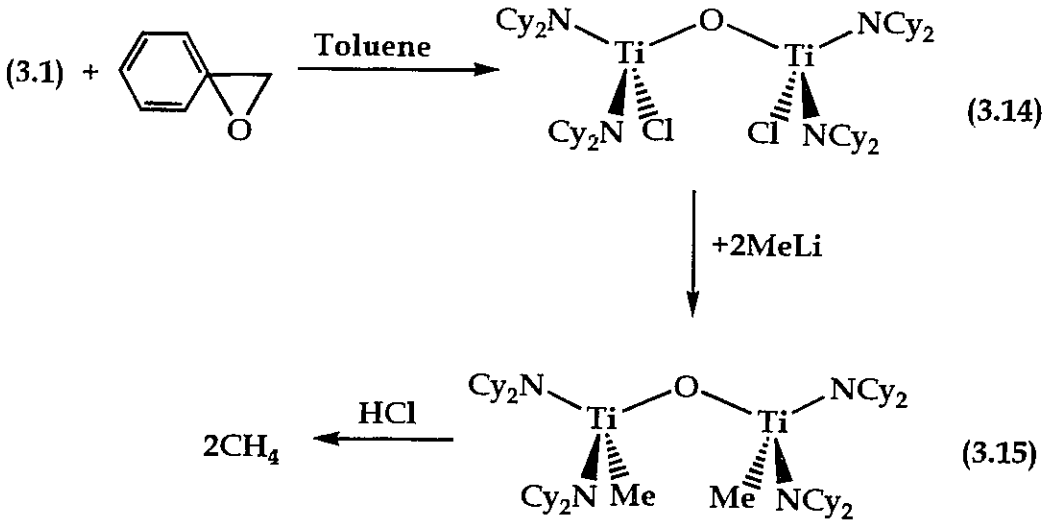
Scheme 3.6

which it decomposed, forming intractable materials. Nevertheless, the reaction of **3.12** with diphenylfulvene resulted in the formation of a neutral Ti(IV) complex $[\{(Me_3Si)_2N\}_2Ti(CH_2Ph)_2]$ **(3.13)** **(Scheme 3.6)** which crystallized as red cubes from hexane in about 59% yield. The complex was characterized by analytical and spectroscopic data. Complex **3.13** could not be synthesized by using the more straightforward synthetic strategy described for the other Ti(IV) alkyls reported above, since the starting $\{(Me_3Si)_2N\}_2TiCl_2$ could not be prepared. However, the reaction of **(3.12)** with diphenylfulvene provided the desired complex **3.13** in good yield *via* a simple electron transfer mechanism. Similar to the other Ti(IV) alkyls

reported in this chapter, the CH_2 benzylic resonances of complex **3.12** were found shifted to considerably lower field of the ^1H NMR spectra.

Complex **3.1** reacted with styrene oxide in toluene at room temperature to form a dinuclear oxo-bridged complex $[(Cy_2N)_2TiCl]_2O$ **(3.14) (Scheme 3.7)** which was isolated as orange crystals. The infrared spectrum showed the Ti-O stretching as a broad intense band at 746 cm^{-1}. The ^1H NMR spectrum of the complex showed only one type of cyclohexyl group, with a multiplet at 3.85 ppm and the characteristic series of multiplets in the range 1.1-2.3 ppm.

The alkylation reaction of **3.14** was achieved only with MeLi. The reaction yielded the corresponding dialkyl complex $[(Cy_2N)_2TiMe]_2O$ **(3.15)** which was characterized on the basis of analytical and spectroscopic data. In addition to the resonances of the cyclohexyl groups shifted to slightly higher field, a new sharp singlet at 0.94 ppm corresponding to the methyl group was observed in the ^1H NMR spectrum. $^{13}C\{^1H\}$, and HMQC spectra also confirmed the formulation. The infrared spectrum showed a Ti-O absorption at 770 cm^{-1}, which is slightly shifted with respect to the starting material **3.14**. Unfortunately, numerous attempts to crystallize this complex to obtain X-ray quality crystals were unsuccessful. However, chemical degradation experiments with gaseous HCl carried out in a closed vessel connected to a Toepler pump yielded the expected amount of methane.



Scheme 3.7

In conclusion, in this chapter we have shown that anionic orgainc amides are versatile supporting ligands for the stabilization of a full series of reactive Ti alkyl derivatives.

III.4 : X-Ray Crystallography

Data were collected at temperatures in the range 23 to -160°C using the ω-2θ scan technique to a maximum 2θ value of 50.0°, for suitable air-sensitive crystals mounted on glass fibres. Cell constants and orientation matrices were obtained from the least-squares refinement of 25 carefully centered high-angle reflections. Redundant reflections were removed from the data set. The intensities of three representative reflections were measured after every 150 reflections to monitor crystal and instrument stability. Data were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were

located in the difference Fourier maps and refined isotropically in the case of favourable observation/parameter ratio. The final cycle of full-matrix least-squares refinement was based on the number of observed reflections with [$I > 2.5\sigma$ (I)]. Neutral atomic scattering factors were taken from Cromer and Waber[20]. Anomalous dispersion effects were included in Fcalc. All calculations were performed using the TEXSAN package on a Digital VAX station. Selected bond distances and angles are given in **Appendix B.**

The molecular structure of **3.10** was confirmed by single crystal X-ray diffraction analysis **(Fig. 3.1)**. The molecule is a monomer with the Ti atom bonded to two Cy_2N groups and engaged into a five-membered metallacycle with an ortho-metallated neophyl group. The Ti atom possesses a slightly distorted tetrahedral geometry [N1-Ti1-N2 = 120.93(8)°, N1-Ti1-C25 = 111.98(8)°, N1-Ti1-C30 = 110.26(8)°, N2-Ti1-C25 = 110.81(8)°, C25-Ti1-C30 = 84.92(9)°], which is bound by two N atoms of the amide groups and two C atoms of one neophyl unit. The neophyl group chelates titanium through the methylene groups and one ortho carbon atom of the phenyl group [Ti1-C25 = 2.121(2)Å, Ti1-C30 = 2.089(2)Å]. The Ti atom was found significantly elevated above the puckered plane [C30-C29-C26-C25 = -19.2(3)°] formed by the four C atoms which compose part of the five-membered ring. Conversely, the metallacycle is nearly coplanar with the phenyl ring of the neophyl group. The two methyl groups borne by the two neophyl β carbon atoms point in opposite directions with respect to the metallacycle plane giving a regular

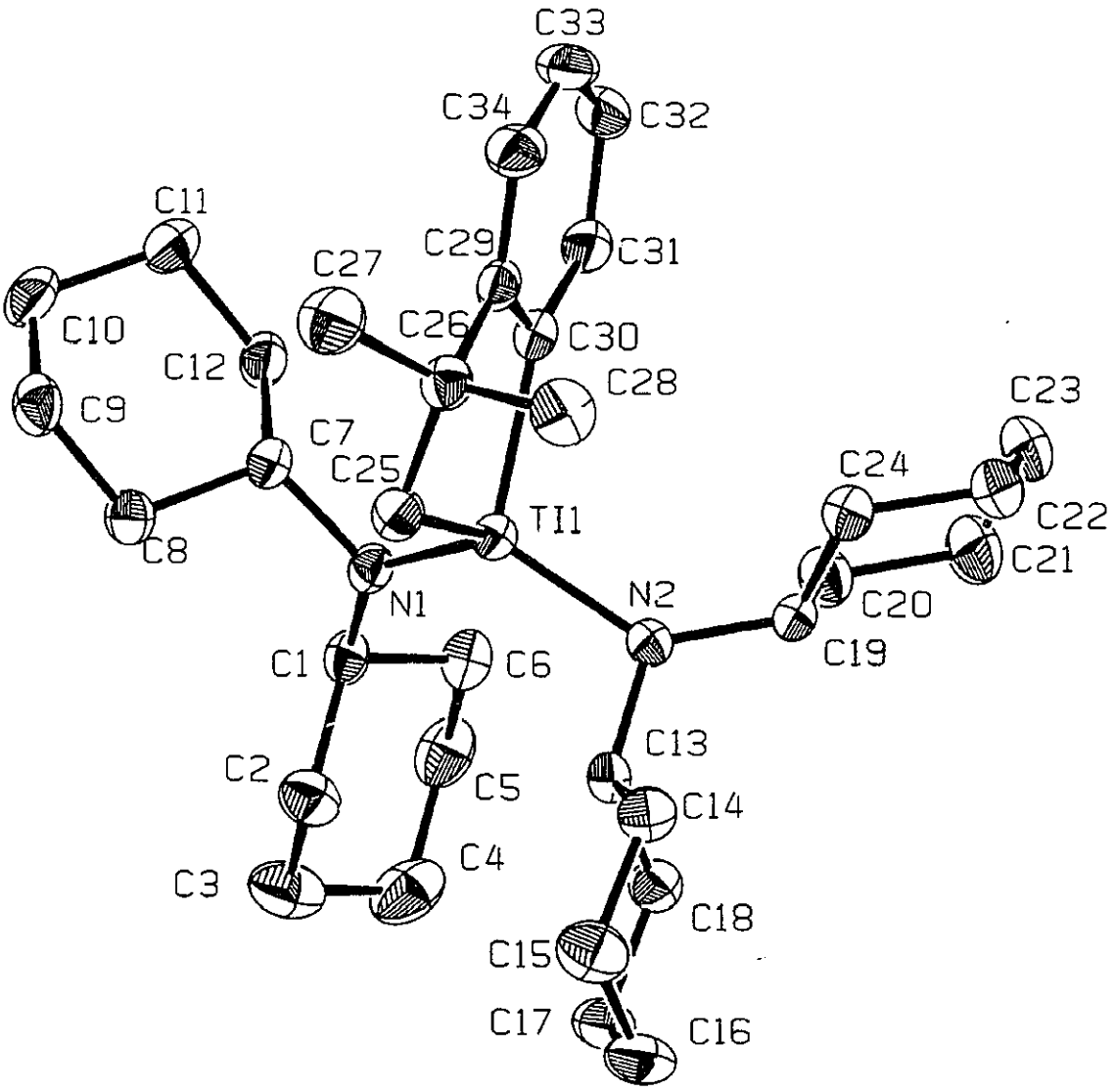


Fig. 3.1. X-Ray Structure of 3.10, $(Cy_2N)_2Ti(CH_2CMe_2C_6H_4)$

Selected Bond Distances (Å) and Bond Angles (deg): Ti1-N1 = 1.896(2), Ti1-N2 = 1.879(2), Ti1-C25 = 2.121(2), Ti1-C30 = 2.089(2), N1-Ti1-N2 = 120.93(8), N1-Ti1-C25 = 111.98(8), N1-Ti1-C30 = 110.26(8), N2-Ti1-C25 = 110.81(8), C25-Ti1-C30 = 84.92(9), Ti1-N1-C1 = 141.3(1), Ti1-N1-C7 = 103.2(1), C1-N1-C7 = 115.5(2).

tetrahedral geometry to the quarternary carbon atom. The distortion around Ti is predominantly caused by the bulky amide ligands whose steric congestion is also indicated by the fact that the geometry of the nitrogen atoms deviates significantly from the regular trigonal plane geometry expected for the sp^2 hybridization [Ti1-N1-C7 = 103.2(1)°, Ti1-N1-C1 = 141.3(1)°, C1-N1-C7 = 115.5(2)°, Ti1-N2-C13 = 108.3(1)°, C13-N2-C19 = 117.2(2)°, Ti1-N2-C19 = 134.5(1)°].

Complex **3.12** is monomeric and also ionic with a $Li(TMEDA)_2$ cationic fragment **(Fig. 3.3)** very similar to that of complex **3.11**[21]. The anion consists of a titanium atom with distorted tetrahedral geometry **(Fig. 3.2)** defined by two N atoms from

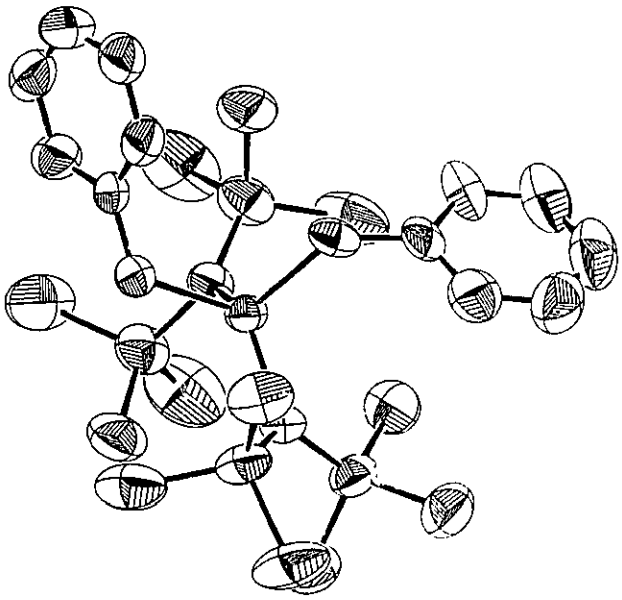


Fig. 3.2. X-Ray Structure of 3.12 anion, $[\{(Me_3Si)_2N\}_2Ti(CH_2Ph)_2]$

Selected Bond Distances (Å) and Bond Angles (deg): Ti1-N1 = 2.036(8), Ti1-N2 =

2.027(8), Ti1-C7 = 2.18(1), Ti1-C14 = 2.18(1), N1-Ti1-N2 = 127.4(3), N1-Ti1-C7 = 108.1(3), N1-Ti1-C14 = 100.0(4), Ti1-N1-Si1 = 116.5(4), Ti1-N1-Si2 = 121.9(4), Si1-N1-Si2 = 121.6(5).

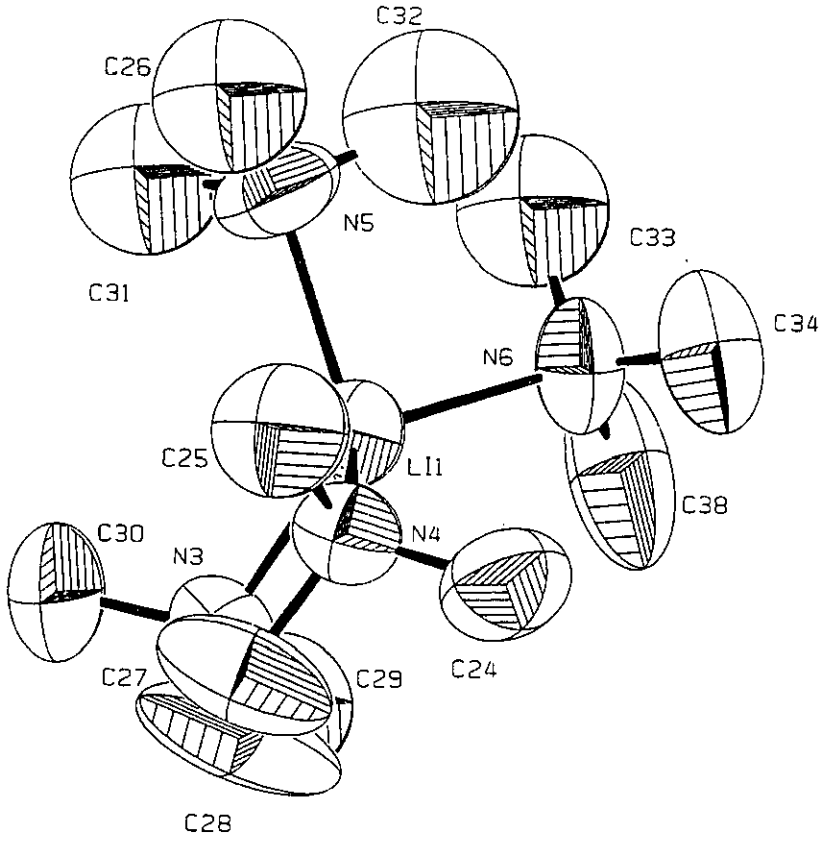


Fig. 3.3. X-Ray Structure of 3.12 cation, [Li(TMEDA)$_2$]

two amide units and two C atoms from the two benzyl substituents [N1-Ti1-N2 = 127.4(3)°, N1-Ti1-C7 = 108.1(3)°, N1-Ti1-C14 = 100.0(4)°, C7-Ti1-C14 = 97.4(4)°]. The nitrogen atoms of the amides show the usual trigonal planar geometry indicative of some extent of Ti-N π bonding [Ti1-N1-Si1 = 116.5(4)°, Ti1-N1-Si2 = 121.9(4)°,

Si1-N1-Si2 = 121.6(5)°]. The Ti-N [Ti1-N1 = 2.036(8)Å, Ti1-N2 = 2.027(8)Å]. The Ti-C bond distances [Ti1-C7 = 2.18(1)Å, Ti1-C14 = 2.18Å] are comparable with those of complex **3.11**. The bond angles subtended at C7 and C14 are as expected for an sp^3 carbon atom [Ti1-C7-H1 = 109.45°, Ti1-C7-H23 = 107.98°, C8-C7-H1 = 107.58°].

The crystal structure of **3.13** revealed the complex to be monomeric. Even in this case the steric bulk of the amide ligands is likely responsible for the significant distortion of the tetrahedral coordination geometry (**Fig. 3.4**) around the titanium atom [N1-Ti2-N2 = 120.6(1)°, N1-Ti2-C13 = 108.4(2)°, N1-Ti2-C20 = 108.1(2)°, C13-Ti2-C20 = 98.4(2)°]. The geometry of the two nitrogen atoms of the amides slightly deviates from the regular trigonal planar geometry [Ti2-N1-Si1 = 124.8(2)°, Ti2-N1-Si2 = 117.5(2)°, Si1-N1-Si2 = 117.5(2)°]. Conversely, the angles subtended at the benzylic carbons, C13 and C20 [Ti2-C13-C14 = 120.7(3)°, Ti2-C20-C21 = 119.2(3)°] deviate severely from the normal tetrahedral angle. The Ti-N [Ti2-N1 = 1.931(3)Å, Ti2-N2 = 1.939(3)Å] and Ti-C [Ti2-C13 = 2.092(5)Å, Ti2-C20 = 2.109(4)Å] bond distances are slightly shorter with respect to complex **3.12** as a probable result of the smaller atomic *radius* of the Ti(IV) atom.

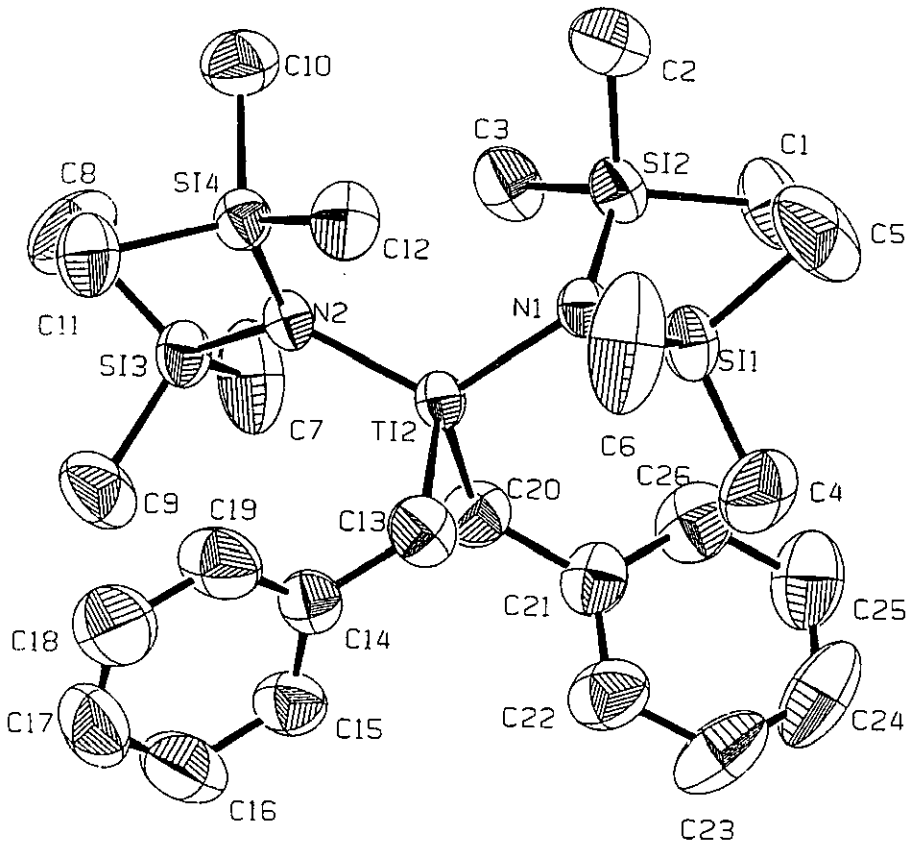


Fig. 3.4. X-Ray Structure of 3.13, $[\{(Me_3Si)_2N\}_2Ti(CH_2Ph)_2]$

Selected Bond Distances (Å) and Bond Angles (deg): Ti2-N1 = 1.931(3), Ti2-N2 = 1.939(3), Ti2-C13 = 2.092(5), Ti2-C20 = 2.109(4), N1-Ti2-N2 = 120.6(1), N1-Ti2-C13 = 108.4(2), N1-Ti2-C20 = 108.1(2), N2-Ti2-C13 = 109.1(2), N2-Ti2-C20 = 110.0(2), Ti2-N1-Si1 = 124.8(2), Ti2-N1-Si2 = 117.5(2), Si1-N1-Si2 = 117.5(2).

The crystal structure determination has proven the complex **3.14** to be dimeric consisting of two identical $(Cy_2N)_2TiCl$ fragments **(Fig. 3.5)** bridged by an oxygen atom. Each titanium atom has tetrahedral geometry [Cl2-Ti1-N2 = 109.9(2)°,

Cl2-Ti1-N1 = 109.2(2)°, Cl2-Ti1-O1 = 109.3(2)°, O1-Ti1-N1 = 113.5(2)°, O1-Ti1-N2 = 108.5(2)°, N1-Ti1-N2 = 106.3(2)°] with two nitrogen atoms from two amides, one

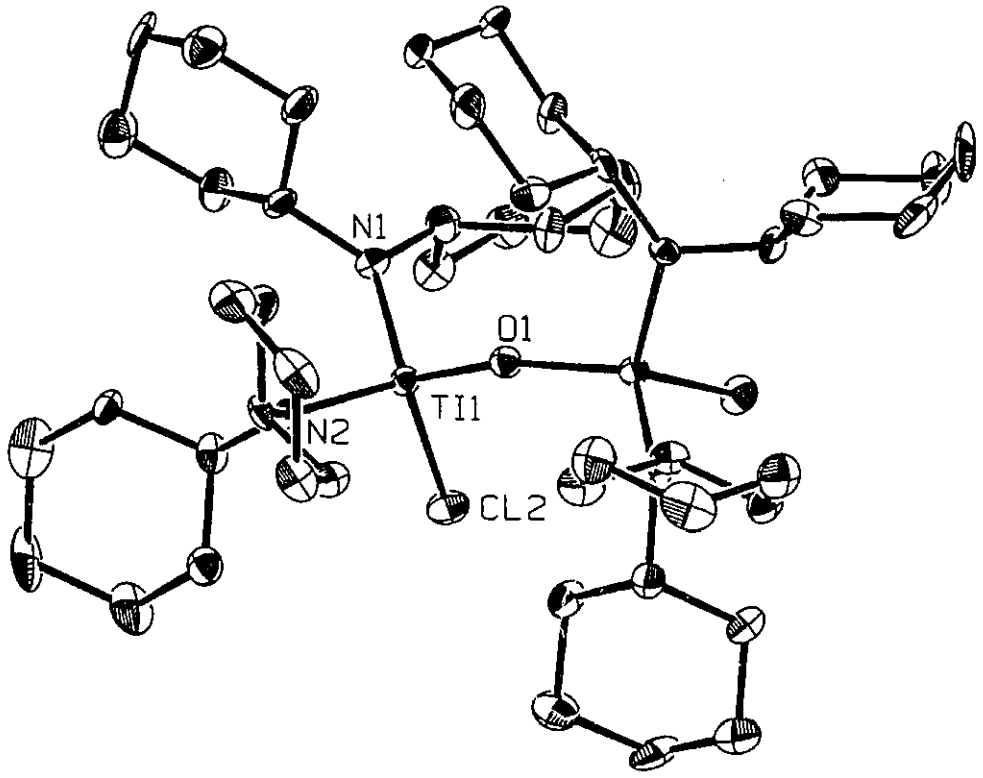


Fig. 3.5. X-Ray Structure of 3.14, $[(Cy_2N)_2TiCl]_2O$

Selected Bond Distances (Å) and Bond Angles (deg): Ti1-Cl2 = 2.296(2), Ti1-O1 = 1.828(2), Ti1-N1 = 1.910(6), Ti1-N2 = 1.876(6), Cl2-Ti1-O1 = 109.3(2), Cl2-Ti1-N1 = 109.2(2), Cl2-Ti1-N2 = 109.9(2), O1-Ti1-N1 = 113.5(2), O1-Ti1-N2 = 108.5(2), N1-Ti1-N2 = 106.3(2), Ti1-O1-Ti1 = 154.9(4).

chloride and the oxygen atom. The nitrogen atoms have a very slightly distorted trigonal planar geometry [Ti1-N1-C1 = 120.6(5)°, Ti1-N1-C7 = 123.5(4)°, C1-N1-C7 =

115.7(5)°]. The short Ti-N distances [Ti-N1 = 1.876(6), Ti1-N2 = 1.910(6)] are as usual. The Ti-O distances are remarkably short [Ti1-O1 = 1.828(2)Å] while the Ti-O-Ti frame is bent with an angle subtended at the oxygen atom [Ti1-O1-Ti2 = 154.9(4)°] which is similar to that of other oxo-bridged compounds[4d, 5k].

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CHAPTER IV

The Stability of V(II) Aryloxides: Synthesis and Characterization of Sterically Protected, Neutral and Monomeric V(II) Aryloxides. Reactivity with the N-N Bond of $(Me_3Si)CH=N=N$.

IV. 1 : Introduction

Disproportionation or electron-transfer reactions are among the most common reaction pathways through which a transition metal complex decomposes, when it is in unstable oxidation state. The most obvious method of preventing unwanted disproportionations, which are occasionally a severe obstacle to synthetic efforts, is to bury the transition metal inside bulky ligands. This would reduce the ability of the transition metal to reorganize the molecule and modify the oxidation state. This strategy, which is based upon the performance of transition metals in bioinorganic systems, has been successfully used in a number of cases. In the chemistry of early transition metals, it has allowed the isolation of transition metals in unstable oxidation states[1] or in unusual coordination geometries,[2] and the trapping and stabilization of many diverse highly-reactive functionalities.[3]

The poor development of the coordination chemistry of divalent vanadium and in particular its alkoxide derivatives, can be attributed to the instability of this oxidation state. For example, simple V(II) aryloxides are extremely rare,[4] despite the

strong interest stimulated by the initial discovery that a few cycles of catalytic transformation of dinitrogen into NH_3 and hydrazine are promoted by *in situ* generated V(II) catecholate or hydroxide, just before irreversible oxidation of the metal center takes place.[5] This suggests that V(II) species supported by oxygen-containing ligands might be very promising starting materials for reactivity studies and therefore encourages further synthetic efforts to prevent oxidation or disproportionation. Interest in the chemistry of V(II) alkoxides has been also stimulated by the fact that these species may conveniently serve as starting materials for the preparation of high-nuclearity oxo/alkoxo vanadates, which have recently been shown to play a relevant role in some important biological processes.[6] The synthetic difficulties generally encountered in the preparation of V(II) complexes seem to be caused by an apparent instability of the divalent state with respect to either disproportionation towards higher and lower oxidation states, or deoxygenation reactions.[7] Attempts to prepare neutral V(II) aryloxides *via* mild-condition ligand replacement reactions in V(II) starting compounds have also been unsuccessful,[8] only two V(II) anionic aryloxides having been reported so far.[4]

In this chapter, we report the synthesis and characterization of the first series of neutral V(II) aryloxides stabilized by sterically demanding or chelating aryloxides. In an attempt to gain insight into their ability to interact with dinitrogen, we have also carried out ligand replacement reactions under mild conditions on a preformed V-(N_2)-V frame of an aryl-dinitrogen vanadium complex $[Mz_2VPy]_2(\mu\text{-}N_2)$ [Mz =

o-$Me_2NCH_2C_6H_4$].[9] We now describe the reaction of this dinitrogen complex and of other V(II) compounds with a series of phenols and corresponding alkali salts together with a preliminary study on the reactivity with the N-N multiple bond of a diazoalkane.

IV. 2 : Experimental Section

All operations were performed under an inert atmosphere in a nitrogen-filled dry-box (Vacuum Atmosphere) or by using standard Schlenk techniques. $[Mz_2Vpyridine]_2(N_2)(thf)_2$ **(4.1)**[9], $Mz_2Vpyridine_2$ **(4.2)**[10], *trans*-$VCl_2(TMEDA)_2$ **(4.3)**[10], $Mes_3V(THF)$[11] and $\{[2,6\text{-}(MeO)_2C_6H_3]_2V\}_2(THF)$[12] were prepared according to published procedures. TMEDA was distilled over molten potassium after refluxing; pyridine was refluxed over CaH_2 and distilled under nitrogen. Phenols (Aldrich) were sublimed before use. NaH (suspension in mineral oil) was washed with hexane, dried and stored under nitrogen in sealed ampoules. Infrared spectra were recorded on a Perkin-Elmer 283 instrument from Nujol mulls prepared in a dry-box. Samples for magnetic susceptibility measurements for complex $\{[2,6\text{-}(t\text{-}Bu)_2\text{-}4\text{-}Me\text{-}C_6H_2O]_2V(pyridine)_2\}.(C_7H_8)_2$ **(4.4)** were weighed inside a dry-box equipped with a microanalytical balance, and sealed into a specially designed teflon capsule. Data were recorded at variable temperatures in the range 100 - 298K by using a Faraday balance (Oxford Instruments) interfaced with an Apple II Computer. Plots of $1/\chi_g$ against T(K) were in satisfactory agreement with the Curie-Weiss law. The magnetic moment was calculated following standard

methods[13] and corrections for underlying diamagnetism were applied to data[14]. Magnetic measurements of all the other complexes were carried out with a Gouy balance (Johnson Matthey) at room temperature in sealed tubes of samples prepared in the dry-box.

Preparation of $\{[2,6\text{-}(t\text{-}Bu)_2\text{-}4\text{-}Me\text{-}C_6H_2O]_2V(pyridine)_2\}.(C_7H_8)_2$ (4.4):

Method A : A THF (20 ml) solution of $[Mz_2VPy]_2(\mu\text{-}N_2)(THF)_2$ **(4.1)** (1.3 g, 1.4 mmol) was treated with $2,6\text{-}(t\text{-}Bu)_2\text{-}4\text{-}Me\text{-}C_6H_2OH$ (1.2 g, 5.6 mmol). The mixture was stirred for about 3 hours and the color changed from red to deep orange. The solvent was removed *in vacuo* and the residual solid was dissolved in pentane (50 mL). Brown-red crystals of **4.4** (0.73 g, 0.9 mmol, 32%) were obtained from pentane solution upon standing at -30°C overnight.

Method B: Addition of neat $2,6\text{-}(t\text{-}Bu)_2\text{-}4\text{-}Me\text{-}C_6H_2OH$ (0.7 g, 3.3 mmol) to a toluene solution (50 mL) of Mz_2VPy_2 **(4.2)** (1.0 g, 1.7 mmol) changed the color from emerald green to deep orange immediately. The solution was concentrated to small volume (20 ml) and layered with hexane. Brown-red crystals of **4.4** (0.5 g, 0.6 mmol, 35%) separated out from toluene-hexane mixture at low temperature.

Method C: A THF solution (50 mL) of $2,6\text{-}(t\text{-}Bu)_2\text{-}4\text{-}Me\text{-}C_6H_2OH$ (4.6 g, 20.9 mmol) was stirred with NaH (0.8 g, 33 mmol). After completion of the reaction, excess NaH was filtered off and $VCl_2(TMEDA)_2$ **(4.3)** (3.7 g, 10.4 mmol) was added

to the colorless solution yielding a green reaction mixture. Addition of pyridine (1.7 g, 21 mmol) changed the color from green to red-brown. The resulting mixture was boiled and refluxed overnight. The solvent was removed *in vacuo* and the residual solid redissolved in toluene (50 mL). NaCl was removed by filtration and toluene solution was concentrated to small volume (20 ml). Layering the toluene solution with hexane provided brown-red crystals of **4.4** (5.2 g, 6.2 mmol, 60 %) upon standing overnight at room temperature.

Elemental Analysis for $C_{54}H_{72}N_2O_2V$: Calcd (Obsvd): C 77.94 (77.88); H 8.72 (8.44); N 3.37 (3.07); V 6.12 (5.89).

Magnetic Moment: $\mu_{eff.}$= 3.71 μ_B.

Infrared Spectrum (Nujol mull, cm^{-1}): 1600(s), 1410(m), 1350(m), 1260(s), 1210(m), 1195(w), 1155(w), 1020(w), 880(m), 860(s), 835(s), 805(m), 780(m), 765(s), 720(w), 705(s), 655(w), 620(w).

Preparation of $(2,6\text{-}Ph_2PhO)_2V(TMEDA)$ (4.5):

The addition of NaH (0.4 g, 16 mmol) to a solution of 2,6-diphenylphenol (2.5 g, 10 mmol) in THF (75 mL) was followed by refluxing overnight. The addition of solid *trans*-$VCl_2(TMEDA)_2$ **(4.3)** (1.8 g, 5.0 mmol) to this solution turned the color red immediately. After stirring for a further one hour, the mixture was filtered. The solvent was removed *in vacuo* and the residual solid redissolved in toluene (30 mL).

NaCl was filtered off and large red crystals of **4.5** (2.5 g, 3.8 mmol, 76 %) separated out overnight at -30°C after layering the toluene solution with hexane.

Elemental Analysis for $C_{42}H_{42}O_2N_2V$: Calcd (Obsvd): C 76.69 (76.55); H 6.44 (6.31); N 4.26 (4.32); V 7.74 (7.12).

Magnetic Moment: $\mu_{eff.} = 3.63\ \mu_B$.

Infrared Spectrum (Nujol mull, cm^{-1}): 1580(s), 1550(m), 1450(s), 1420(s), 1405(w), 1350(w), 1300(s), 1280(m), 1245(s), 1175(w), 1120(w), 1110(w), 1075(w), 1060(m), 1040(w), 1005(m), 995(w), 950(s), 930(w), 915(w), 860(s), 800(s), 750(s), 740(s), 725(m), 710(w), 700(s), 600(s), 585(s), 550(m), 510(m), 500(m).

Preparation of $(2,6\text{-}Ph_2PhO)_2V(pyridine)_3$ (4.6):

Method A: A THF solution (25 ml) of $(2,6\text{-}Ph_2PhO)_2V(TMEDA)$ (1.6 g, 2.4 mmol) was allowed to react with pyridine (2 ml). Not much color change was observed and changing the solvent to toluene yielded large deep red crystals of **4.6** (1.1 g, 1.4 mmol, 58 %).

Method B: A toluene solution (50 ml) of Mz_2VPy_2 **(4.2)** (1.0 g, 1.7 mmol) was treated with one equivalent of pyridine and neat Ph_2PhOH (0.8 g, 3.3 mmol). The color changed from emerald-green to deep brown and large deep red crystals of **4.6**

separated upon standing overnight at -30°C.

Method C: A red solution of $(Mz_2VPy)_2(\mu\text{-}N_2)(THF)_2$ **(4.1)** (1.5 g, 1.6 mmol) in toluene (50 ml) was treated with pyridine and Ph_2PhOH as above, but deep red crystals of **4.6** were isolated in low yield (11%).

Elemental Analysis for $C_{51}H_{41}O_2N_3V$: Calcd (Obsvd): C 78.65 (78.33); H 5.31 (5.29); N 5.40 (5.18); V 6.54 (6.33).

Magnetic Moment: $\mu_{eff.} = 3.72\ \mu_B$.

Infrared Spectrum (Nujol mull, cm^{-1}): 1580(s), 1495(s), 1420(m), 1380(s), 1300(m), 1260(m), 1205(m), 1180(w), 1150(w), 1065(w), 1045(w), 1010(w), 980(w), 940(w), 800(s), 760(s), 750(m), 735(s), 700(s), 600(m), 505(m).

Preparation of $[2\text{-}(OCH_3)C_6H_4O]_2V(TMEDA)$ (4.7):

Method A: A THF solution (70 ml) of guaiacol (3.3 g, 27 mmol) was refluxed with NaH (1.0 g, 40 mmol) along with continuous stirring. When the reaction was complete, the excess NaH was filtered off and *trans*-$VCl_2(TMEDA)_2$ **(4.3)** (4.8 g, 13.5 mmol) added to the clear filtrate. The color turned green and the reaction mixture was stirred for 3 hours. The solvent was evaporated to dryness and toluene (50 ml) was added to the resulting solid. The mixture was filtered to remove NaCl followed by layering with ether (20 ml). Brown-orange crystals of **4.7** (2.8 g, 6.8 mmol, 52%)

were isolated at room temperature.

Method B: A light blue suspension of *trans*-$VCl_2(TMEDA)_2$ (1.9 g, 5.3 mmol) in THF (70 mL) was treated with neat guaiacol (1.3 g, 11 mmol) in the presence of a small excess of TMEDA (1.7 g, 14 mmol). The orange colored mixture was boiled and the solvent was removed *in vacuo*. Toluene was added to the residual solid, the insoluble solid filtered off and the filtrate layered with ether. Brown-orange crystals of **4.7** (1.3 g, 3.1 mmol, 58%) separated upon standing overnight at room temperature.

Elemental Analysis for $C_{20}H_{30}O_4N_2V$: Calcd (Obsvd): C 58.11 (58.03); H 7.31 (7.29); N 6.78 (6.38); V 12.32 (12.23).

Magnetic Moment: $\mu_{eff} = 3.83\ \mu_B$.

Infrared spectrum (Nujol mull, cm^{-1}): 1590(s), 1460(s), 1325(s), 1300(s), 1250(m), 1200(s), 1160(s), 1110(m), 1060(w), 1020(s), 950(w), 930(w), 900(w), 850(m), 840(w), 830(w), 800(m), 745(s), 730(m), 595(m), 430(m).

Preparation of $[2\text{-}(OCH_3)C_6H_4O]_2V(py)_2$ (4.8):

A toluene solution (40 ml) of $[2\text{-}(OCH_3)C_6H_4O]_2V(TMEDA)$ **(4.7)** (0.8 g, 1.9 mmol) was treated with pyridine (1.5 ml) which changed the color of solution from green-yellow to violet. The toluene solution was concentrated to small volume (15

ml) and then layered with hexane. Violet microcrystalline complex **4.8** (0.3 g, 0.6 mmol, 34%) was obtained upon standing overnight at room temperature.

Elemental Analysis for $C_{24}H_{24}O_4N_2V$: Calcd (Obsvd): C 63.30 (63.01); H 5.31 (5.11); N 6.15 (6.00); V 11.19 (11.07).

Magnetic Moment: $\mu_{eff} = 3.53\ \mu_B$

Infrared Spectrum (Nujol mull, cm^{-1}): 1570 (m), 1430 (m), 1310(sh), 1290(m), 1260(sh), 1240(sh), 1195(sh), 1155(sh), 1090(sh), 1010(w), 840(m), 830(m), 730(w), 675(sh), 575(m), 400(w).

Preparation of $(2,6\text{-}Me_2C_6H_3O)_3V(Py)_2$ (4.10):

Neat $2,6\text{-}Me_2C_6H_3OH$ (0.85 g, 4.0 mmol) was added to a toluene solution (50 ml) of Mz_2VPy_2 **(4.2)** (1.0 g, 2.0 mmol) and the color changed from emerald green to deep orange. Bright orange crystals of **4.10** (0.3 g, 0.5 mmol, 25%) separated out overnight at -10°C after the toluene solution had been concentrated to ~20 ml.

Preparation of $[(t\text{-}BuO)_2V]_2(\mu\text{-}t\text{-}BuO)(\mu\text{-}O)$ (4.11):

Method A: A toluene solution (100 ml) of $Mes_3V(THF)$ (1.4 g, 2.9 mmol) was treated with freshly distilled t-BuOH (0.65 g, 8.7 mmol) which changed the color from deep blue to deep purple. The solvent was evaporated to dryness *in vacuo* and the oily residue was sublimed *in vacuo* (2 mm Hg, 120-150°C), yielding deep purple

crystals of **4.11** (0.54 g, 1.1 mmol, 69%).

Method B: The same procedure as above was followed using $\{[2,6\text{-}(MeO)_2C_6H_3]_2V\}_2(THF)_2$ (1.0 g, 1.2 mmol) as starting material yielding **4.11** (0.12 g, 0.25 mmol, 20%).

Elemental Analysis for $C_{20}H_{45}O_6V_2$: Calcd (Obsvd): C 49.69 (49.27); H 9.38 (9.01); V 21.07 (20.81).

Magnetic Moment: $\mu_{eff} = 2.71\ \mu_B$

Infrared Spectrum (Nujol mull, cm^{-1}): 2940(s), 2900(s), 2830(s), 1560(w), 1445(s), 1382(s), 1351(s), 1239(w), 1216(m), 1175(s), 1090(w), 980(s), 930(w), 894(m), 825(w), 795(m), 778(s), 761(s), 719(w), 649(s), 590(s), 492(m), 472(w), 401(w).

Preparation of $(C_6H_5O)_3V(TMEDA)$ (4.12):

A solution of C_6H_5OH (1.7 g, 18 mmol) in THF (70 mL) was boiled overnight over NaH (0.64 g, 26 mmol). The excess NaH was filtered off and *trans*-$VCl_2(TMEDA)_2$ (3.2 g, 9.0 mmol) was added to the solution. The color turned green-orange and stirring was continued for two hours. After evaporation of the solvent *in vacuo,* the residual solid was redissolved in toluene and the residual solution was layered with hexane after filtration. Green crystals of **4.12** (2.2 g, 4.9

mmol, 54 %) separated out upon standing at -30°C overnight.

Elemental Analysis for $C_{24}H_{31}O_3N_2V$: Calcd (Obsvd): C 64.57 (63.12); H 7.00 (7.12); N 6.27 (6.12); V 11.41 (11.21).

Magnetic Moment: $\mu_{eff} = 2.78\ \mu_B$.

Infrared Spectrum (Nujol mull, cm^{-1}): 1580(sh), 1318(m), 1330(m), 1260(br), 1190(w), 1160(sh), 1120(w), 1065(m), 1040(w), 1020(sh), 990(sh), 955(sh), 890(br), 850(w), 830(sh), 800(sh), 760(sh), 725(m), 695(sh), 575(sh), 520(w).

Preparation of $\{[2\text{-}(CH_3O)C_6H_4]_2V\}_2[\mu\text{-}N\text{-}N{=}CH(SiMe_3)]_2$.toluene (4.13):

A solution of $[2\text{-}(OCH_3)C_6H_4O]_2V(TMEDA)$ **(4.7)** (1.2 g, 3.0 mmol) in toluene (40 mL) was treated with $(Me_3Si)CHN_2$ (1.48 ml, 3.0 mmol). The initial green-orange color slowly turned red-brown. After stirring 24 hours at room temperature, the resulting deep red-orange solution was layered with hexane and allowed to stand overnight at room temperature. Black microcrystals of **4.13** (0.6 g, 0.7 mmol, 46%) separated out.

Elemental Analysis for $C_{43}H_{56}O_8N_4V_2Si_2$: Calcd (Obsvd): C 56.45 (56.12); H 6.17 (5.91); N 6.12 (5.94); V 11.13 (10.93).

^{1}H NMR Spectrum [200 MHz, C_6D_6, δ(ppm)]: 7.40 (s, 1H, C-H diazo), 7.10 (m,

toluene and C_6D_6), 7.02 (m, toluene), 6.83 (m, 4H, guaiacol), 6.52 (pseudot, 2H, guaiacol), 6.36 (pseudod, 2H, guaiacol), 3.77 (s, 6H, guaiacol), 2.10 (s, 3H, toluene), -0.05(s, 9H, Me_3Si).

Preparation of $\{[2\text{-}(CH_3O)C_6H_4]_2V\}_2[(\mu\text{-}NNCH(SiMe_3)]_2/\{[2\text{-}(CH_3O)C_6H_4]_2V\}_2$ $[\mu\text{-}2\text{-}(CH_3O)C_6H_4]_2$ (4.14):

A toluene solution of **4.13**, prepared as above and by using similar amounts, was boiled for a few minutes and then worked up in the usual manner. Dark orange crystals of the co-crystallite separated upon standing overnight at room temperature (24%).

Infrared Spectrum (Nujol mull, cm^{-1}): 1595(w), 1360(m), 1310(m), 1300(s), 1265(sh), 1235(sh), 1195(m), 1160(m), 1090(sh), 1030(s), 1010(sh), 1000(sh), 980(s), 910(m), 835(m), 750(sh), 730(sh), 720(sh), 710(sh), 615(w), 580(m).

Preparation of $[V(C_{10}H_7O)_2TMEDA]$ (4.15):

A solution of 1-naphthol (3.0 g, 20.8 mmol) in THF (75 ml) was stirred with NaH (0.75 g, 31 mmol) for about 30 min. The excess NaH was removed by filtration and the resulting solution was treated with *trans*-VCl_2TMEDA_2 (3.7 g, 10.4 mmol). The red-brown reaction mixture was stirred for two hours and then evaporated *in vacuo*. After addition of toluene (50 ml), the mixture was filtered and the resulting solution was layered with ether (30 ml). Red-brown crystals (2.2 g, 4.8 mmol, 46 %)

separated out after one day at room temperature.

Elemental Analysis for $C_{26}H_{30}N_2O_2V$: Calcd (Obsvd): C 68.86 (68.78); H 6.67 (6.59); N 6.18 (6.03); V 11.23 (11.15).

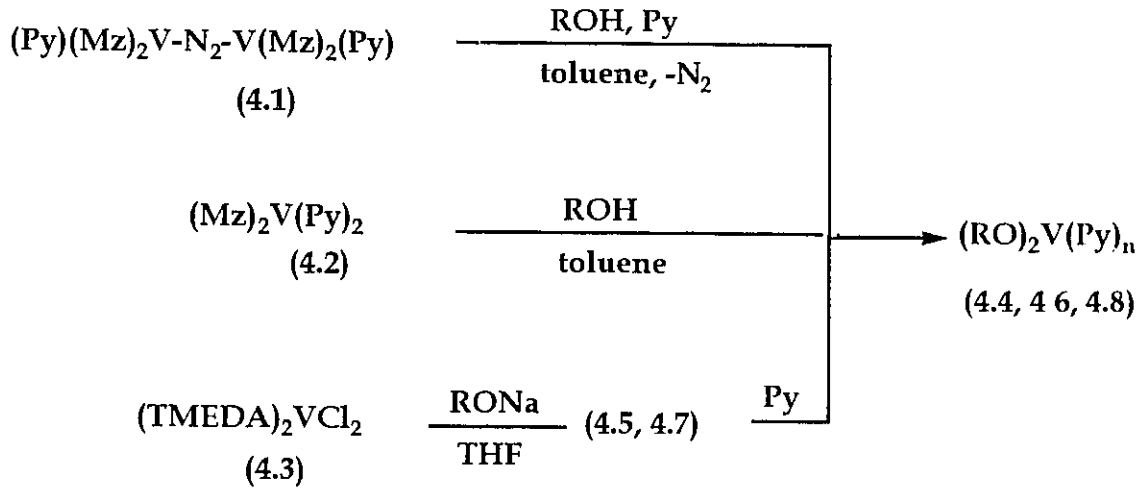
Magnetic Moment: $\mu_{eff} = 3.57\ \mu_B$.

Infrared Spectrum (Nujol mull, cm^{-1}): 1590(w), 1550(m), 1480(sh), 1460(br), 1410(s), 1390(m), 1375(br), 1360(s), 1345(s), 1310(s), 1290(sh), 1255(m), 1215(sh), 1140(sh), 1125(m), 1105(s), 1070(sh), 1050(m), 1015(sh), 995(m), 945(m), 870(sh), 770(sh), 750(br), 700(sh), 640(m), 575(m), 560(m).

IV. 3 : Results and Discussion

According to **Scheme 4.1**, the structure of final product, V(aryloxide)$_n$, does not depend on the nature of the starting materials or the reaction pathway used for their preparation. The reactions of $(Mz_2VPy)_2(N_2)$ **(4.1)** and Mz_2VPy_2 **(4.2)** as starting materials with ROH [R = 2,6-(t-Bu)$_2$-4-Me-C_6H_2; 2,6-Ph_2-C_6H_3; 2-$(CH_3O)C_6H_4$] proceeded in similar manners in toluene at low temperature, producing the same final product, except that N_2 was evolved in the case of complex **4.1**. The yield was better in the case of Mz_2VPy_2, and was improved in the case of $(Mz_2VPy)_2(N_2)$, if a small excess of pyridine was added. The reactions of $VCl_2(TMEDA)_2$ **(4.3)** with the corresponding sodium aryloxides proceeded in an entirely different manner,

yielding the same final product after treatment with pyridine, as obtained by the reactions of **4.1** and **4.2**. The intermediate TMEDA adducts $(RO)_2V(TMEDA)$ were also isolated and characterized for ROH = 2,6-$Ph_2C_6H_3OH$ **(4.5)** and 2-$(OCH_3)C_6H_4OH$ **(4.7)**. The reactions of $VCl_2(TMEDA)_2$ with sodium aryloxides were relatively slow, requiring long reaction times or refluxing in some cases. As an example, in the preparation of complex $\{[2,6\text{-}(t\text{-}Bu)_2\text{-}4\text{-}Me\text{-}C_6H_2O]_2V(pyridine)_2\}.(C_7H_8)_2$ **(4.4)**, which required extensive refluxing time, another crop of crystals was isolated only after one hour of stirring, which on structural characterization showed the starting *trans*-$VCl_2(TMEDA)_2$ and complex **4.4** co-crystallised[15] in the same unit cell in 1:1 ratio.



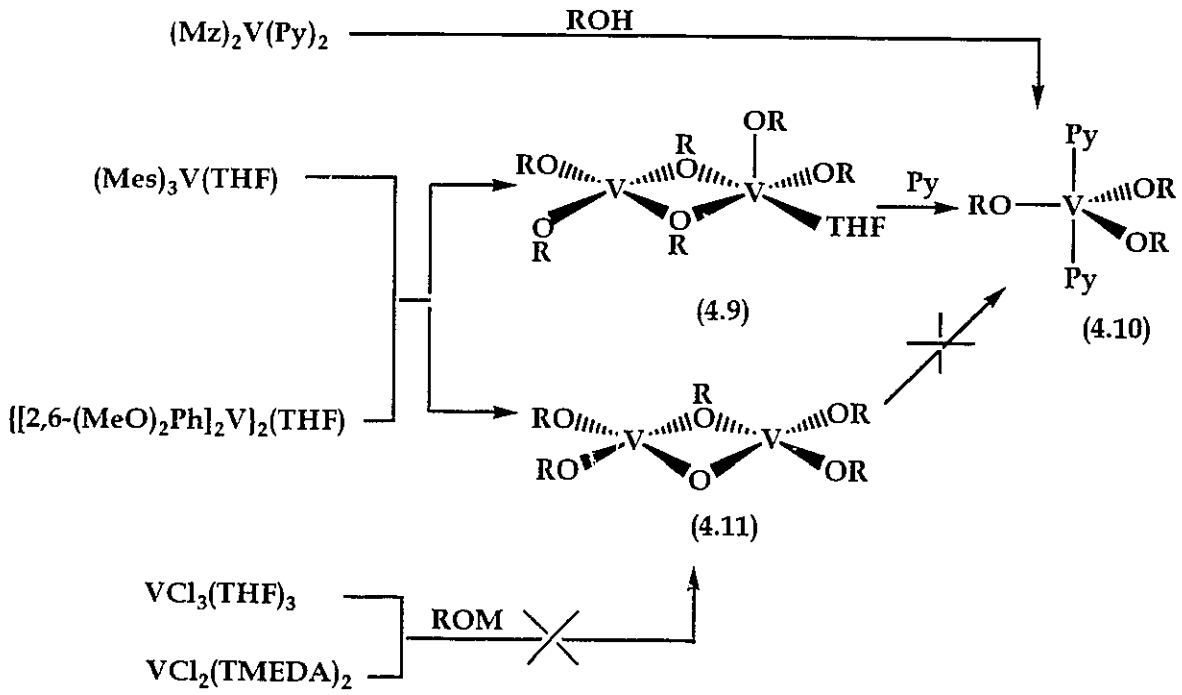
R = 2,6-$(t\text{-}Bu)_2$-4-Me-C_6H_2 (4.4)

2,6-$Ph_2C_6H_3$ (4.5, 4.6)

2-(OCH_3)-C_6H_4 (4.7, 4.8)

Scheme 4.1

As illustrated in **Scheme 4.2**, the oxidation state and nuclearity of the final product is independent of the nature and oxidation state of the starting material, since by using V(II) or V(III), dimeric or monomeric starting material, similar final



R = 2,6-Me_2Ph (4.9, 4.10)

t-Bu (4.11)

M = Li, Na, K

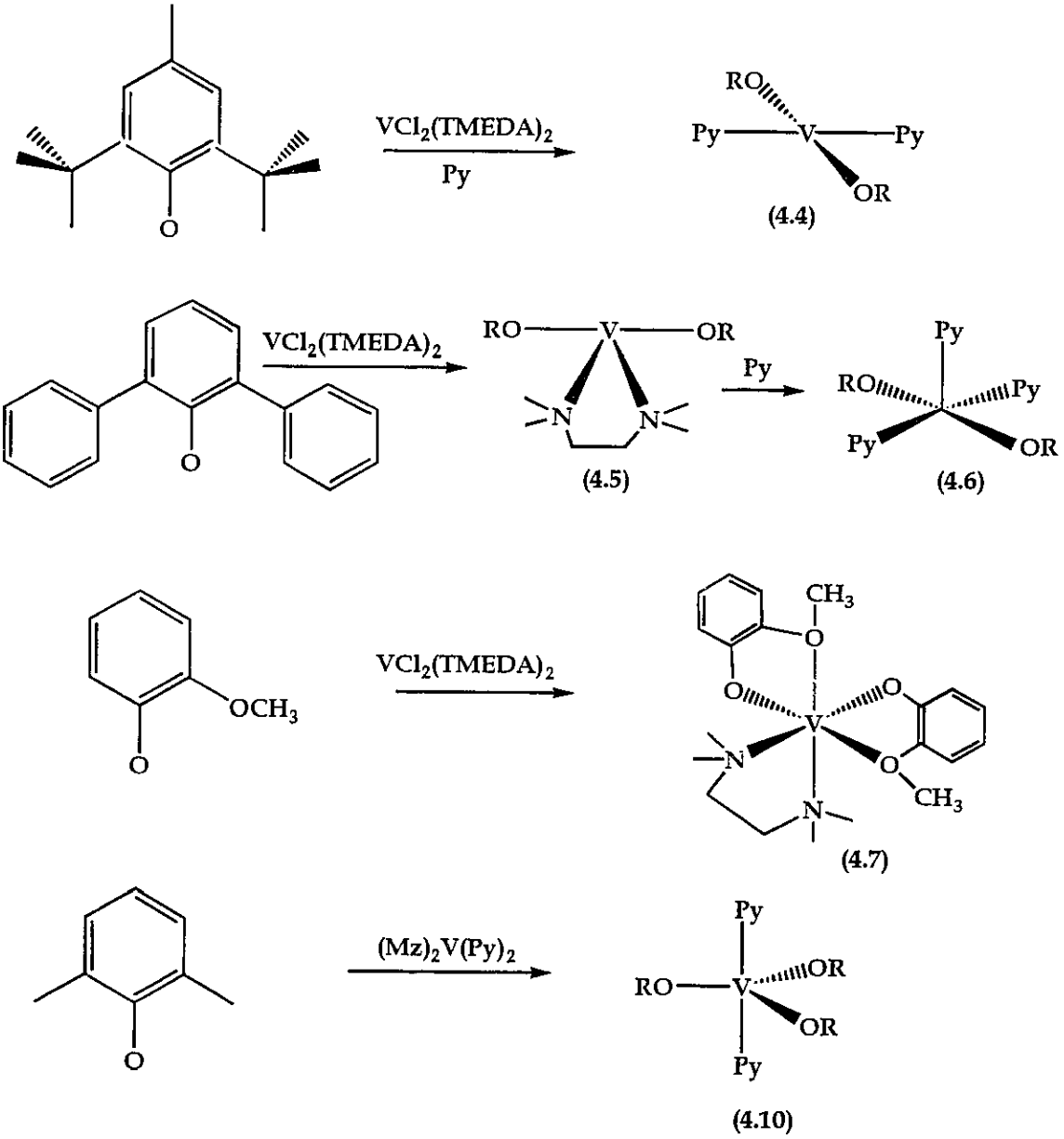
Scheme 4.2

products were obtained. The nuclearity of the product does depend on the coordinating ability of the solvent used, for example, both monomeric and dimeric V(III) species $V(OR)_3L_n$ [R = 2,6-Me_2Ph, L = THF, Py] were obtained using different solvents. The pyridine complex could also be obtained by the reaction of Mz_2VPy_2

or $(Mz_2VPy)_2(N_2)$ with neat 2,6-Me_2PhOH. When aliphatic and less bulky alcohols such as t-BuOH were used, a different reaction occurred and an oxidation and deoxygenation reaction took place giving the mixed valence V(III)/V(IV) dimeric complex $[(t\text{-}BuO)_2V]_2(\mu\text{-}O)[\mu\text{-}(Ot\text{-}Bu)]$ **(4.11)**[16]. However in this case, no evidence was found to indicate whether coordinating solvents like THF or Py (Lewis Bases) have any effect on the nuclearity of the complex. Complex **4.11** could not be prepared from the reaction of $VCl_3(THF)_3$ or $VCl_2(TMEDA)_2$ with t-BuOM (M = Li, Na, K), instead pink-purple hexane-insoluble microcrystalline solids, probably metallates, were obtained from these reactions. Even Mz_2VPy_2 gave poorly defined deep orange microcrystalline product on reaction with t-BuOH. Summing up the results in **Scheme 4.3**, it can be said that the oxidation state of the final product depends on the steric bulk of the organic alkoxide moiety.

In the case of a sterically less demanding phenol, a V(III) complex was obtained and characterized on the basis of magnetic and analytical data, whereas for sterically more demanding phenols e.g. 2,6-$(t\text{-}Bu)_2$-4-MeC_6H_2OH and 2,6-Ph_2PhOH, the original oxidation state of +2 is preserved.

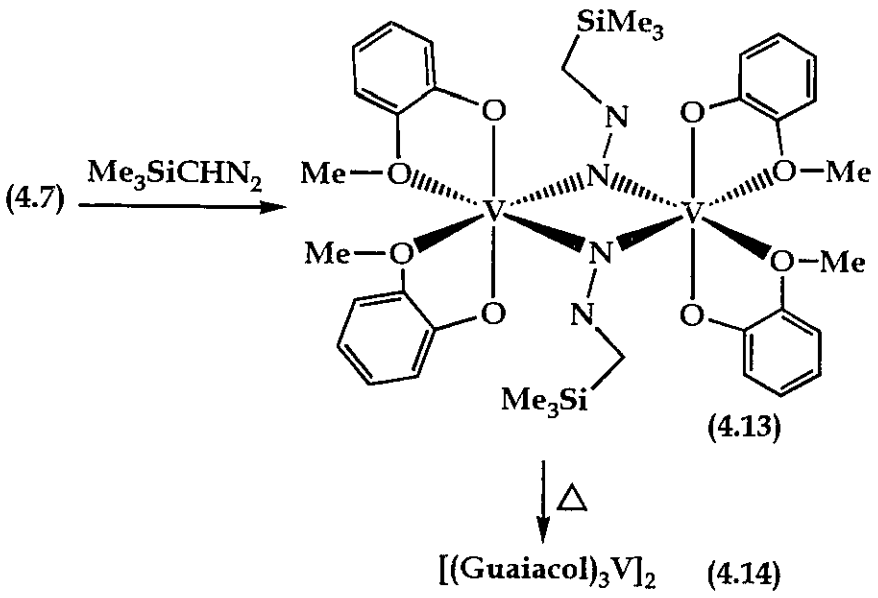
For the reactions of $(Mz_2VPy)_2(N_2)$ with various phenols dinitrogen is released indicating the impossibility of stabilizing the dinitrogen complexes using organic ligands with oxygen as the donor atom. This result contradicts the catalytic activity displayed by *in situ* generated V(II) hydroxide and catecholate. As the first series of



Scheme 4.3

V(II) aryloxides were now readily available, we investigated the reactivity of V(II) aryloxides with diazoalkanes. These contain a N-N multiple bond, and so have a structure and electronic configuration which could be viewed as an alkylated

dinitrogen moiety which has been reduced by two electrons. The reaction of **4.7** with $(Me_3Si)CHN_2$ was slow at room temperature, requiring at least 24 hours to complete **(Scheme 4.4)** and there was no appreciable gas evolution during the reaction time. Black crystals of diamagnetic and dimeric $\{2\text{-}(CH_3O)C_6H_4]_2V\}_2[\mu\text{-}N\text{-}N{=}CH(SiMe_3)]_2$ **(4.13)** were isolated from a toluene/hexane mixture. Complex **4.13** is thermally unstable, rapidly decomposing in boiling toluene into a complicated mixture, in which the $\{[2\text{-}(CH_3O)C_6H_4O]_3V\}_2$ dimer was the only clearly identifiable product.



Scheme 4.4

Although attempts to grow crystals suitable for X-ray analysis failed, complex **4.13** co-crystallized very conveniently with $\{[2\text{-}(CH_3O)C_6H_4O]_3V\}_2$ in a 1:1 ratio forming well-formed black-brown cubes of the co-crystallite $\{2\text{-}(CH_3O)C_6H_4]_2V[\mu\text{-}N\text{-}N{=}CH(SiMe_3)]\}_2/\{[2\text{-}(CH_3O)C_6H_4O]_3V\}_2$ **(4.14)**. An X-ray

crystal structure determination subsquently illustrated the structures of both compounds. The diamagnetism of **4.13**, together with the remarkably short V-V distance [V2-V2a=2.498(1)Å] as determined in the solid state structure, indicate a significant extent of direct V-V bonding betwen the two metal atoms. Furthermore, the well-resolved ^{1}H-NMR spectrum of **4.13** indicates that the dinuclear structure is retained in a solution of hydrocarbon solvents (C_6D_6). However, due to the fact that the dinuclear frame can easily be cleaved *via* coordination of a Lewis base[18] (py), and that a V-V distance as short as 2.4 Å has been demonstrated to be non-bonding[19], we suggest that the intermetallic contact may be just the result of optimization of bond distances and angles as determined by the two bridging nitrogen atoms of the diazo moieties. In other words, the short V-V distance should be regarded as a ligand artifact in spite of the fact that it is indeed one of the shortest ever found among dinuclear compounds of tetravalent vanadium[20].

IV. 4 : X-ray crystallography

Data were collected at temperatures in the range 25 to -160°C using the ω-2θ scan technique to a maximum 2θ value of 50.0° , for suitable air-sensitive crystals mounted on glass fibres. Cell constants and orientation matrices were obtained from the least-squares refinement of 25 carefully centered high-angle reflections. Redundant reflections were removed from the data set. The intensities of three representative reflections were measured after every 150 reflections to monitor crystal and instrument stability. Data were corrected for Lorentz and polarization

effects but not for absorption. The structures were solved by direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were located in the difference Fourier maps and refined isotropically in the case of favourable observation/parameter ratio. The final cycle of full-matrix least-squares refinement was based on the number of observed reflections with [$I > 2.5\sigma(I)$]. Neutral atomic scattering factors were taken from Cromer and Waber[17]. Anomalous dispersion effects were included in Fcalc. All calculations were performed using the TEXSAN package on a Digital VAX station. Selected bond distances and angles are given in **Appendix C**.

The structures of complexes **4.4**, **4.5**, **4.6**, **4.7** and **4.14** were determined by X-Ray analysis. Complex **4.4** has almost perfect square planar geometry around the vanadium atom [N1-V1-O1 = 93.39(8)°] with both aryloxide ligands *trans* to each other (***Fig.* 4.1**). The V-O distance [V1-O1 = 1.916(2)Å] is somewhat short, causing steric congestion around the vanadium atom. As a result of this, the V-N distance [V1-N1 = 2.235(10)Å] is slightly longer than in VCl_2Py_4[21] but comparable to the V-N distance in Mz_2VPy_2[10]. This is a result of steric congestion as well as partial π-bond character in the V-O bond. The oxygen and carbon atoms of the aryloxide ligand are in alignment with vanadium metal [V1-O1-C6 = 167.8(4)°].

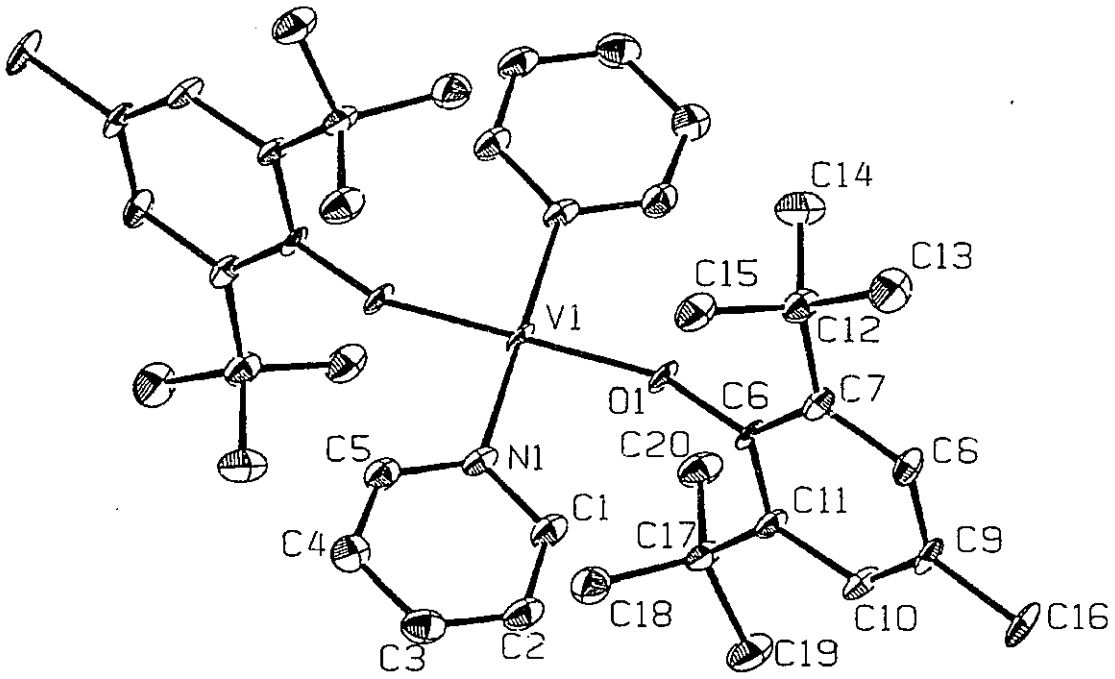


Fig. 4.1. X-Ray structure of 4.4, $\{[2,6\text{-}(t\text{-}Bu)_2\text{-}4\text{-}Me\text{-}C_6H_2O]_2V(pyridine)_2\}.(C_7H_8)_2$

Selected Bond Distances (Å) and Bond Angles (deg): V1-O1 = 1.916(2), V1-N1 = 2.235(2), O1-C6 = 1.351(3), O1-V1-N1 = 93.39(8), N1-V1-N1a = 180.00, O1-V1-O1a = 180.00.

In complex **4.5**, the geometry around vanadium is very unusual and can be described as saddle-shaped with one TMEDA molecule on one side of the O-V-O plane [O2-V1-O1 = 173.4(1)°] and an open coordination site on the other side **(Fig. 4.2)**. The [N1-V1-N2 = 82.4(1)°] angle is also slightly compressed, but otherwise the V-O [V1-O1 = 2.000(3)Å] and V-N [V1-N1 = 2.256(3)Å] distances are normal and compare well with those of other V(II) aryloxides[4,8] and TMEDA derivatives[10, 22]. This complex can be regarded as a molecule in which vanadium atom has regular

octahedral geometry, if the short V...H nonbonding distances [V...H(118) = 2.504Å, V...H(217) = 2.544Å] observed between the vanadium atom and the two ortho hydrogen atoms of the aryloxide ligands are considered real interactions. The octahedron is composed of two oxygen atoms from the aryloxides at apical *trans*

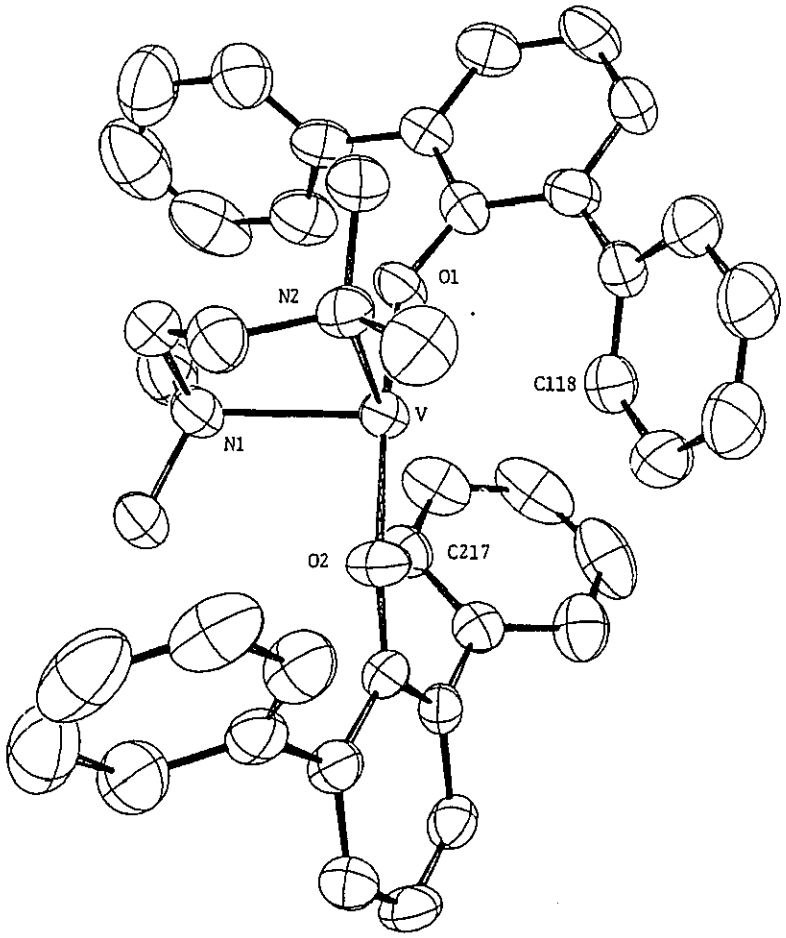


Fig. 4.2. X-Ray structure of 4.5, (2,6-Ph_2PhO)$_2$V(TMEDA)

Selected Bond Distances (Å) and Bond Angles (deg): V1-O1 = 2.000(3), V1-O2 = 2.038(3), V1-N1 = 2.256(3), V1-N2 = 2.202(4), O1-V1-O2 = 173.41(13), O1-V1-N1 =

92.23(15), O1-V1-N2 = 95.70(15), N1-V1-N2 = 82.41(13), V1...H118 = 2.504, V1...H218 = 2.544.

positions, two nitrogen atoms of one TMEDA molecule at *cis* equatorial positions and two agostic hydrogen atoms at equatorial positions. It may be that these agostic interactions are the result of the geometry of the bulky aryloxide ligands and so do not help to stabilize the metal center.

Complex **4.6** also has an unusual square-pyramidal geometry[23] at V(II). The basal plane is formed by two oxygen atoms of two aryloxide ligands and two nitrogen atoms of two pyridine molecules and the apical position is occupied by the third pyridine molecule **(Fig. 4.3)**. The angle O1-V1-O1a = 156.3(2)° is quite narrow compared to the similar angle in complex **4.5** suggesting the geometry to be somewhere between a square-pyramidal and trigonal bipyramidal. The V-N and V-O [V1-O1 = 2.025(4)Å] distances compare well with other compounds and even the V-N distances for axial or equatorial pyridine nitrogens are not significantly different [V1-N1 = 2.103(8), V1-N2 = 2.198(5)]. The two nitrogen atoms of the basal pyridine molecules are almost aligned with the vanadium atom [N2-V1-N2a = 170.5(3)°]. Differently from the case of the closely related (pyrrolyl)$_2$Cr(py)$_3$[24], no significant differences have been found in the V-N bond distances formed with the metal by the equitorial and axial pyridine.

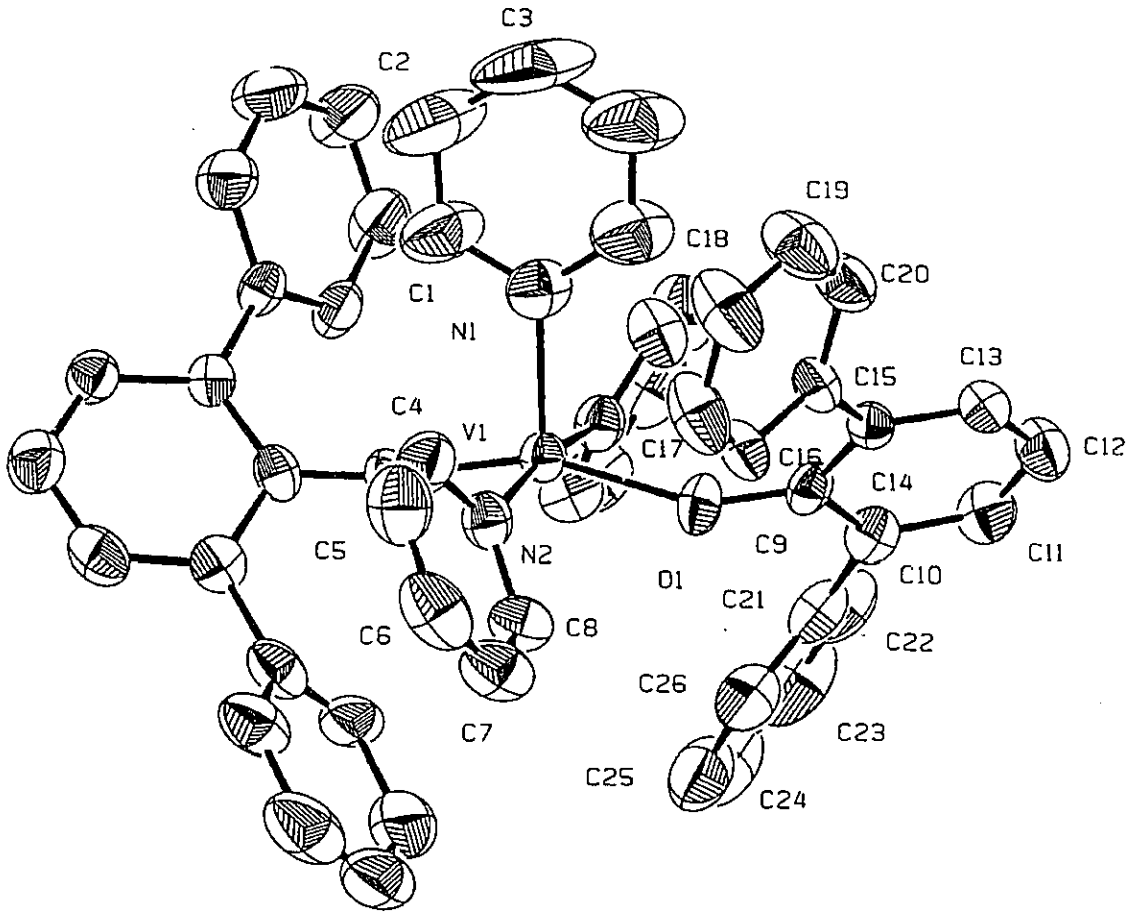


Fig. 4.3. X-Ray Structure of 4.6, $(2,6\text{-}Ph_2PhO)_2V(pyridine)_3$

Selected Bond Distances (Å) and Bond Angles (deg): V1-N1 = 2.103(8), V1-N2 = 2.198(5), V1-O1 = 2.025(4), N1-V1-N2 = 94.7(1), N1-V1-O1 = 101.9(1), O1-V1-O1a = 156.3(2), N2-V1-N2a = 170.5(3), O1-V1-N2 = 93.0(2).

In complex 4.7 vanadium has a slightly distorted octahedral geometry and the octahedron is formed by four oxygen atoms of two guaiacolate ligands and two nitrogen atoms of one TMEDA molecule (**Fig. 4.4**). The V-O and V-N [V1-O1 =

2.068(4)Å, V1-N1 = 2.245(4)Å] distances are as expected and compare well with other similar compounds. The angles subtended at vanadium by all three chelating ligands are slightly compressed from 90° [O1-V1-O4 = 77.3(1)°, O2-V1-O3 = 76.0(1)°, N1-V1-N2 = 82.0(2)°] and are all similar.

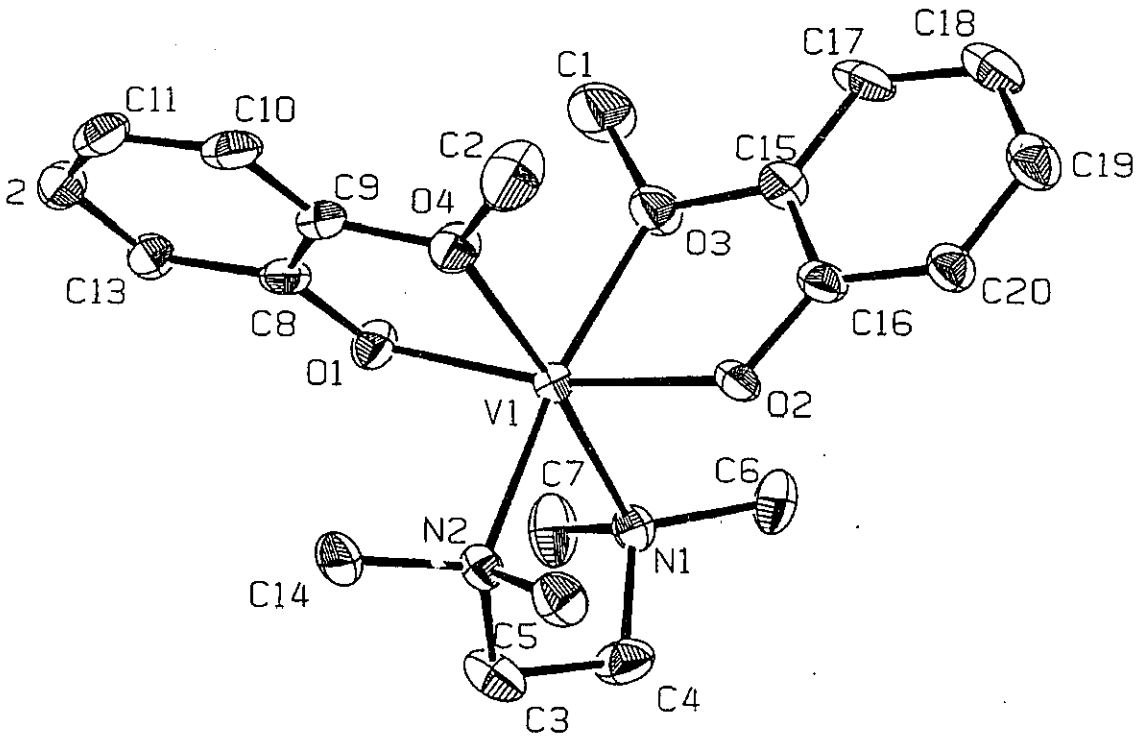


Fig. 4.4. X-Ray Structure of 4.7, [2-(OCH$_3$)C$_6$H$_4$O]$_2$V(TMEDA)

Selected Bond Distances (Å) and Bond Angles (deg); V1-O1 = 2.068(4), V1-O2 = 2.105(3), V1-O3 = 2.172(4), V1-O4 = 2.163(4), V1-N1 = 2.245(4), V1-N2 = 2.208(4), O1-V1-O3 = 95.1(1), O1-V1-O2 = 168.7(1), O1-V1-O4 = 77.3(1), O1-V1-N1 = 97.1(1), O1-V1-N2 = 94.3(2), N1-V1-N2 = 82.0(2).

The structure of the cocrystallite **4.14** is composed by two independent $[2\text{-}(CH_3O)C_6H_4O]_3V\}_2[\mu\text{-}N\text{-}N{=}CH(SiMe_3)]_2$ and $[2\text{-}(CH_3O)C_6H_4O]_3V\}_2$ molecules. The dimeric structure of the first unit is made by two $(Guaiacol)_2V$ moieties bridged by the terminal nitrogen atoms of two bridging $(Me_3Si)CHN_2$ units **(Fig. 4.5)**. The V_2N_2 core is planar [torsion angle V2-N1-N1a-V2a = 0.00°] and is characterized by a short V-V distance [V2-V2a=2.498(1)Å]. The angle formed by the bridging nitrogen with the two vanadium atoms [V2-N1-V2a = 85.1(1)°] deviates significantly from that expected for an sp^2 nitrogen atom. The V-N distance is rather short [V2-N1 = 1.847(3)Å] and together with the trigonal planar geometry of the bridging atom suggests some extent of π-bonding with the two metals. In agreement with these considerations, the N-N distance of the diazo moiety [N1-N2 = 1.377(4)Å] is only slightly shorter than expected for a N-N single bond.[25] In agreement with a significant degree of N-N double bond reduction, the N-N-C array is bent [N1-N2-C36 = 117.6(3)°]. The $(Guaiacol)_2V$ unit is normal with the expected V-O bond distances and angles [V2-O7 = 1.894(3)Å, V2-O8 = 2.264(2)Å] which compare well with those of complex **4.7**. The coordination geometry of vanadium is distorted octahedral [N1-V2-N1a = 94.9(1)°, O9-V2-O10 = 75.9(1)°, O7-V2-O8 = 74.90(9)°]. The second molecule cocrystallized is also dimeric and is similarly composed by two $(guaiacol)_2V$ units [V1-O3=2.177(2)Å, V1-O4=1.920(2)Å, O3-V1-O4=77.00(9)°] bridged by two oxygen atoms of two guaiacols **(Fig. 4.6)**. Apart from the significant differences in the dimetallic core [V1-V1a=3.089(2)Å,

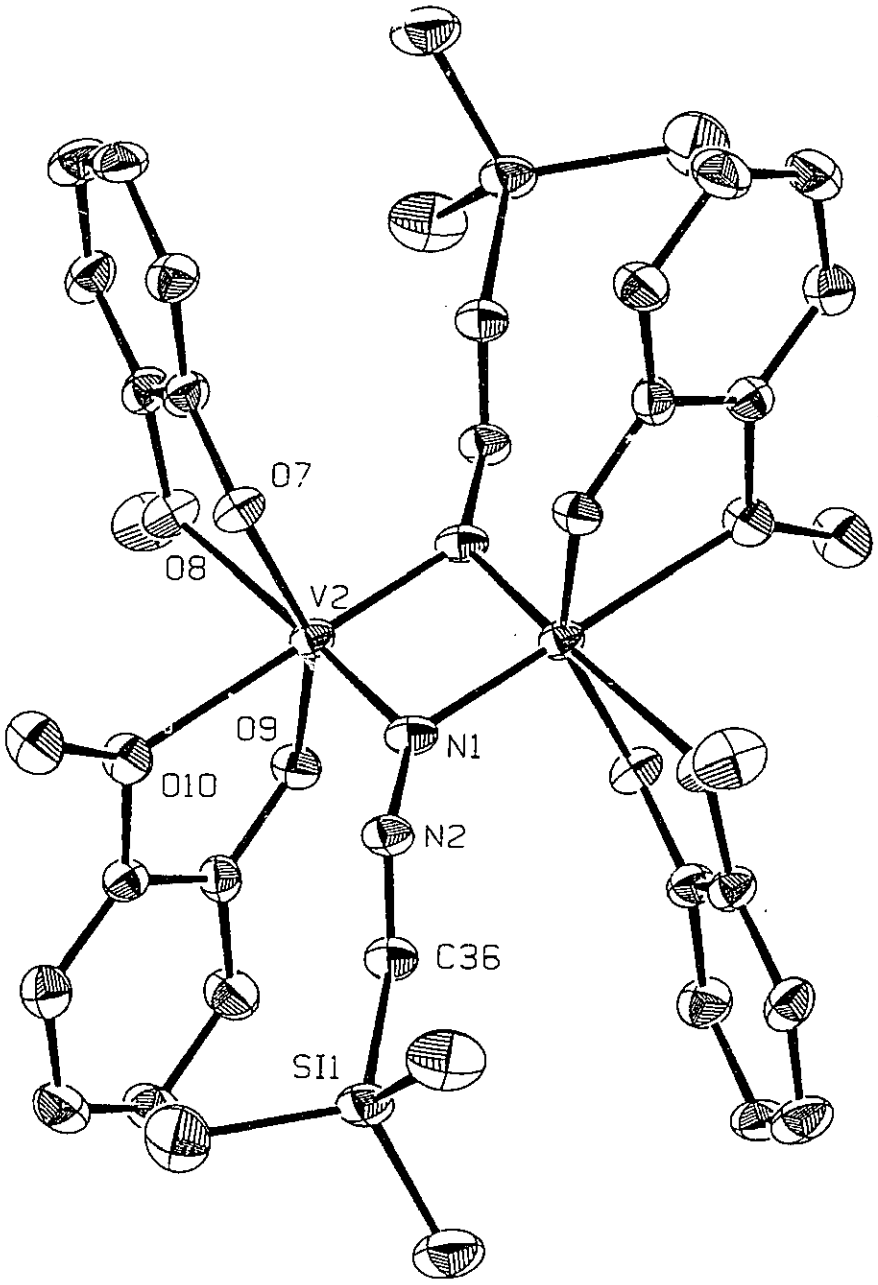


Fig. 4.5. X-Ray Structure of 4.13, $\{[2\text{-}(CH_3O)C_6H_4]_2V\}_2$ [μ-N-N=CH($SiMe_3$)]$_2$. toluene (first molecule)

Selected Bond Distances (Å) and Bond Angles (deg): V2-O7 = 1.894(3), V2-O8 = 2.264(2), V2-N1 = 1.847(3), N1-N2 = 1.377(4), V2-V2a = 2.498(1), N1-V2-N1a =

94.9(1), O9-V2-O10 = 75.9(1), O7-V2-O8 = 74.90(9), N1-N2-C36 = 117.6(3).

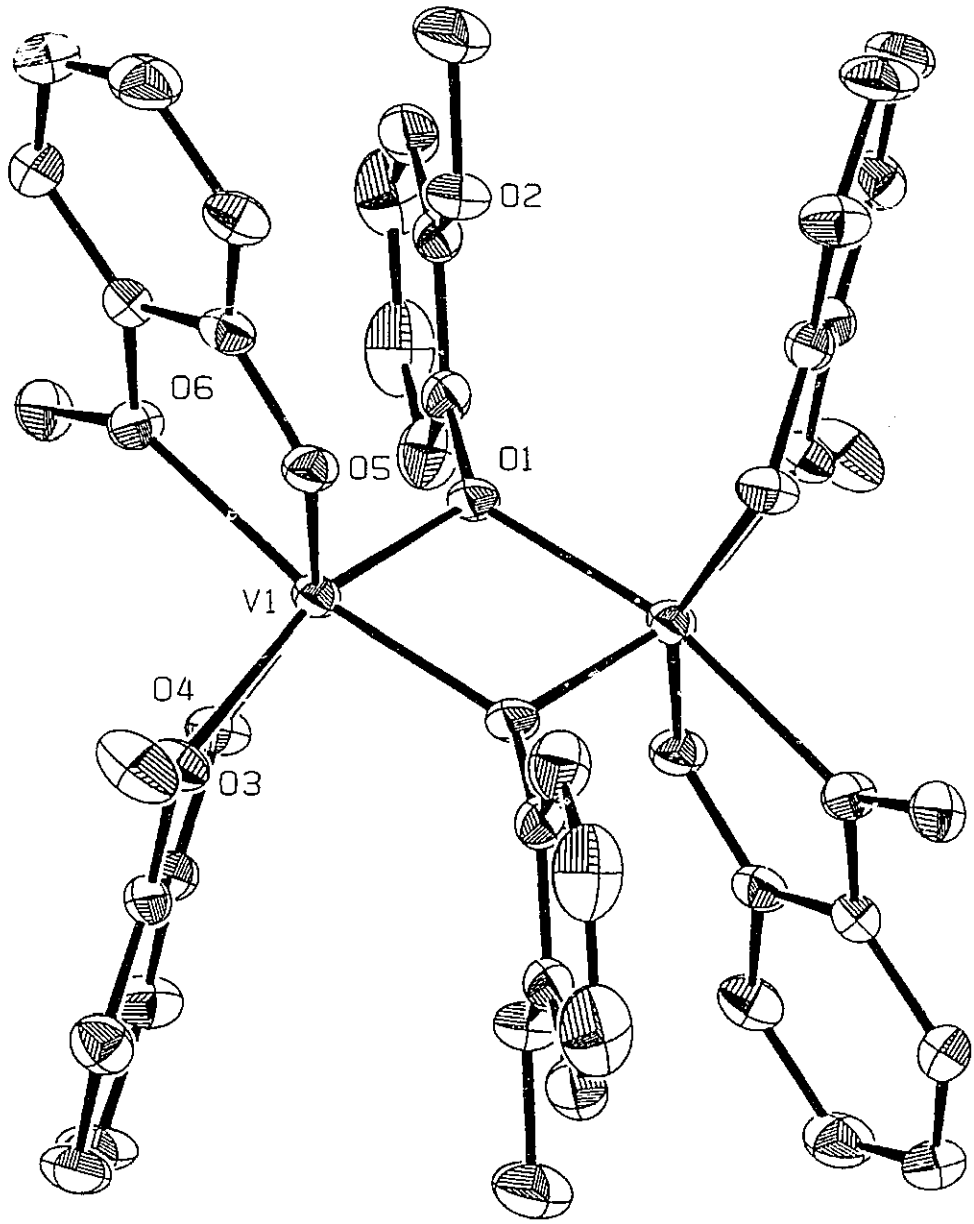


Fig. 4.6. X-Ray Structure of 4.14, {[2-(CH_3O)C_6H_4]$_2$V}$_2$[(μ-NNCH($SiMe_3$)]$_2$/ {[2-(CH_3O)C_6H_4]$_2$V}$_2$[μ-2-(CH_3O)C_6H_4]$_2$ (second molecule)

Selected Bond Distances (Å) and Bond Angles (deg): V1-O3 = 2.177(2), V1-O4 =

1.920(2), V1-V1a = 3.089(2), V1-O1 = 1.974(2), O3-V1-O4 = 77.00(9), V1-O1-V1a = 102.1(1), O1-V1-O1a = 77.8(1).

V1-O1=1.974(2)Å, V1-O1-V1a=102.1(1)°, O1-V1-O1=77.8(1)°], the bond distances and angles of the (guaiacol)$_2$V fragment compare well with those of complex **4.13**.

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16. $C_{20}H_{45}O_6V_2$, M=438.46, orthorhombic, C_{2221}, a=12.712(3)Å, b=15.234(2)Å, c=17.829(3)Å, V=3453(6)Å^3, Z=4, l=0.71069Å, R = 0.13, R_w=0.16, for 70 parameters and 616 out of 1493 unique reflections.

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CHAPTER V

Synthesis and Characterization of a Series of V(II) and V(III) Amidinates: Effect of Ligand Steric Hindrance on the V-V Distances.

V.1 : Introduction

Multiple bonds between first row early transition metals display one of the most intriguing features of inorganic chemistry. In spite of the fact that these bonds display the shortest ever found intermetallic distances,[1,2] thus suggesting the existence of strong bonds, today it is ascertained that these bonds are generally very weak[3], unlikely to be able to hold together dinuclear frames in the absence of bridging interactions[4], easily cleaved to form monomeric species[5] and therefore dominated by ligand features[6]. The paradoxical weakness of these bonds, especially spectacular in the chemistry of divalent chromium, has ignited in the past some theoretical controversy about the existence of these bonds and about whether or not the definition of chemical bond is appropriate for these short and very short metal-metal contacts.

Very short M-M contacts have been also found in the chemistry of divalent vanadium. However, the three-center chelating ligands (two donor atoms, three atom bite, four π-electrons and negative charge) which have been almost invariably employed to promote the formation of very short M-M multiple bonds, possess a unique ability to assemble dimers and to enforce very short M-M contacts[7,8] even ir

the absence of direct M-M bond[9]. As in the case of divalent chromium, it is therefore possible that efficient magnetic couplings between the two metals (antiferromagnetism, superexchange, etc.) may significantly shield the intermetallic repulsions. This would allow the formation of very short V-V contacts without there being a significant attraction force between the two transition metals. Even in this case the intermetallic contact may be just the result of ligand geometry optimization[10]. Moreover, theoretical work has predicted the existence of V-V triple bonds at distances of about 2.2 Å although the singly bonded configuration has been calculated to be considerably more stable than the triply bonded one[8b]. Moreover, an efficient magnetic coupling is apparently the only intermetallic interaction present in the diamagnetic and dinuclear $[(COT)V]_2$ with a V-V distance of about 2.4 Å. These observations thus suggest that short and even very short V-V contacts may not necessarily be diagnostic of the existence of V-V multiple bonds and that there is the possiblity that the intermetallic contacts might be ligand artifacts in spite of very short intermetallic distance.

The preferred coordination geometry of the transition metal, as imposed by the electronic configuration, is a factor which can prevail over the binucleating ability of the ligand[11]. In other words, while it is rather easy for three center chelating ligands to interface two monomeric square-planar metal complexes, such as in the case of Cr(II) units, it is far more difficult to assemble dimeric structures with short metal-metal contacts with divalent vanadium atoms. The octahedral coordination

geometry, as imposed by the d^3 electronic configuration of V(II), obviously disfavors lantern-type dinuclear structures unless severe distortions occur on the bridging donor atom coordination geometry. Such distortions have been observed in two of the three existing examples of divanadium complexes of three-center chelating ligands with short and very short V-V distances[7,8a]. However, the square-planar coordination geometry of divalent vanadium, although rare, is documented in a few examples[12] where large ligand steric hindrance is capable of prevailing over the unfavorable crystal field stabilization energy. Therefore, the employment of sterically demanding three-center chelating ligands might be the best synthetic strategy to assemble divanadium species with very short V-V distances.

In order to gain some insight into the nature of the vanadium-vanadium interaction in divanadium system with very short metal-metal contacts, we have now investigated the chemistry of V(II) and V(III) complexes of sterically demanding amidinates. Amidinate anions provide in fact a large series of three-center chelating ligands where a variety of substituents allow the steric hindrance to be finely tuned. Therefore, the influence of the geometry of this versatile class of ligands can be studied to determine both the nuclearity and the extent of intermetallic separation. In this chapter the synthesis, characterization and chemical behavior of a novel series of monomeric and dimeric V(II) and V(III) amidinate complexes is described.

V.2 : Experimental Section

All operations were performed under an inert atmosphere in a nitrogen-filled dry-box (Vacuum Atmosphere) or by using standard Schlenk techniques. VCl_3THF_3, *trans*-$VCl_2(TMEDA)_2$[13], $\{[(Me_3Si)N]_2C(Ph)\}Li$[14], and CyN(H)-(H)C=NCy[15], were prepared according to published procedures. MeLi and $(Me_3Si)_2NLi$ were prepared following standard procedures. CyNCNCy and $(Me_3Si)_2NH$ (Aldrich) were used as received. NMR spectra were recorded on a Varian Gemini 200 and on a Bruker AMX-500 spectrometer by using vacuum-sealed samples prepared in a dry-box. Solvents for NMR spectroscopy were dried over the appropriate drying agent, vacuum-transferred into appropriate ampoules and stored inside a dry-box. Infrared spectra were recorded on a Perkin-Elmer 283 instrument from Nujol mulls prepared in a dry-box. Samples for magnetic susceptibility measurements were weighed out inside a dry-box equipped with an analytical balance, and sealed into precalibrated tubes. Magnetic measurements were carried out with a Guoy balance (Johnson Matthey) at room temperature. The magnetic moment was calculated following standard methods[16], and corrections for underlying diamagnetism were applied to data[17]. Satisfactory combustion analysis data were obtained for all the complexes. Complexes 5.1-5.5 were synthesized by Dr. S. Hao.

Preparation of [CyN-C(H)-NCy]Li.C_6H_{14}:

A solution of CyN-C(H)-N(H)Cy (13.3 g, 64 mmol) in hexane (160 mL) was treated with a solution of n-BuLi in hexane (26 mL, 2.5M, 64 mmol) at room

temperature. The resulting light yellow solution was allowed to stand overnight at room temperature upon which colorless crystals of [CyN-C(H)-NCy]Li precipitated out (11.0 g, 51 mmol, 80%).

Infrared Spectrum [Nujol mull, cm^{-1}]: 1565(s), 1330(s), 1295(s), 1260(m), 1230(m), 1150(w), 1100(m), 1060(m), 1030(w), 990(w), 890(m), 840(m), 805(m), 785(w), 720(m), 600(w), 580(m).

^{1}H-NMR [C_6D_6, 200 MHz, δ(ppm)]: 8.38 (s, 1H, C-H form.), 2.81 (pseudoquintet, 2H, Cy), 1.89 (m, 4H, Cy), 1.71-1.24 (series of lines, 16H, Cy).

Preparation of [CyN-C(CH_3)-NCy]Li(Et_2O):

A solution of CyNCNCy (2.1 g, 10.2 mmol) in diethyl ether (30 mL) cooled to -70°C was treated with a solution of MeLi in ether (7.3 mL, 1.4 M, 10.2 mmol). Colorless crystals of [CyN-C(CH_3)-NCy]Li(Et_2O) (2.4 g, 7.9 mmol, 77%) separated out from the resulting yellowish solution upon reaching room temperature.

Infrared Spectrum [Nujol mull, cm^{-1}] : 1510(vs), 1410(s), 1350(s), 1305(w), 1250(m), 1160(m), 1130(w), 1070(sh), 1050(s), 1020(w), 990m), 1030(w), 990(w), 950(w), 920(m), 890(m), 840(w), 820(w), 795(m), 720(w), 650(m), 600(m), 570(m), 495(br), 460(w), 410(m).

^{1}H-NMR [C_6D_6, 200 MHz, δ(ppm)] : 3.26 (q, J=7.0Hz, 4H, Et_2O) 3.18 (bd s, 2H,

Cy), 1.99 (m, 4H, Cy), 1.89 (s, 3H, CH_3), 1.85-1.45 (series of multiplets, Cy), 1.09 (t J=7.0Hz, 6H, Et_2O).

Preparation of [CyN-C(CH_2Ph)-NCy]Li(Et_2O):

A solution of CyNCNCy (4.0 g, 19.4 mmol) in diethyl ether (70 mL) cooled to -40°C was treated with $PhCH_2Li$(TMEDA) (4.25 g, 19.4 mmol). After standing overnight at room temperature, the resulting yellowish solution was concentrated to small volume by evaporation of the solvent *in vacuo*, and hexane (40 mL) was added. Pale-yellow microcrystalline [CyN-C(CH_2Ph)-NCy]Li(Et_2O) (2.8 g, 7.4 mmol, 38%) separated upon standing at -30°C for four days .

Infrared Spectrum [Nujol mull, cm^{-1}]: 3077(sh), 3054(sh), 3020(sh), 2788(sh), 1592(s), 1500(s), 1498(s), 1457(s), 1407(m), 1376(m), 1355(s), 1342(m), 1294(m), 1257(m), 1159(s), 1132(m), 1064(m), 1022(m), 944(s), 887(m), 835(w), 790(m), 771(w), 732(s), 703(s), 651(w), 619(w), 582(br), 543(m).

^{1}H-NMR [C_6D_6, 200 MHz, δ(ppm)] : 7.50, 7.24, 7.05 (m, 5H, Ph,) 3.79 (s, 2H, CH_2 ,Bz), 3.27 (q, J=7.0Hz, 4H, Et_2O), 3.21 (bd s, 2H, Cy), 1.85 (m, 4H, Cy), 1.60 (m, 4H, Cy), 1.31 (m, 4H, Cy), 1.11 (t, J=7.0Hz, 6H, Et_2O).

Preparation of [V(CyN-C(H)-NCy)$_2$Cl]$_2$ (5.1):

A suspension of VCl_3THF_3 (8.25 g, 22.1 mmol) in THF (100 ml) was boiled in the

presence of [CyN-C(H)-NCy]Li.C_6H_4 (9.33 g, 43.6 mmol). After stirring overnight the solvent was evaporated *in vacuo* and the deep red solid was extracted with hexane to give red microcrystalline (7.6 g, 7.6 mmol, 69%) solid.

Infrared Spectrum [Nujol mull, cm^{-1}]: 1558(s), 1529(s), 1454(s), 1411(m), 1374(s), 1364(sh), 1350(m), 1334(m), 1313(m), 1260(s), 1228(s), 1189(m), 1151(m), 1118(m), 1096(s), 1082(sh), 1064(m), 1046(w), 1020(m), 992(w), 968(w), 920(w), 887(m), 845(m), 803(w), 788(w), 764(w), 728(s), 694(m), 680(m), 510(m), 478(w), 464(w), 454(w), 432(s).

^{1}H-NMR [C_6D_6, 200 MHz, δ(ppm)] : 9.4 (1H, Δν1/2 = 40Hz, C-H_{form}), 6.6 (2H, Δν1/2 = 63Hz, Cy), 6.2 (2H, Δν1/2 = 50Hz, Cy), 2.8 (4H, Δν1/2 = 15Hz, Cy), 2.1 (2H, Δν1/2 = 15Hz, Cy), 1.88 (2H, Δν1/2 = 9Hz, Cy), 1.6 (4H, Δν1/2 = 20Hz, Cy), 1.3 (4H, Δν1/2 = 10Hz, Cy), 0.8 (4H, Δν1/2 = 20Hz, Cy).

Magnetic Moment: μ_{eff}= 1.22 μ_B per dimer.

Elemental Analysis for $C_{26}H_{46}N_4ClV$: Calcd (Obsvd): C 62.32 (62.19); H 9.25 (9.13); N 11.18 (11.01).

Preparation of [CyN-C(H)-NCy]$_2$V(TMEDA) (5.2):

A suspension of *trans*-$VCl_2(TMEDA)_2$ (4.44 g, 12.5 mmol) in toluene (100 mL) was stirred and heated to the boiling point of the solvent in the presence of

[CyN-C(H)-NCy]Li (4.33 g, 20.2 mmol). The resulting deep yellow suspension was cooled to room temperature and filtered to discard a white solid. The resulting dark yellow solution was concentrated to small volume until crystallization of a dark yellow solid started. The suspension was boiled to redissolve the solid and slowly cooled to room temperature. Dark yellow air-sensitive crystals of **5.2** were obtained upon standing two days at room temperature (3.0 g, 5.0 mmol, 40%).

Infrared Spectrum [Nujol mull, cm^{-1}]: 3005(m), 1570(s), 1545(s), 1450(s), 1400(m), 1370(s), 1350(m), 1340(s), 1270(s), 1250(m), 1230(s), 1180(sh), 1160(s), 1155(sh), 1120(s), 1110(s), 1090(br), 1060(m), 1040(w), 1020(m), 1010(m), 980(m), 960(sh), 950(m), 880(s), 840(w), 790(s), 770(w), 720(w), 590(w), 565(w), 475(w), 450(w), 440(w), 390(br).

Magnetic Moment: μ_{eff}= 3.88 μ_B

Elemental Analysis for $C_{32}H_{62}N_6V$: Calcd (Obsvd): C 66.06 (65.98); H 10.74 (10.66); N 14.44 (14.11).

Preparation of $[(CyN\text{-}C(H)\text{-}NCy)_2V]_2$ (5.3):

Method A : A suspension of *trans*-$VCl_2(TMEDA)_2$ (2.23 g, 6.3 mmol) in toluene (100 mL) was refluxed and stirred overnight in the presence of [CyN-C(H)-NCy]Li(C_6H_{14}) (2.86 g, 13.4 mmol). The resulting deep-yellow suspension was filtered at 80°C to eliminate a grey solid (0.2 g). The resulting dark

yellow solution was concentrated to small volume until crystallization of an emerald-green solid started. The suspension was boiled to redissolve the solid and slowly cooled to room temperature. Emerald-green air-sensitive crystals of **5.3** were obtained upon standing two days (0.4 g, 0.4 mmol, 13%).

Method B : A solution of **5.1** (1.3 g, 1.3 mmol) in THF (50 ml) was heated to the boiling point of THF with potassium metal (0.14 g, 3.6 mmol) and then stirred overnight. The deep red color changed into dark green. The solvent was evaporated *in vacuo* and the residual solid was dissolved in toluene (20 ml). The solution was filtered to remove any KCl formed and green microcrystals of **5.3** (0.5 g, 0.54 mmol, 42%) separated when the filtrate was allowed to stand at -30°C for two days.

Method C : A solution of **5.1** (1.71 g, 1.7 mmol) in THF (50 ml) was heated to the boiling point with potassium metal (0.23 g, 5.9 mmol) in the presence of TMEDA (2.0 ml, 13.8 mmol). After stirring overnight, the color changed to dark green and replacing the solvent with toluene (25 ml) gave a green microcrystalline solid (0.7 g, 0.75 mmol, 44%) after standing for two days at -30°C.

Method D : A solution of **5.1** (1.22 g, 1.2 mmol) in toluene (50 ml) was heated to about 100°C with potassium metal (0.14 g, 3.6 mmol) and stirred overnight. Green microcrystals of **5.3** (0.6 g, 0.65 mmol, 53%) separated at -30°C, after concentrating the solution to about 20 ml.

Method E : A solution of **5.2** (1.1 g, 1.9 mmol) in toluene was refluxed overnight and then allowed to stand at -30°C. Green crystals of **5.3** (0.6 g, 0.65 mmol, 68%) were obtained from dark yellow solution after two days.

Method F : A deep blue solution of $V(CyNCHNCy)_2Py_2$ (0.3 g, 0.48 mmol) in toluene (20 ml) was refluxed for about half an hour resulting into green solution, which when concentrated and cooled to -30°C gave green crystals of **5.3**.

Infrared Spectrum [Nujol mull, cm^{-1}]: 2805 (s), 1585(s), 1550(m), 1460(s), 1370(m), 1360 (m), 1340(s), 1325(s), 1290(m), 1250(m), 1185(w), 1150(s), 1120(m), 1100(s), 1080(m), 1070(sh), 1020(w),980(m), 890(m), 840(m), 780(w), 725(w), 690(w), 510(m), 490(m), 450(w), 425(s), 390(m).

^{1}H-NMR [C_6D_6, 200 MHz, δ(ppm)] : 9.85 (s, 4H, form), 2.75 (pseudo quintet, 8H, Cy), 1.99 (s, 3H, toluene), 1.90 (pseudo d, 16H, Cy), 1.75 (pseudo d, 16H, Cy), 1.63 (pseudo d, 8H, Cy), 1.20 (m, 40H, Cy).

Elemental Analysis for $C_{52}H_{92}N_8V_2$: Calcd (Obsvd): C 67.07 (66.98); H 9.96 (9.73); N 12.03 (11.89).

Preparation of $V(CyN\text{-}C(H)\text{-}NCy)_2Py_2$ (5.4):

A suspension of **5.3** (0.6 g, 0.65 mmol) in pyridine (15 ml) was heated at about 100°C for half an hour. After cooling the deep blue solution slowly to room

temperature, blue crystals of **5.4** (0.3 g, 0.48 mmol, 37%) were obtained overnight.

Infrared Spectrum [Nujol mull, cm^{-1}]: 2747(m), 1664(w), 1565(s), 1480(m), 1453(s), 1436(s), 1376(m), 1364(s), 1344(s), 1311(m), 1258(s), 1228(s), 1171(s), 1145(m), 1118(m), 1088(s), 1064(w), 1040(m), 998(w), 985(w), 956(w), 920(w), 885(m), 842(w), 749(s), 722(w), 685(s), 668(w), 548(w), 455(w).

Magnetic Moment: μ_{eff}= 3.81 μ_B.

Elemental Analysis for $C_{36}H_{56}N_6V$: Calcd (Obsvd): C 69.31 (69.22); H 9.05 (8.88), N 13.47 (13.38).

Preparation of $[C_6H_{11}NC(Me)NC_6H_{11}]_2VCl$ (5.5):

A suspension of VCl_3THF_3 (2.3 g, 6.2 mmol) in THF (75 ml) was stirred overnight at room temperature in the presence of $[(C_6H_{11})NC(Me)N(C_6H_{11})]Li.Et_2O$ (3.75 g, 12.4 mmol). The resulting blood-red solution was evaporated to dryness and the residual solid was redissolved in toluene (40 mL). After filtration, the solution was concentrated and layered with hexane. Red crystals of **5.5** (0.8 g, 1.5 mmol, 24%) separated upon standing two days at room temperature.

Magnetic Moment: μ_{eff} = 2.77 μ_B.

Elemental Analysis for $C_{28}H_{50}N_4ClV$: Calcd (Obsvd): C 63.56 (63.49); H 9.53

(9.48); N 10.59 (10.50).

Preparation of $[(C_6H_{11})NC(Me)N(C_6H_{11})]_3V$ (5.6):

Method A : A suspension of VCl_2TMEDA_2 (1.8 g, 5.1 mmol) in toluene (100 mL) was refluxed and stirred overnight in the presence of [CyN-C(Me)-NCy]Li.Et_2O (3.06 g, 10.1 mmol). After filtration, the resulting brown-orange solution was allowed to stand overnight at -30°C upon which dark-orange crystals of **5.6** (1.5 g, 2.1 mmol, 41%) separated.

Infrared Spectrum [Nujol mull, cm^{-1}]: 1490(sh), 1450(vs), 1375(sh), 1360(s), 1340(m), 1310(w), 1290(s), 1270(s), 1235(w), 1190(sh), 1180(sh), 1140(m), 1080(sh), 1000(s), 900(m), 890(w), 880(m), 840(w), 820(m), 800(m), 650(m), 600(w), 570(w), 500(w).

Magnetic Moment: μ_{eff}= 2.78 μ_B.

Method B : A suspension of $VCl_3(THF)_3$ (3.83 g, 10.3 mmol) in THF (120 mL) was stirred at room temperature for 5 hours in the presence of [CyN-C(Me)-NCy]Li (6.17 g, 20.4 mmol). The resulting deep-red solution was boiled, cooled to room temperature and evaporated to dryness. The residual solid was redissolved in toluene (50 mL) and the insoluble material was eliminated by filtration. After the addition of finely dispersed potassium (0.50 g, 12.8 mmol), the mixture was stirred at 80°C overnight. The dark-yellow suspension was filtered at c.a. 60°C and slowly

cooled at room temperature. Brown needles of **5.6** (3.4 g, 4.8 mmol, 46%) were obtained upon standing a few days at room temperature.

Infrared Spectrum [Nujol mull, cm^{-1}]: 1490(s), 1460(s), 1360(s), 1340(s), 1330(m), 1310(w), 1250(m), 1240(m), 1190(s), 1170(s), 1140(w), 1080(s), 100(m), 890(w), 880(m), 840(m), 820(m), 800(m), 650(m), 600(w), 570(w), 500(w).

Magnetic Moment: μ_{eff}= 2.88 μ_B.

Elemental Analysis for $C_{42}H_{75}N_6V$: Calcd (Obsvd): C 70.55 (70.41); H 10.57 (10.38); N 11.75 (11.69).

Preparation of $[(C_6H_{11})NC(Me)N(C_6H_{11})]_2V(THF)_2$ (5.7):

A suspension of VCl_3THF_3 (2.95 g, 7.9 mmol) in THF (70 ml) was stirred overnight at room temperature in the presence of $C_6H_{11}NC(Me)N(Li)C_6H_{11}.Et_2O$ (4.77 g, 15.8 mmol). Thinly smashed metallic lithium (0.06 g, 8.5 mmol) was added to the resulting blood-red solution. The flask was evacuated and sealed. Stirring was continued under argon for additional 24 hours. The resulting brown solution was warmed and filtered while warm to remove the excess of lithium. Light-green crystals of **5.7** (2.4 g, 3.7 mmol, 46%) were obtained upon standing at room temperature overnight.

Infrared Spectrum [Nujol mull, cm^{-1}]: 1380(s), 1360(m), 1340(s), 1255(s),

1190(m), 1170(s), 1140(br), 1080(sh), 1050(sh), 1000(s), 920(m), 890(m), 840(m), 820(m), 705(m), 720(s), 650(s), 570(sh), 495(s).

Magnetic Moment: μ_{eff}= 3.85 μ_B.

Elemental Analysis for $C_{34}H_{62}N_4O_2V$: Calcd (Obsvd): C 66.96 (66.85); H 10.25 (10.17); N 9.19 (9.09).

Preparation of $[(C_6H_{11})NC(CH_2Ph)N(C_6H_{11})]_2V(THF)_2$ (5.8):

A suspension of $VCl_2(TMEDA)_2$ (2.3 g, 6.5 mmol) in THF (60 mL) was stirred and boiled for a few minutes in the presence of $[(C_6H_{11})NC(CH_2Ph)N(C_6H_{11})]_2Li(Et_2O)$ (4.9 g, 13.0 mmol). The resulting yellowish-green suspension was filtered while hot, concentrated to small volume (30 mL) and layered with hexane. Emerald-green crystals of **5.8** (1.8 g, 2.3 mmol, 35%) separated upon standing two days at room temperature.

Infrared Spectrum [Nujol mull, cm^{-1}]: 1650(br), 1605(m), 1500(sh), 1375(sh), 1365(sh), 1310(s), 1265(m), 1240(s), 1200(m), 1170(sh), 1140(s), 1075(br), 1030(m), 1000(s), 935(m), 900(m), 890(sh), 875(s), 840(m), 785(sh), 740(sh), 725(sh), 705(sh), 690(m), 655(m), 600(m).

Magnetic Moment: μ_{eff}= 3.81 μ_B.

Elemental Analysis for $C_{48}H_{74}N_4O_2V$: Calcd (Obsvd): C 72.97 (72.91); H 9.44 (9.38); N 7.09 (7.00).

Preparation of $[(Me_3Si)NC(Ph)N(SiMe_3)]_2V(THF)_2$ (5.9):

A suspension of VCl_2TMEDA_2 (2.0 g, 5.6 mmol) in THF (60 ml) was stirred for 3 hours at room temperature in the presence of $[(Me_3Si)NC(Ph)N(SiMe_3)]Li.TMEDA$ (4.03 g, 11.3 mmol). The resulting orange-brown suspension was boiled to redissolve the orange microcrystalline solid formed during the stirring, and very slowly cooled to room temperature. Orange crystals of **5.9** (3.0 g, 4.5 mmol, 80%) were obtained upon standing overnight at room temperature.

Infrared Spectrum [Nujol mull, cm^{-1}]: 1255(s), 1240(sh), 1175(m), 1075(s), 1050(sh), 1000(m), 975(sh), 915(sh), 885(s), 830(br), 790(m), 750(br), 720(s), 700(sh), 670(m), 600(sh), 495(sh).

Magnetic Moment: $\mu_{eff} = 3.77\ \mu_B$.

Elemental Analysis for $C_{34}H_{62}N_4O_2Si_4V$: Calcd (Obsvd): C 56.55 (56.45); H 8.65 (8.58); N 7.76 (7.61).

Preparation of $[(Me_3Si)NC(Ph)N(SiMe_3)]VCl_2(TMEDA)$ (5.10):

Addition of $[(Me_3Si)NC(Ph)N(SiMe_3)]Li(TMEDA)$ (13.6 g, 35 mmol) to a stirred suspension of $VCl_3(THF)_3$ (13.2 g, 35 mmol) in toluene (200 ml) turned the color

greenish-yellow. The stirring was continued overnight and the reaction mixture was filtered while hot. The resulting solution was concentrated to half the volume and then layered by diethylether (100 ml). Green microcrystalline **5.10** (11.62 g, 66%) separated upon standing overnight at -30°C.

Infrared Spectrum [Nujol mull, cm^{-1}]: 1247(s), 1067(sh), 1016(sh), 1000(sh), 981(s), 954(sh), 843(s, br), 805(sh), 784(m), 768(br), 704(s), 511(s).

Magnetic Moment: $\mu_{eff} = 2.66\ \mu_B$.

Elemental Analysis for $C_{19}H_{39}N_4Si_2Cl_2V$: Calcd (Obsvd): C 45.50 (45.44); H 7.84 (7.78); N 11.17 (11.07).

Preparation of $[(Me_3Si)NC(Ph)NSiMe_3)]_2VCl$ (5.11):

A suspension of $VCl_3(THF)_3$ (5.1 g, 13.7 mmol) in toluene (100 ml) at room temperature was treated with $[(Me_3Si)NC(Ph)N(SiMe_3)]Li(TMEDA)$ (10.6 g, 27.4 mmol). The color turned greenish-yellow upon mixing and stirring was continued overnight. After removal of the solvent *in vacuo*, the residual solid was heated *in vacuo* at 120-130°C for 3 hours. The resulting solid was dissolved in toluene (100 ml) and after filtration, the clear orange solution was concentrated to small volume (40 ml). Layering with hexane (100 ml) and leaving the solution at -30°C overnight completed the crystallisation of **5.11** (6.35 g, 10.4 mmol, 76%).

Infrared Spectrum [Nujol mull, cm^{-1}]: 3060(w), 1508(s), 1248(s), 1169(m), 1075(w), 1008(w), 973(vs), 923(w), 842(s), 764(s), 727(m), 704(s), 615(w), 535(s), 445(w).

Magnetic Moment: μ_{eff} = 2.95 μ_B.

Elemental Analysis for $C_{26}H_{46}N_4Si_4ClV$: Calcd (Obsvd): C 50.91 (50.85); H 7.56 (7.44); N 9.13 (9.02).

Preparation of $\{[Me_3SiNC(Ph)NSiMe_3]_2V\}_2(N_2)$ (5.12):

Method A: A solution of **5.11** (6.35 g, 10.4 mmol) in toluene (60 ml) was treated with $NaHBEt_3$ (10.5 ml, 1M in toluene), which turned the color brown along with a vigorous gas evolution. The suspension was stirred overnight at room temperature during which a slow uptake of gas occurred. The mixture was filtered, evaporated to dryness and the residual solid was redissolved in hexane. Dark-green crystals of **5.12** (2.69 g, 43%) separated almost immediately.

Infrared Spectrum [Nujol mull, cm^{-1}]: 3060(w), 1500(sh), 1248(s), 1173(m), 1073(w), 1001(s), 982(s), 912(m), 843(s), 763(s), 701(s), 604(m), 522(s), 498(m), 443(w).

Magnetic Moment: μ_{eff} = 0.91 μ_B per dimer.

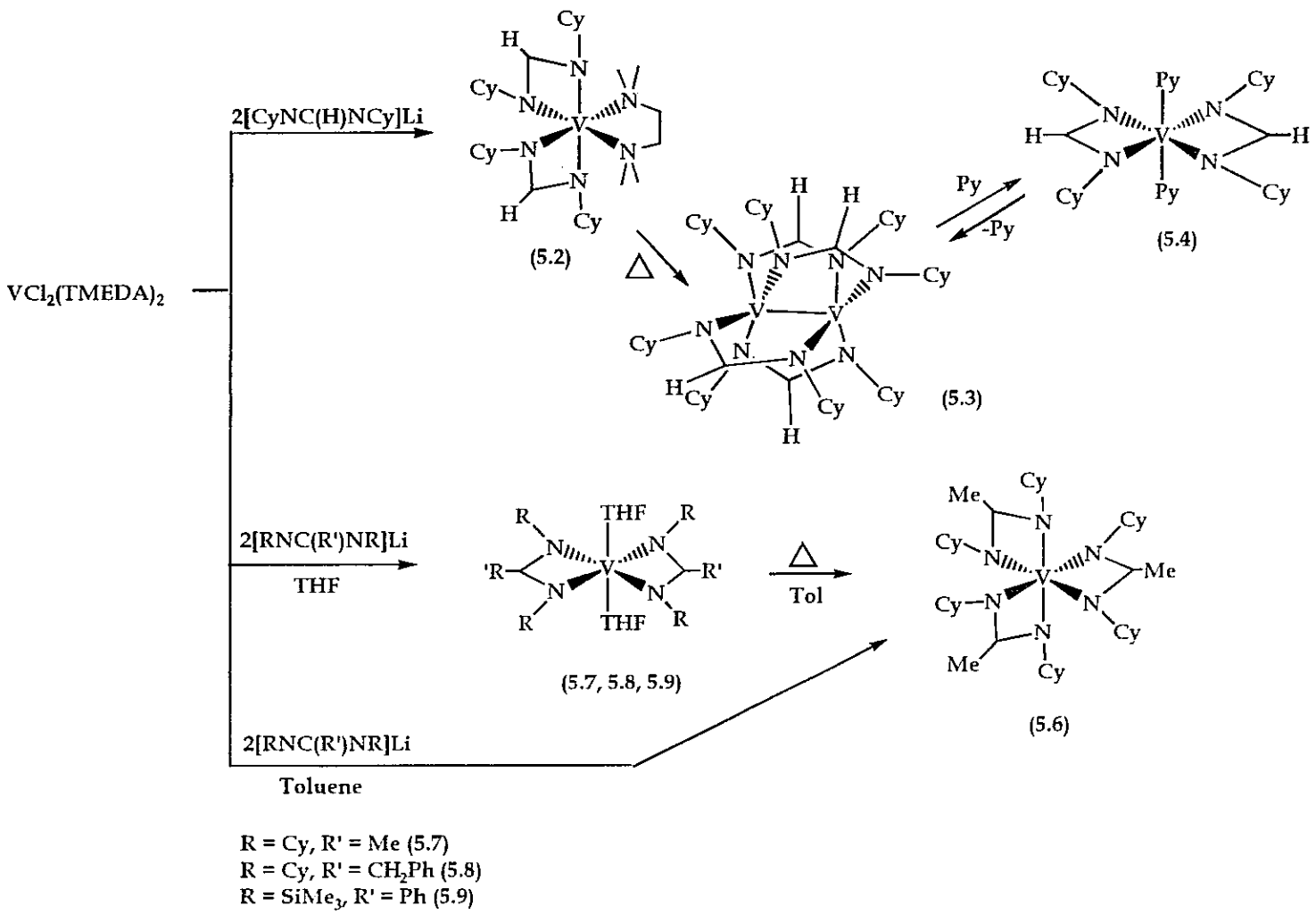
^{1}H-NMR [C_6D_6, 200 MHz, δ(ppm)] : 7.69 (5H, $\Delta\nu 1/2$ = 66 Hz,Ph), 0.36 (18H,

$\Delta\nu 1/2$ = 84 Hz, Me_3Si).

Elemental Analysis for $C_{52}H_{92}N_{10}Si_8V_2$: Calcd (Obsvd): C 52.75 (52.66); H 7.83 (7.71); N 11.17 (11.01).

V.3 : Results and Discussion

The reaction of $VCl_2(TMEDA)_2$ with two equivalents of [RNC(R')NR]Li gave different products depending upon the nature of R and R' substituents e.g. for R = Cy and R' = H, complex $[CyN\text{-}C(H)\text{-}NCy]_2V(TMEDA)$ **(5.2)** was isolated in good yield as dark-yellow very air-sensitive crystals. The formulation confirmed by X-ray diffraction analysis was consistent with analytical and magnetic moment data. However, for R = Me_3Si and R' = Ph, complex $[(Me_3Si)NC(Ph)N(SiMe_3)]_2V(THF)_2$ **(5.9)** with the solvent molecules in *trans* position was obtained. Isostructural complexes have been obtained using R = Cy and R' = Me **(5.7)** or Bz **(5.8)**. The important role played by the steric hindrance of amidinates in determining the nuclearity and the stability of V(II) and V(III) complexes is quite clear from the following scheme of reactions **(Scheme 5.1).** Also the fact that one molecule of TMEDA is retained in the formamidine derivative **5.2** while its complete replacement by two molecules of THF observed in the case of amidinates or benzamidinates (**5.7, 5.8, 5.9**) can be explained on the basis of larger steric hindrance of these ligands since the reaction conditions employed in all these complexes are identical. The replacement of TMEDA with two molecules of THF in **5.7, 5.8** and **5.9**


VCl2(TMEDA)2
2[CyNC(H)NCy]Li
(5.2)
(5.3)
(5.4)
Py
-Py
2[RNC(R')NR]Li
THF
(5.7, 5.8, 5.9)
Tol
(5.6)
2[RNC(R')NR]Li
Toluene
R = Cy, R' = Me (5.7)
R = Cy, R' = CH2Ph (5.8)
R = SiMe3, R' = Ph (5.9)

Scheme 5.1

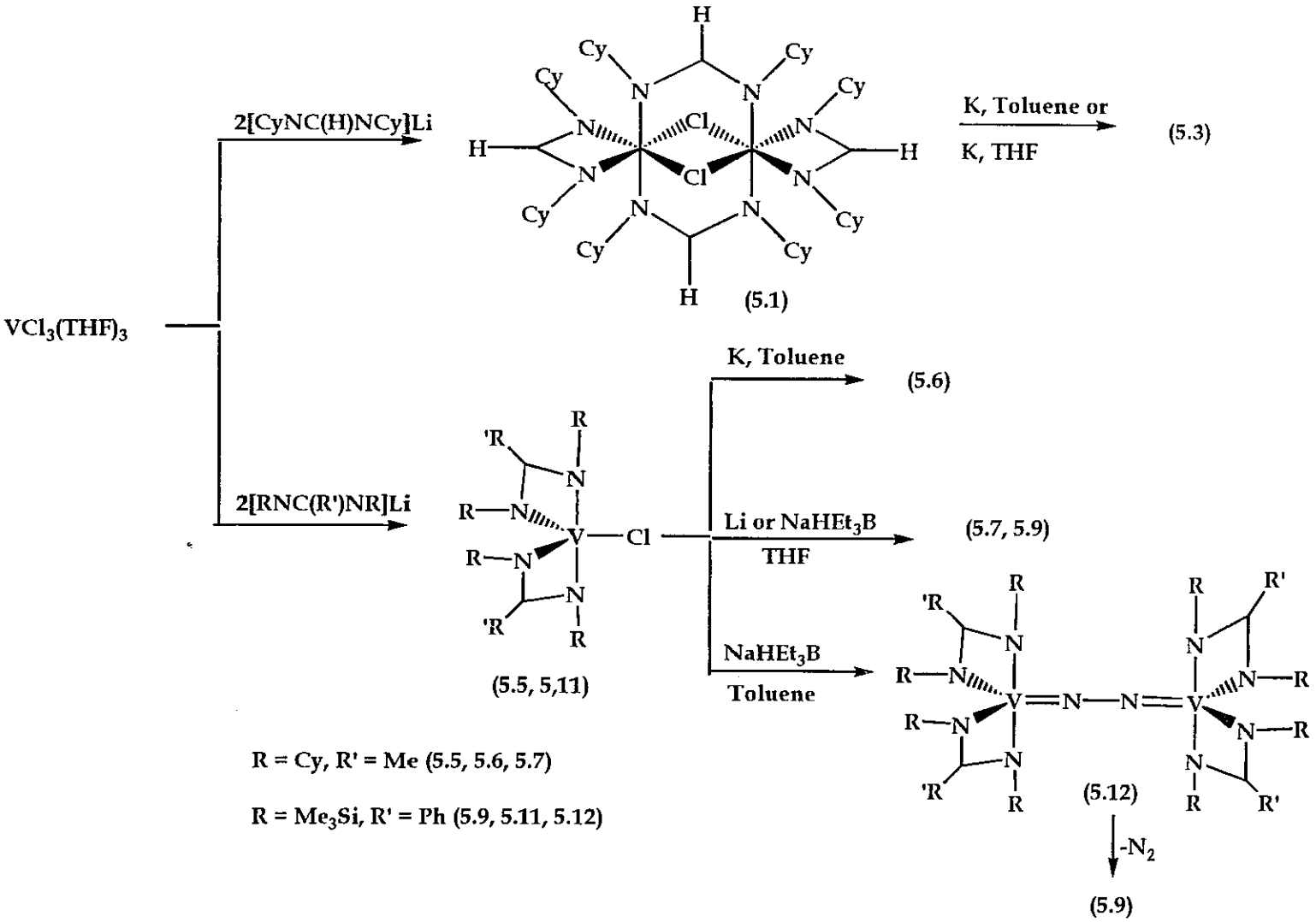
is somewhat surprising since it contradicts the suspected inability of amines, and of chelating amines in particular, to dissociate and consequently to strongly stabilize monomeric V(II) complexes instead of dimeric aggregation. Although all these complexes (**5.2, 5.7, 5.8** and **5.9**) show thermal stability at room temperature in the solid state, they are unstable in non-polar solvents and undergo thermolysis to form different products. The most remarkable difference between these complexes in terms of chemical behaviour, is illustrated by the thermolysis of complex **5.2.** Dimeric, diamagnetic, lantern-type $[\{CyNC(H)NCy\}_2V]_2$ **(5.3)** was obtained as light-green crystals in good yield through thermal dissociation of TMEDA. However, no dimeric structure with a V-V bond was obtained when amidinate or benzamidinate derivatives were used. The thermal dissociation of coordinated THF molecules in **5.7** yielded only the monomeric V(III) complex $[CyNC(Me)NCy]_3V$ **(5.6).**

Complex **5.3** could also be prepared using $VCl_3(THF)_3$ as the starting material. Reaction with two equivalents of [CyNC(H)NCy]Li in toluene gave another dimeric, almost diamagnetic $[\{CyNC(H)NCy\}_2VCl]_2$ (**5.1**) as orange air-stable crystals[19] which on further reduction with metallic potassium in THF or toluene gave the green dimer **5.3**. However, both the V(II) and V(III) dimers **5.3** and **5.1** display different reactivity with coordinating solvents. While complex **5.1** was unreactive towards THF or pyridine, complex **5.3** could easily and reversibly be cleaved by pyridine forming thermally robust, blue, paramagnetic and monomeric

$[CyNC(H)NCy]_2V(Py)_2$ **(5.4)**. Refluxing **5.4** in toluene resulted in the re-formation of **5.3**.

Conversely, the reaction of $VCl_3(THF)_3$ with two equivalents of [CyNC(Me)NCy]Li in THF gave monomeric and paramagnetic $[C_6H_{11}NC(Me)NC_6H_{11}]_2VCl$ **(5.5)**. **(Scheme 5.2)** Also further reduction of **5.5** with metallic K gave different products depending upon the solvents used. For example, the reduction in toluene yielded complex $[(C_6H_{11})NC(Me)N(C_6H_{11})]_3V$ **(5.6)** possibly *via* disproportionation of an intermediate $[(C_6H_{11})NC(Me)N(C_6H_{11})]_2V$ species, probably square-planar, and obviously unable to dimerize. The formation of this intermediate is also suggested by the fact that a monomeric octahedral $[(C_6H_{11})NC(Me)N(C_6H_{11})]_2V$[*trans*-$(THF)]_2$ was obtained when the reduction of **5.5** was carried out in THF. Complex **5.6** could also be obtained directly by reacting $VCl_2(TMEDA)_2$ with two equivalents of lithium acetamidinate salt in non-polar medium e.g. in toluene.

The diamagnetism of **5.3** altogether with the very short V-V distance (the shortest ever found) might indicate the existence of a direct M-M bond with high degree of multiplicity (triple). Since the replacement of the formamidinic hydrogen with the methyl group of the acetamidine ligand cannot be reasonably expected to be able to significantly modify the electronic configuration of the complex, it is evident that only the larger steric hindrance may be responsible for the failure of the acetamidinate ligand to form a dimeric species. On the other hand, complex **5.3** has

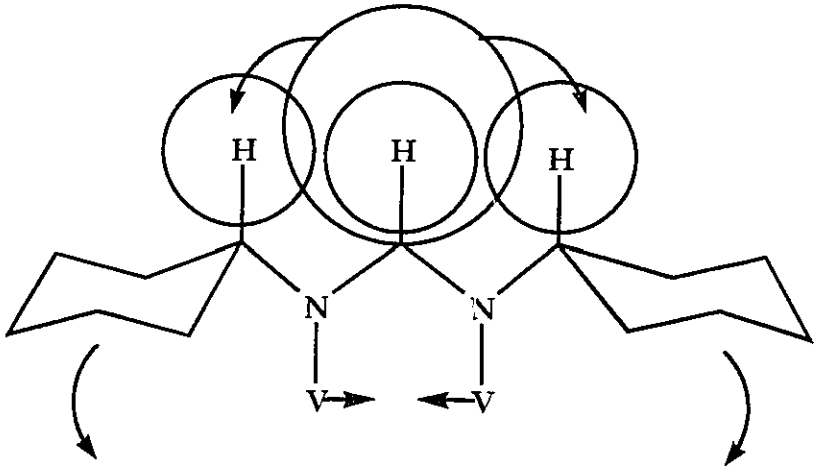

VCl3(THF)3
2[CyNC(H)NCy]Li
(5.1)
K, Toluene or
K, THF
(5.3)
2[RNC(R')NR]Li
(5.5, 5,11)
K, Toluene
(5.6)
Li or NaHEt3B
THF
(5.7, 5.9)
NaHEt3B
Toluene
(5.12)
-N2
(5.9)
R = Cy, R' = Me (5.5, 5.6, 5.7)
R = Me3Si, R' = Ph (5.9, 5.11, 5.12)

Scheme 5.2

an intermetallic distance [V-V = 1.962(2)Å] which, although only slightly, is yet significantly shorter than in the isostructural [(p-tolylformamidinate)$_2$V]$_2$ [V-V =1.978(2)Å]. As in the case of the lantern-type compounds of divalent chromium, this indicates that the increase in ligand steric hindrance results in shorter M-M rather than longer bonds. This is the converse of what could be expected on the basis of the behavior of multiple bonds between main group elements where stronger steric interactions within the molecule usually result in increased bond distances. The X-ray crystal structure of **5.3** has indicated the presence of short H..H non-bonding contacts between the formamidinic hydrogen and other hydrogen atoms of the cyclohexyl groups [ranging from 2.13Å to 2.39Å]. Similar distances have also been determined in the monomeric [(Cy)NC(Me)N(Cy)]$_2$V(TMEDA) [ranging from 2.06 to 2.24]. Similar contacts in biscyclopentadienyl dinuclear species have shown destabilization energy profiles which sharply rise up to 36 Kcal mol^{-1} as the distance becomes shorter[20]. Assuming that comparable destabilization energy also arises from the H..H non bonding contacts of **5.3**, and since the cyclohexyl-cyclohexyl hydrogen atom contacts are definitely longer [ranging from 2.5 to 3.15Å], it is reasonable to assume that the geometry of the ligand is determined primarily by the shortest H..H contacts, i.e. the contacts formed by the formamidinic hydrogen with the two cyclohexyl methyne hydrogens. **(Scheme 5.3)** The increase in steric hindrance introduced by the methyl group of the acetamidinic ligand pushes away the two cyclohexyl "wings" thus resulting in a considerable

distortion of the N-C-N framework.

This is confirmed by the X-ray analysis of the monomeric **(5.5 and 5.6)** which



Scheme 5.3

indeed has shown that short H..H contacts are formed by the H of the methyl groups with some of the hydrogens of the lateral cyclohexyl groups. The reaction of $VCl_3(THF)_3$ with $[Me_3SiNC(Ph)NSiMe_3]Li.TMEDA$ gave a thermally robust $[Me_3SiNC(Ph)NSiMe_3]VCl_2(TMEDA)$ **(5.10)**[19] which yielded the monomeric and paramagnetic $[Me_3SiNC(Ph)NSiMe_3]_2VCl$ **(5.11)** only after forcing the reaction with a second equivalent of the ligand. The reaction conditions required evaporation of the solvent and heating for three hours at 120°C *in vacuo* in solid state followed by the recrystallization of the residue from toluene.

Although complex **5.11** was isostructural with that found for the acetamidinate, there are still a few noticeable differences. Reaction of $VCl_2(TMEDA)_2$ with

[($Me_3SiNC(Ph)NSiMe_3$]Li.TMEDA yielded the monomeric and paramagnetic V(II) derivative **5.9** isostructural with **5.7** and **5.8**. However, attempts to dissociate THF by heating *in vacuum* did not lead to oxidation and formation of [$Me_3SiNC(Ph)NSiMe_3$]$_3$V analogous to **5.6**, probably due to steric hindrance. Instead the reaction produced a green crystalline material, the precursor of the dinitrogen complex, which was stable under Ar but which rapidly turned brown upon exposure to dinitrogen even in the solid state. Although a full characterization of this complex could not be obtained due to its enormous reactivity, recrystallization from toluene under N_2 allowed the isolation and characterization of the new V(II) dinitrogen complex [{$Me_3SiNC(Ph)NSiMe_3$}$_2$V]$_2$(μ-N_2) (**5.12**). On the basis of the reaction with N_2 we tentatively propose a tetrahedrally distorted square-planar structure similar to Cr(II) derivative [$Me_3SiNC(Ph)NSiMe_3$]$_2$Cr[21]. A similar result was obtained by carrying out the reaction of $VCl_2(TMEDA)_2$ with [$Me_3SiNC(Ph)NSiMe_3$]Li.TMEDA in toluene rather than in THF. However, in order to obtain **5.12** using this route, the reaction mixture had to undergo a prolonged heating at 120°C in vacuum in solid state after removal of the solvent *in vacuo*. This unusual procedure is probably necessary to assure the complete removal of TMEDA.

Complex **5.12** was also obtained by carrying out the reduction of **5.11** with a solution of $NaHBEt_3$ in toluene which gave the same green crystalline precursor of the dinitrogen complex under Ar. Even in this case, recrystallization of the green

solid under N_2 gave the dinitrogen complex in good yield. The coordination of the dinitrogen appears to be quite labile since simple treatment with THF released an almost quantitative amount of N_2 during chemical degradation experiments carried out with a Toepler pump. Complex **5.12** is one of the rare cases[22] where coordination of dinitrogen on a V(II) metal center occurs with a non-organometallic complex.

V.4 : X-ray crystallography

Data were collected at temperatures in the range -150 to -160°C using the ω-2θ scan technique to a maximum 2θ value of 50.0°, for suitable air-sensitive crystals mounted on glass fibers. Cell constants and orientation matrices were obtained from the least-squares refinement of 25 carefully centered high-angle reflections. Redundant reflections were removed from the data set. The intensities of three representative reflections were measured after every 150 reflections to monitor crystal and electronic stability. Data were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were located in the difference Fourier maps and refined isotropically in the case of favorable observation/parameter ratio. The final cycle of full-matrix least-squares refinement was based on the number of observed reflections with $[I > 2.5\sigma(I)]$. Neutral atomic scattering factors were taken from Cromer and Waber[18]. Anomalous dispersion effects were included in Fcalc. All calculations were performed using the TEXSAN package on a Digital VAX station. Selected bond distances and angles are

given in **Appendix D.**

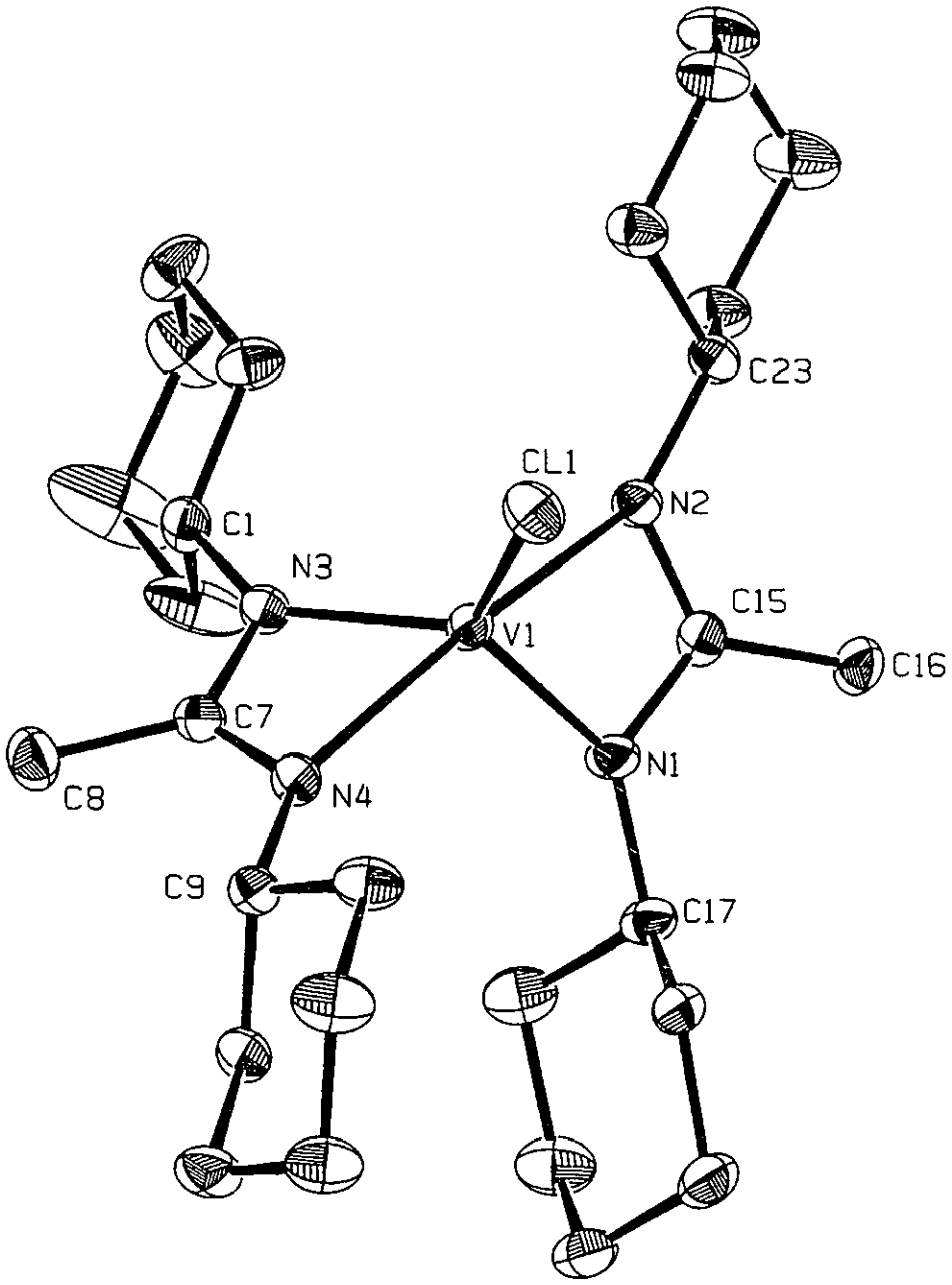


Fig. 5.1. X-Ray Structure of 5.5, $[C_6H_{11}NC(Me)NC_6H_{11}]_2VCl$

Selected Bond Distances (Å) and Bond Angles (deg): V1-Cl1 = 2.300(1), V1-N1 =

1.944(2), V1-N2 = 2.158(2), V1-N3 = 1.960(2), V1-N4 = 2.147(2), Cl1-V1-N1 = 123.00(8), Cl1-V1-N2 = 95.47(7), Cl1-V1-N3 = 123.57(7), Cl1-V1-N4 = 96.50(7), N1-V1-N3 = 113.4(1), N3-V1-N4 = 64.60(9), N2-V1-N4 = 167.77(8).

The coordination geometry of the vanadium atom in this monomeric complex **5.5** may be described in terms of a severely distorted trigonal bipyramid **(Fig. 5.1)** with one chlorine and two nitrogen atoms from two acetamidinate ligands defining the equatorial plane [Cl1-V1-N1 = 123.00(8)°, Cl1-V1-N3 = 123.75(7)°, Cl1-V1-N4 = 96.50(7)°, Cl1-V1-N2 = 95.47(7)°] and the other two nitrogen atoms cited on the two apical sites [N2-V1-N4 = 167.77(8)°]. The angle subtended at the acetamidinate carbon atom by the two nitrogen atoms [N1-C15-N2 = 111.6(2)°, N3-C7-N4 = 111.2(3)°] is significantly narrower than in the formamidinate complexes which probably results from the H..H non bonding contacts formed by the methyl of the acetamidinate group with the cyclohexyl groups.

The monomeric complex **5.6** is formed by a vanadium atom placed in the center of a distorted octahedron **(Fig. 5.2)** bound by the six nitrogen atoms of three acetamidinate ligands [N1-V1-N2 = 63.7(1)°, N3-V1-N4 = 63.5(1)°, N5-V1-N6 = 63.6(1)°]. The three metallacycles are planar [V1-N1-C1-N2 = 1.3(3)°, V1-N3-C2-N4 = 3.5(3)°, N5-V1-C29-N6 = 1.1(2)°] and impose an overall propeller-shape geometry on the central vanadium atom. The angles subtended at the acetamidinate carbon atoms deviate from the normal value expected for a sp^2 carbon atom as a probable

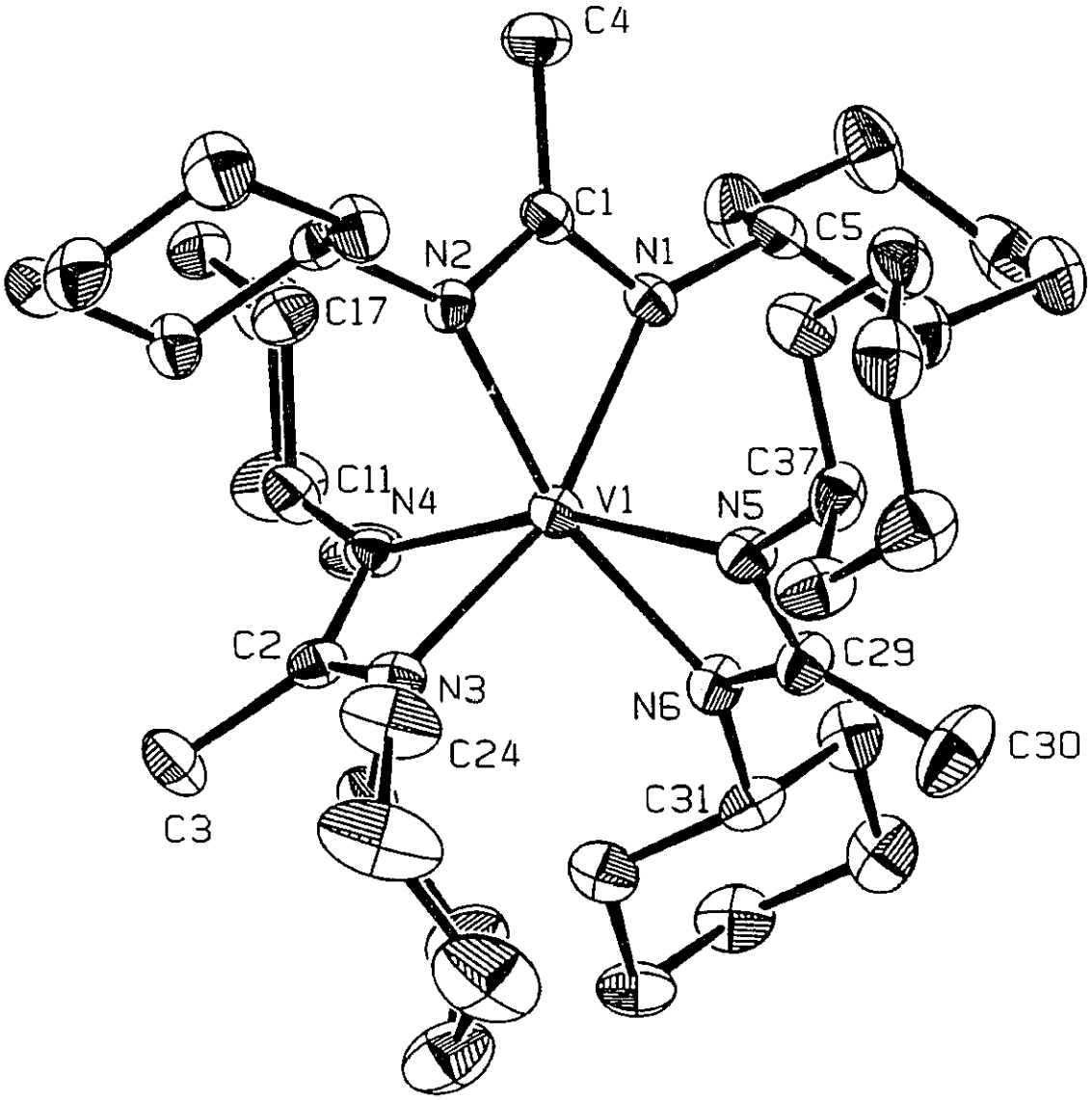


Fig. 5.2. X-Ray Structure of 5.6, $[(C_6H_{11})NC(Me)N(C_6H_{11})]_3V$

Selected Bond Distances (Å) and Bond Angles (deg): V1-N1 = 2.099(3), V1-N2 = 2.091(3), V1-N3 = 2.075(3), V1-N4 = 2.091(4), N1-V1-N2 = 63.7(1), N3-V1-N4 = 63.5(1), N5-V1-N6 = 63.6(1), N1-V1-N5 = 91.9(1), N1-C1-N2 = 112.1(3), N3-C2-N4 = 112.2(4).

result of the H..H short non-bonding contacts formed by the central methyl hydrogen atoms and some of the hydrogens of the cyclohexyl groups [av. H..H = 1.94Å].

The molecular structure of complex **5.9** reveals the molecule to be monomeric with the vanadium atom placed in the center of a regular octahedron **(Fig. 5.3)** generated by a twofold crystallographic axis and defined by four nitrogen atoms of the two equatorial benzamidinate ligand [N1-V1-N2 = 61.4(1)°, N1-V1-N1a = 172.0(2)°] and the two oxygens of two axial molecules of THF placed *trans* with

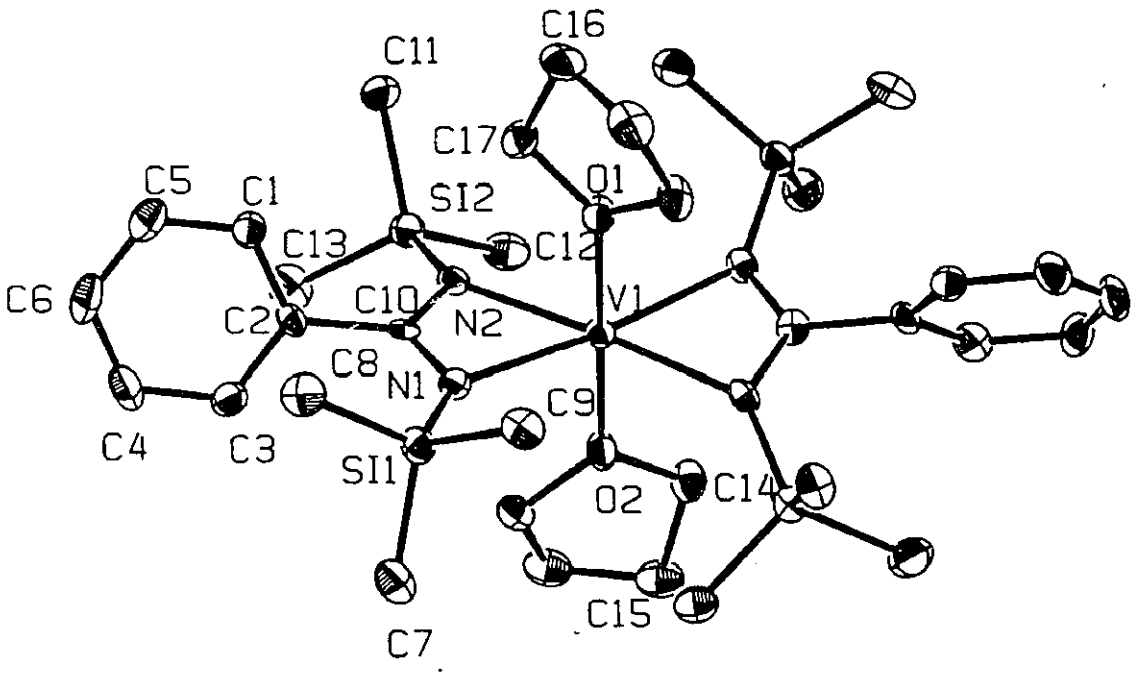


Fig. 5.3. X-Ray Structure of 5.9, $[(Me_3Si)NC(Ph)N(SiMe_3)]_2V(THF)_2$

Selected Bond Distances (Å) and Bond Angles (deg): V1-N1 = 2.221(4), V1-N2 =

2.232(3), V1-O1 = 2.174(4), V1-O2 = 2.147(4), O1-V1-O2 = 180.0(0), N1-V1-N2 = 61.4(1), N1-V1-O1= 86.01(9), N1-C10-N2 = 118.1(4).

respect to each other [O1-V1-O2 = 180.0°, O1-V1-N1 = 86.01(9)°, O1-V1-N2 = 92.52(9)°]. The V-N [V1-N1 = 2.221(4)Å, V1-N2 = 2.232(3)Å] and the V-O [V1-O1 = 2.174(4)Å, V1-O2 = 2.147(4)Å] bond distances compare well with those of the other amidinate complexes reported in this chapter. The four-membered rings formed by the chelating benzamidinate ligands are almost planar [V1-N1-C10-N2 = 4.0(4)°].

Complex **5.11** is monomeric with the vanadium atom placed at the center of a

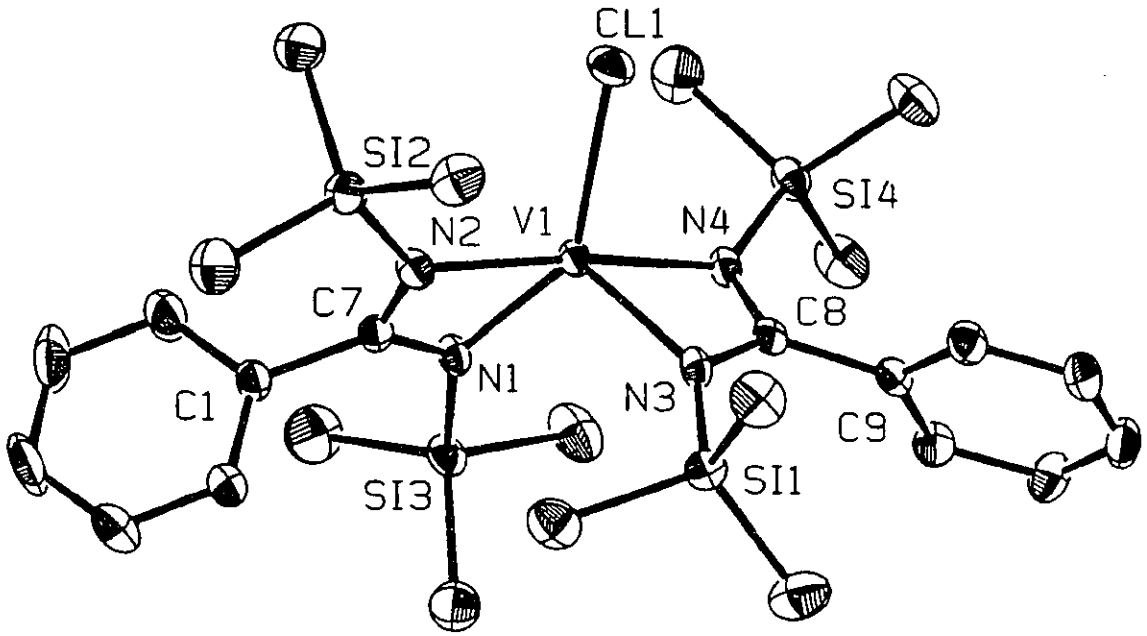


Fig. 5.4. X-Ray Structure of 5.11, $[(Me_3Si)NC(Ph)NSiMe_3)]_2VCl$

Selected Bond Distances (Å) and Bond Angles (deg): V1-Cl1 = 2.306(2), V1-N1 =

2.005(3), V1-N3 = 1.969(3), V1-N2 = 2.111(2), V1-N4 = 2.114(2), N1-V1-N3 = 106.9(1), Cl1-V1-N1 = 139.71(8), Cl1-V1-N3 = 113.4(9), Cl1-V1-N4 = 91.82(8), Cl1-V1-N2 = 95.69(8).

trigonal bipyramid **(Fig. 5.4)**. The equatorial plane is defined by one chlorine atom [V1-Cl1 = 2.306(2)Å] and two nitrogen atoms [V1-N1 = 2.005(3)Å, V1-N3 = 1.969(3)Å] of two benzamidinate anions [Cl1-V1-N1 = 139.71(8)°, Cl1-V1-N3 = 113.40(9)°, N1-V1-N3 = 106.9(1)°] while the remaining two nitrogen atoms occupy the axial positions [Cl1-V1-N2 = 139.71(8)°, Cl1-V1-N4 = 91.82(8)°, N2-V1-N4 = 171.59(9)°].

Molecule **5.12** is a dimeric dinitrogen complex where two $[Me_3SiNC(Ph)NSiMe_3]_2V$ units are linked by an end-on bridging dinitrogen molecule **(Fig. 5.5)**. The V-N_2-V array is almost linear [V1-N1-N2 = 173.7(4)°, V2-N2-N1 = 179.3(4)°] forming rather short V-N distances [V1-N1 = 1.756(5)Å, V2-N2 = 1.757(5)Å] which might indicate significant reduction of the dinitrogen molecule. The short N-N distance [N1-N2 = 1.235(6)Å] also indicates that partial reduction of the N-N multiple bond has occurred. If the vanadium atom is considered as lying at the center of a distorted square-pyramid, then the basal plane is bound by the four nitrogen atoms of two benzamidinate groups [N2-V2-N3 = 98.9(2)°, N2-V2-N4 = 127.5(2)°, N2-V2-N5 = 97.3(2)°, N2-V2-N6 = 119.4(2)°] with the vanadium atom significantly elevated above the basal plane [distance of V2 from

the N3-N4-N5-N6 plane = 0.73(6)Å].

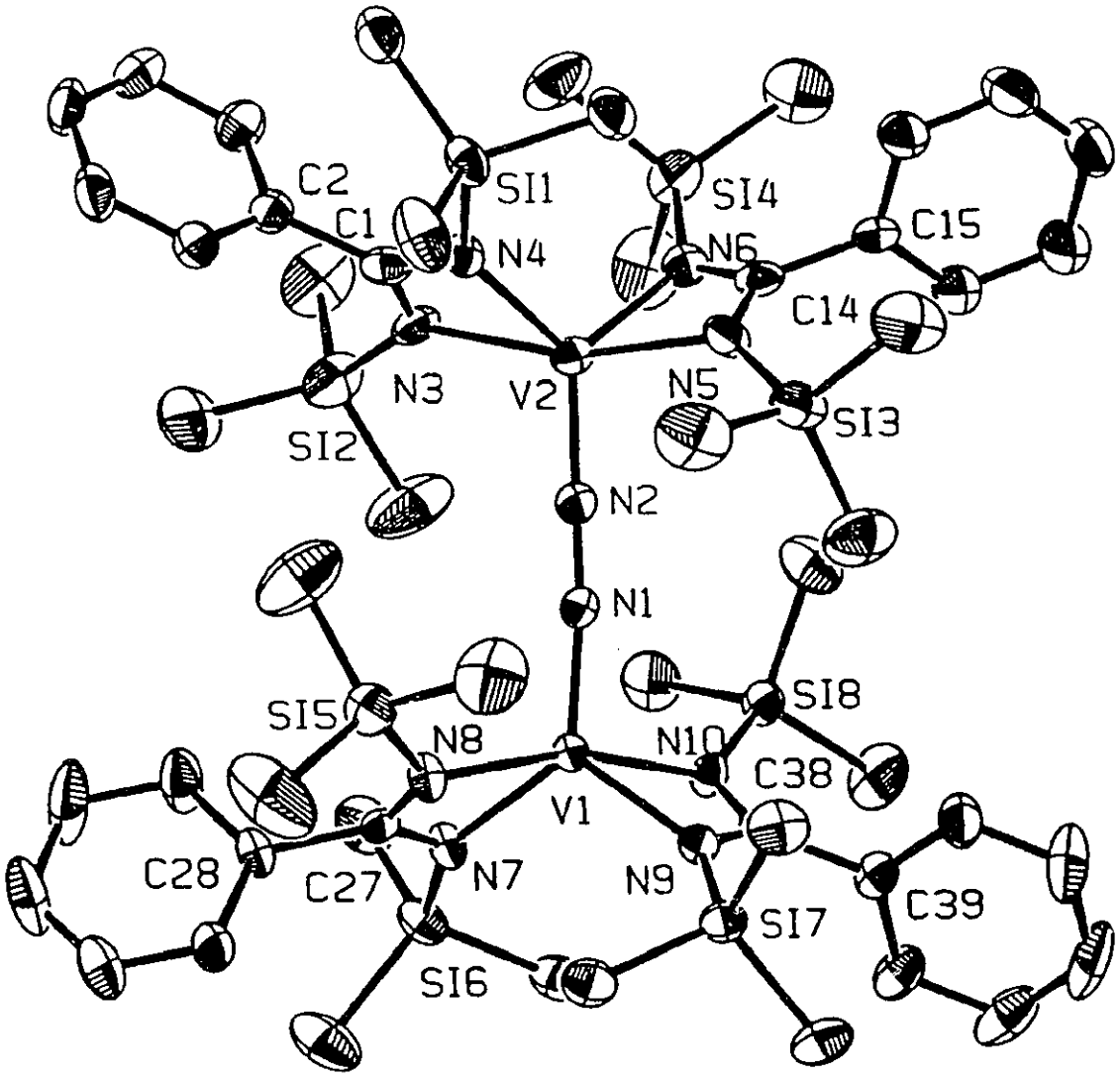


Fig. 5.5. X-Ray Structure of 5.12, $\{[Me_3SiNC(Ph)NSiMe_3]_2V\}_2(N_2)$

Selected Bond Distances (Å) and Bond Angles (deg): V1-N1 = 1.756(5), V2-N2 = 1.757(5), N1-N2 = 1.235(6), V1-N7 = 2.074(5), V1-N8 = 2.137(5), N7-V1-N9 = 116.0(2), N7-V1-N1 = 129.2(2), N1-V1-N9 = 114.7(2), N1-V1-N8 = 97.4(2), N1-V1-N10 =

97.7(2).

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19. Crystal data for **5.1**: orthorhombic Fddd, a = 27.295Å, b = 28.761Å, c = 15.716Å, Dc = 0.950, μ = 4.808, R = 9.7, R_w = 10.8, G.o.F. = 3.84 for 168 parameters and 1722 obervations. V1-V1a = 2.81(2)Å. **5.10**: Monoclinic, P21/c, a = 10.171Å, b = 12.996Å, c = 20.185Å, b = 92.41°, Dc = 1.250, μ =

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CHAPTER VI

Synthesis, Reactivity and Stability of Di- and Trivalent Samarium Amides

VI. 1 : Introduction

In the past few years, lanthanide chemistry has been one of the most rapidly developing areas of organometallic chemistry.[1] A significantly low radial extension and ionic character is a distinctive characteristic of these elements. This means that the chemical behavior is mainly determined by electrostatic and steric factors rather than by the interactions between the metal and ligand orbitals. In other words, the choice of the ligand donor atom and the tuning of its steric bulk are central to the stabilization of these complexes and to prevent unwanted features such as decomposition, disproportionation and ligand scrambling.

Among the lanthanides that exist in the +2 oxidation state (Eu^{+2}, Yb^{+2}, Sm^{+2}), samarium is the most reactive, due to its high reduction potential (-1.55V),[2] and consequently its complexes are the most difficult to stabilize. Cyclopentadienyl anion[3] and the cyclooctatetraenyl dianion[4] are two classes of ligands which have been successfully used for the stabilization of Sm(II) species. In particular, $(C_5Me_5)^-$ has allowed the isolation of some of the most highly reactive organolanthanide derivatives[5] providing new classes of complexes[6], unusual structural types[7] and spectacular reactivity patterns[8]. More recently, the sterically demanding

tris(pyrazolyl)borate, which similar to the Cp* is a 6e⁻ donor and has similar steric requirements, has also proved to be able to stabilize the Sm(II)[9] metal center. Apart from these ligands, only less than a handful of compounds, containing divalent samarium, have been reported with oxygen,[10] nitrogen[11] and phosphorous[12] donor based ligands.

Recently, we have reported that a tetraanionic porphyrinogen ligand promoted the formation of either, an unusual Sm dinitrogen complex,[13] or a divalent bissamarium species, [14] depending upon the reaction conditions. These findings suggested to us that N-donor based ligands might be suitable for the stabilization of the Sm(II) metal center and may well provide promising reactivity patterns. With this respect, anionic dialkylamides are one of the most versatile families of ligands.[15] A feature that makes these ligands especially attractive is the basicity, which is important for both the stabilization of wide range of oxidation states and for promoting di- and poly-nuclear aggregation, through bridging interactions of the nitrogen donor atom. Another attractive characteristic of these ligands is a virtually unlimited possibility of adjusting the steric hindrance by selecting the appropriate organic moieties bound to nitrogen. Surprisingly enough, the chemistry of Sm(II) amides is limited to a few reports.[11b]

These observations prompted us to start a project on the synthesis, characterization and reactivity of Sm(II) amides. Since some difficulties were

anticipated for the employment of $SmI_2(THF)_2$ as a starting material, we have also preliminarily explored the preparation of selected Sm(III) amide complexes which might be further reduced towards divalent species.

VI. 2 : Experimental Part

All operations were performed under an inert atmosphere of a nitrogen filled drybox or by using standard Schlenk-type glassware in combination with a nitrogen-vacuum line. $SmCl_3(THF)_3$[16] and $SmI_2(THF)_2$[17] were prepared according to the literature procedures. Cy_2NH, $i\text{-}Pr_2NH$ and TMEDA (Aldrich) were distilled prior to use over Na and K metals. The corresponding lithium salts (R_2NLi) were prepared by treating the hexane solutions of the amines with stoichiometric amounts of n-BuLi. NpLi and NfLi were obtained by refluxing the solutions of the corresponding chlorides with finely dispersed metallic lithium under Ar atmosphere. The NaH and KH suspensions in mineral oil (Aldrich) were washed with hexane, dried, and stored under nitrogen in sealed ampoules. $NaBHEt_3$ was used as received (Aldrich). Infrared spectra were recorded on a Mattson 3000 FTIR instrument from Nujol mulls prepared inside the dry-box. Samples for magnetic susceptibility measurements were prepared inside the dry-box and the measurements were carried out at room temperature using a Gouy balance (Johnson Matthey). Magnetic moments were calculated by following standard methods[18] and corrections for underlying diamagnetism were applied to the data[19]. Elemental analyses were carried out by using a Perkin Elmer Series II CHN/O 2400-analyzer.

Preparation of $[(Cy_2N)_2Sm(\mu\text{-}Cl)(THF)]_2$ (6.1):

The addition of Cy_2NLi (15.7g, 83.8 mmol) at room temperature to a stirred solution of $SmCl_3(THF)_3$ (19.8g, 41.8 mmol) in THF (150 ml) turned the color of the solution orange. The stirring was continued for additional 3 hours followed by removal of the solvent *in vacuo*. The residual crystalline solid was redissolved in toluene (150 ml) and LiCl was filtered out. Orange crystals of **6.1** (20.8 g, 33 mmol, 81%) separated upon allowing the filtrate to stand overnight at -30°C.

Elemental Analysis for $C_{56}H_{105}N_4O_2Sm_2Cl_2$: Calcd (obsvd): C 54.37 (53.99), H 8.47 (8.19), N 4.53 (4.44).

Magnetic Moment: $\mu_{eff} = 2.30\ \mu_B$.

Infrared Spectrum (Nujol mull, cm^{-1}): 2661(m), 1454(sh), 1376(s), 1249(m), 1157(w), 1145(sh), 1120(sh), 1025(s, br), 983(m), 944(sh), 919(w), 877(m, br), 842(m), 798(m), 777(m), 725(m), 665(sh), 651(sh), 597(m), 572(m), 493(m).

Preparation of $[(i\text{-}Pr_2N)_2SmCl_3(LiTMEDA)_2]$ (6.2):

The addition of TMEDA (4.5 ml, 29.8 mmol) to a solution of $SmCl_3(THF)_3$ (7.0g, 14.8 mmol) in THF (60 ml), followed by the addition of lithium diisopropylamide (3.2g, 29.8 mmol), quickly turned the color of the solution orange. The stirring was continued for about 3 hours. The solvent was evaporated *in vacuo* and the residual

oil was redissolved in toluene (80 ml). After removal of LiCl by filtration and standing at -30°C for two days, the resulting solution yielded orange crystals of **6.2** (3.3g, 4.7 mmol, 32%).

Elemental Analysis for $C_{24}H_{60}N_6SmCl_3Li_2$: Calcd (obsvd): C 40.98 (40.77), H 8.60 (8.48), N 11.95 (12.05).

Magnetic Moment: $\mu_{eff} = 1.58\ \mu_B$

Infrared Spectrum (Nujol mull, cm^{-1}): 1461(sh), 1405(w), 1376(m, br), 1351(m), 1290(m), 1251(w), 1180(sh), 1130(w), 1114(w), 1101(m), 1062(m), 1035(m), 1016(m), 948(m), 917(sh), 842(w), 792(sh), 769(w), 723(w), 586(w), 518(w), 482(m).

Preparation of $(Cy_2N)_6Sm_4Cl_6(THF)_2$ (6.3):

A suspension of $[(Cy_2N)_2Sm(\mu\text{-}Cl)(THF)]_2$ (2.1 g, 1.7 mmol) in toluene (40 ml) was warmed and stirred at 60°C for about 24 hours. The resultant clear orange solution was evaporated to dryness *in vacuo* and the residual solid redissolved in hexane. Dark red crystals of **6.3** (0.8 g, 0.39 mmol, 47%) separated upon standing overnight at room temperature.

Elemental Analysis for $C_{80}H_{148}N_6Cl_6O_2Sm_4$: Calcd (obsvd): C 47.10 (46.88), H 7.31 (7.19), N 4.12 (4.33).

Magnetic Moment: $\mu_{eff} = 4.25\ \mu_B$.

Infrared Spectrum (Nujol mull, cm^{-1}): 1455(sh, br), 1376(m), 1342(w), 1247(m), 1157(w), 1141(m), 1118(sh, br), 1081(w), 1033(m, br), 981(m), 943(sh), 889(sh), 840(m), 798(m), 775(m), 723(w), 655(sh), 615(w), 572(m), 495(sh), 440(m), 420(m).

Preparation of $[(Cy_2N)_4SmLi(THF)].THF$ (6.4):

Method A : A stirred orange suspension of **6.1** (5.5 g, 4.4 mmol) in diethylether (140 ml) was treated with NpLi (0.7 g, 8.9 mmol) at room temperature. The reaction was very slow and the stirring was continued for about 20 hours. The solvent was evaporated to dryness *in vacuo* and the residual solid was redissolved in hexane (30 ml). Filtration of LiCl followed by cooling of the clear orange solution at -30°C yielded yellow crystals of **6.4** (1.3 g, 1.36 mmol, 17%) over a period of one week.

Method B : A stirred orange suspension of **6.1** (4.9 g, 4.0 mmol) in diethyl ether (140 ml) was treated with NfLi (1.21 g, 8.5 mmol) at room temperature and the stirring was continued for about 24 hours. The solvent was evaporated to dryness *in vacuo* and the residual solid was redissolved in hexane (30 ml). The resulting solution was filtered to remove LiCl and allowed to stand at -30°C over a period of one week upon which yellow crystals of **6.4** (1.1g, 1.15 mmol, 28%) separated.

Elemental Analysis for $C_{56}H_{106}N_4O_2LiSm$: Calcd (obsvd): C 65.64 (64.99), H

10.43 (10.34), N 5.47 (5.12).

Magnetic Moment: $\mu_{eff} = 2.07\ \mu_B$.

Infrared Spectrum (Nujol mull, cm^{-1}): 1452(sh), 1376(sh), 1340(m), 1261(w), 1197(w), 1176(m), 1130(m), 1103(m), 1087(w), 1047(sh), 983(w), 960(w), 944(sh), 917(w), 887(sh), 842(m), 796(m), 723(w), 655(m), 626(m), 613(sh), 568(w), 495(m), 470(m).

Preparation of [$Sm(Cy_2N)_3THF$].toluene (6.5):

Method A : The addition of Cy_2NLi (1.3 g, 7.1 mmol) to the stirred solution of $SmCl_3(THF)_3$ (1.2 g, 2.5 mmol) in THF (30 ml) at room temperature turned the color instantaneously pale yellow. The solvent was evaporated *in vacuo* and the residual crystalline solid was redissolved in toluene (30 ml). After filtration of LiCl, the clear solution was allowed to stand at -30°C for two days upon which pale yellow single crystals of **6.5** (0.9 g, 1.18 mmol, 72%) separated.

Method B : A stirred solution of **6.1** (1.3 g, 1.0 mmol) in THF (40 ml) was treated with lithium naphthalenide (3.3 mmol) prepared under Ar in THF, at -78°C. The reaction was instantaneous and the color of the solution became burgundy red. During the warming to room temperature, the color turned orange-brown. The solvent was evaporated *in vacuo* and the residual oil redissolved in toluene (20 ml).

A small amount of black solid was removed by filtration and the resultant clear solution was allowed to stand seven days at -30°C upon which yellow crystals of **6.5** (0.3 g, 0.4 mmol, 20%) separated.

Elemental Analysis for $C_{47}H_{82}N_3OSm$: Calcd (obsvd): C 65.98 (65.33), H 9.66 (9.61), N 4.91 (4.78).

Magnetic Moment: $\mu_{eff} = 1.60\ \mu_B$.

Infrared Spectrum (Nujol mull, cm^{-1}): 2661(m), 1450(br, s), 1376(m), 1340(w), 1240(m), 1195(w), 1174(w), 1143(sh), 1118(sh), 1085(m), 1064(m), 1030(br, s), 983(m), 960(w), 944(sh), 920(m), 887(m), 867(m), 840(m), 796(m), 775(m), 727(sh), 694(m), 655(sh), 646(w), 620(sh), 573(sh), 489(sh), 465(m), 440(m).

Preparation of $(Ph_2N)_4Sm[Na(TMEDA)]_2$ (6.6):

A clear solution of Ph_2NH (4.1 g, 24.0 mmol) in THF (70 ml) was stirred with NaH (1.2 g, 50.0 mmol) and refluxed for 6 hours. After removal of excess NaH by filtration, the addition of $SmI_2.TMEDA_2$ (3.85 g, 6.0 mmol) turned the color dark brown. The reaction mixture was stirred for 24 hours and dark green crystals of **6.6** (3.8 g, 3.6 mmol, 60%) were obtained from the resulting dark brown solution, upon standing two days at -30°C.

Elemental Analysis for $C_{60}H_{72}N_8SmNa_2$: Calcd (obsvd): C 65.42 (65.27), H 6.59

(6.39), N 10.17 (10.34).

Magnetic Moment: μ_{eff} = 3.61 μ_B.

Infrared Spectrum (Nujol mull, cm^{-1}): 1577(sh), 1560(s), 1460(sh, br), 1376(m), 1330(s), 1305(sh), 1199(s), 1170(m), 1076(s), 1037(s), 1020(s), 987(m), 948(s), 883(s), 864(w), 827(w), 804(m), 788(w), 750(sh), 694(sh), 516(sh), 495(m).

Preparation of $[(Ph_2N)_2Sm(THF)_4]$·THF (6.7):

A solution of Ph_2NH (1.8 g, 10.7 mmol) in THF (50 ml) was stirred and refluxed with KH (0.7 g, 17.5 mmol) for one hour and then filtered. A solution of $SmI_2(THF)_2$ (2.9 g, 5.3 mmol) in THF (50 ml) was added at room temperature under N_2. The reaction mixture was stirred for 24 hours and the color turned very dark grey. The resulting solution was concentrated and allowed to stand two days at -30°C upon which dark blue crystals of **6.7** separated (3.4 g, 3.9 mmol, 75%).

Elemental Analysis for $C_{44}H_{60}N_2O_5Sm$: Calcd (obsvd): C 62.37 (61.82), H 7.14 (6.81), N 3.31 (3.54).

Magnetic Moment: μ_{eff} = 3.80 μ_B.

Infrared Spectrum (Nujol mull, cm^{-1}): 1577(sh), 1461(s, br), 1378(sh), 1346(m), 1297(br), 1261(m), 1197(s), 1167(m), 1082(m), 1025(m), 987(s), 874(w), 800(m),

749(sh), 702(sh), 694(sh), 523(m), 500(m).

Preparation of $(Ph_2N)_4SmNa(TMEDA)$ (6.8):

The addition of trimethylsilyl azide (0.2 ml) to a stirred solution of **6.6** (1.14 g, 1.0 mmol) in THF (50 ml) immediately changed the color to orange. After removal of the solvent by evaporation *in vacuo*, the oily residue was dissolved in toluene (20 ml). The resulting solution was filtered and layered with hexane (20 ml) yielding orange single crystals of **6.8** (0.5 g, 0.5 mmol, 52%).

Elemental Analysis for $C_{54}H_{56}N_6SmNa$: Calcd (obsvd): C 67.39 (67.23), H 5.86 (5.80), N 8.73 (9.06).

Magnetic Moment: $\mu_{eff} = 1.65\ \mu_B$.

Infrared Spectrum (Nujol mull, cm^{-1}): 1581(sh), 1567(sh), 1470(sh, br), 1376(m), 1330(w), 1305(br), 1286(br), 1193(m), 1174(m), 1080(s), 1025(s), 991(m), 910(s), 888(br, w), 817(m, br), 748(sh), 694(sh), 49(w), 520(sh), 497(sh).

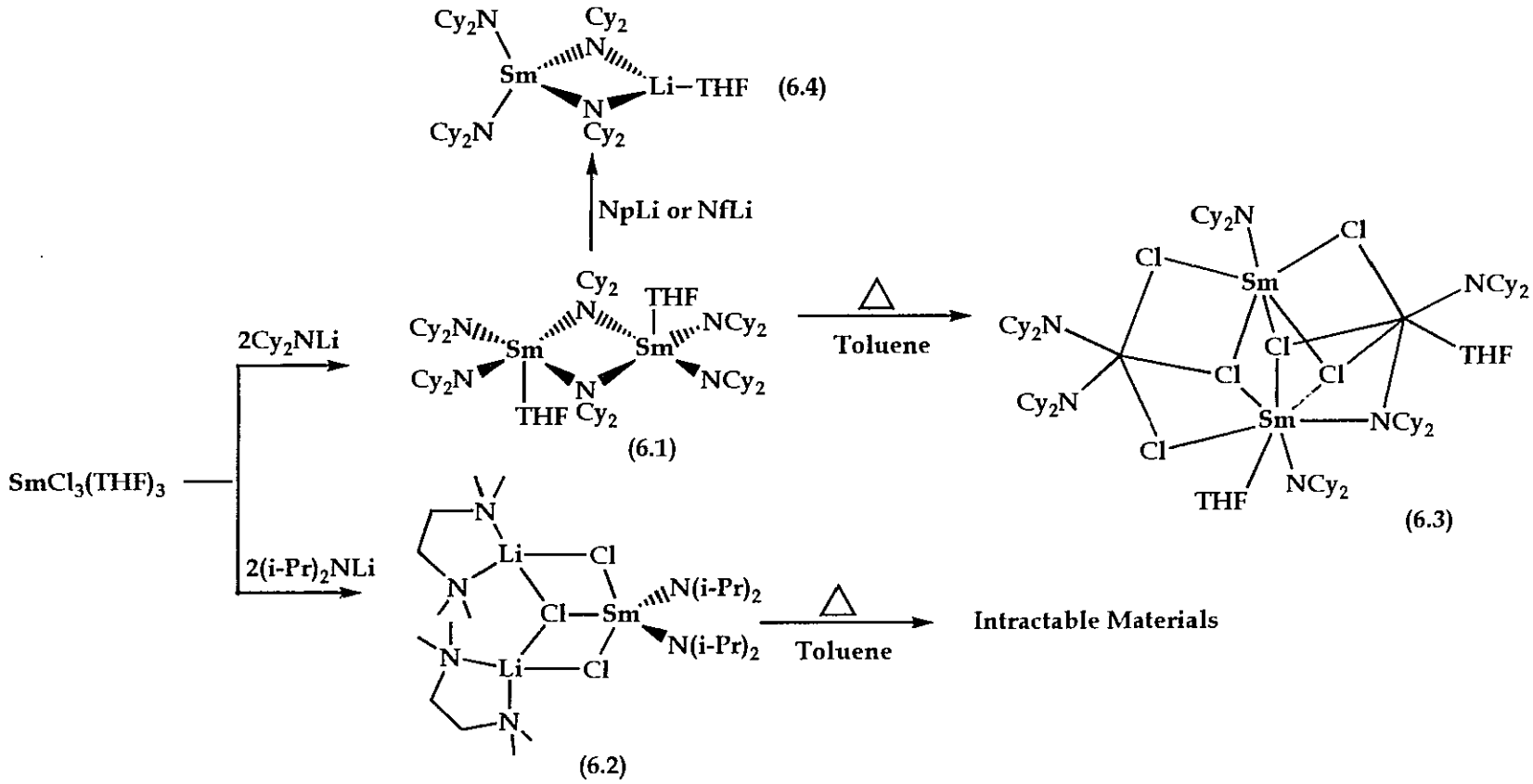
VI. 3 : Results and Discussion

The reaction at room temperature of $SmCl_3(THF)_3$ with two equivalents of Cy_2NLi formed an orange-yellow air-sensitive solution from which orange crystals of dimeric $[(Cy_2N)_2Sm(\mu\text{-}Cl)(THF)]_2$ **(6.1)** were isolated in good yield upon crystallization from toluene **(Scheme 6.1)**. While the formulation was inferred from

combustion analysis data, the magnetic moment (μ_{eff} = 2.30 μ_B) was significantly higher than expected for the f^5 electronic configuration of a Sm(III) metal center. The structure of **6.1** was elucidated by X-ray crystal structure.

Similar reaction of $SmCl_3(THF)_3$ with diisopropylamide lithium, which may be considered comparable to the cyclohexyl substituents in terms of steric hindrance, showed a remarkably different behavior. When the reaction was carried out under comparable reaction conditions, intractable materials were obtained. However, a new crystalline complex $[(i\text{-}Pr_2N)_2SmCl_3(LiTMEDA)_2]$ **(6.2)** was isolated only when the reaction was carried out in the presence of TMEDA. The formula, indicated by combustion analysis and X-ray fluorescence data, suggested a monomeric structure for the complex. The molecular structure was elucidated by single crystal X-ray diffraction analysis.

Both complexes **6.1** and **6.2** showed thermal instability in solution, where a slow reaction occurred in solution of non-polar solvent. However, the two complexes are indefinitely stable at room temperature in the solid state. As expected, the reaction can be greatly accelerated by heating at 60°C. Unfortunately in the case of **6.2**, the product of the thermolysis could not be isolated due to very high solubility. However, in the case of complex **6.1**, dark-red crystals of $(Cy_2N)_6Sm_4Cl_6(THF)_2$ **(6.3)** were isolated in good yield from a red-orange solution. The combustion analysis and X-ray fluorescence data were consistent with a formulation which indicated


Cy2N
Cy2
Sm
N
Li–THF
(6.4)
NpLi or NfLi
THF
NCy2
2Cy2NLi
Toluene
(6.1)
Cl
(6.3)
SmCl3(THF)3
2(i-Pr)2NLi
N(i-Pr)2
Intractable Materials
(6.2)

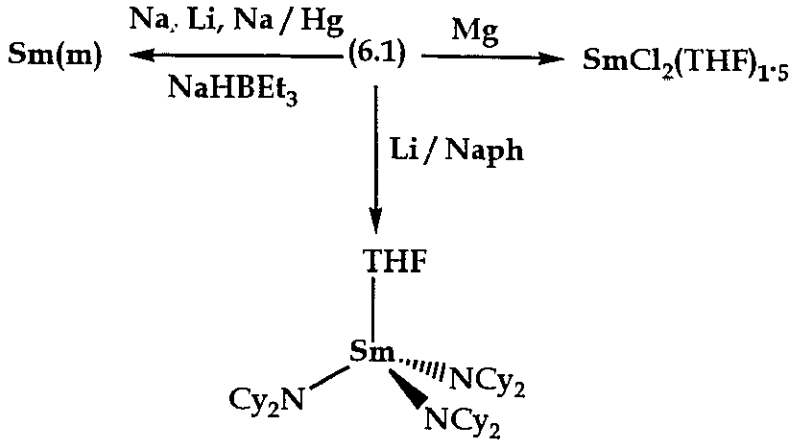
Scheme 6.1

partial loss of coordinated THF thus indicating a probable higher level of nuclearity. The structure was elucidated by an X-ray single crystal structure determination.

Attempts to replace the bridging chlorides in complex **6.1** with NpLi or NfLi did not afford the corresponding alkyl derivative but rather yielded the same product $[(Cy_2N)_4SmLi(THF)].THF$ **(6.4).** The formulation was indicated by combustion analysis and X-ray fluorescence data which showed the absence of chlorine. The light color of the product suggested that the samarium atom was probably in the trivalent oxidation state. These observations indicated that a ligand scrambling occurred at the time of chlorine removal during the alkylation reaction. Accordingly, the yield of complex **6.4** was always rather poor, yet significant.

Attempts to reduce Sm(III) dimer **(6.1)** using a variety of reducing agents (Na, Li, Na/Hg, $NaHBEt_3$) invariably led to either metallic Sm or some intractable materials **(Scheme 6.2).** Interestingly enough, the reduction of **6.1** with Mg powder gave high yield of a deep-green very air-sensitive solid whose combustion analysis and X- ray fluorescence data were consistent with the formulation $SmCl_2(THF)_{1.5}$. Conversely, reduction with Li/Naphthalide gave metallic Sm and yellow crystals of $[Sm(Cy_2N)_3THF].toluene$ **(6.5)** probably as a result of the formation of an unstable $Sm(Cy_2N)_2$ species followed by disproportionation into Sm(III) and Sm^0. Complex **6.5** was more conveniently prepared by reaction of $SmCl_3(THF)_3$ with three equivalents of Cy_2NLi. Attempts to remove THF from the coordination sphere of the

samarium atom and to prepare a solvent-free $Sm(Cy_2N)_3$ species by azeotropic removal of THF in toluene were unsuccessful, as only a highly soluble intractable oil was obtained.



(6.5)

Scheme 6.2

The failure to prepare Sm(II) amides *via* reduction of Sm(III) precursors possibly indicates that these species may posses an intrinsic instability towards disproportionation. This is further emphasized by the fact that the utilization of $SmI_2(TMEDA)_2$ as starting material yielded, upon reaction with two equivalents of R_2NLi, unidentified complexes, but whose light-yellow color strongly indicated the presence of the metal in the +3 oxidation state. Similar to the case of the Zr(III) compounds,[20] the instability of these particular Sm(II) amides might be ascribed to their ability to form dinuclear structures which readily disproportionate to metallic Sm and anionic Sm(III) species. Another possibility is that metallacyclic structures, similar to those observed in the case of V[21] and Nb[22] amide derivative would be

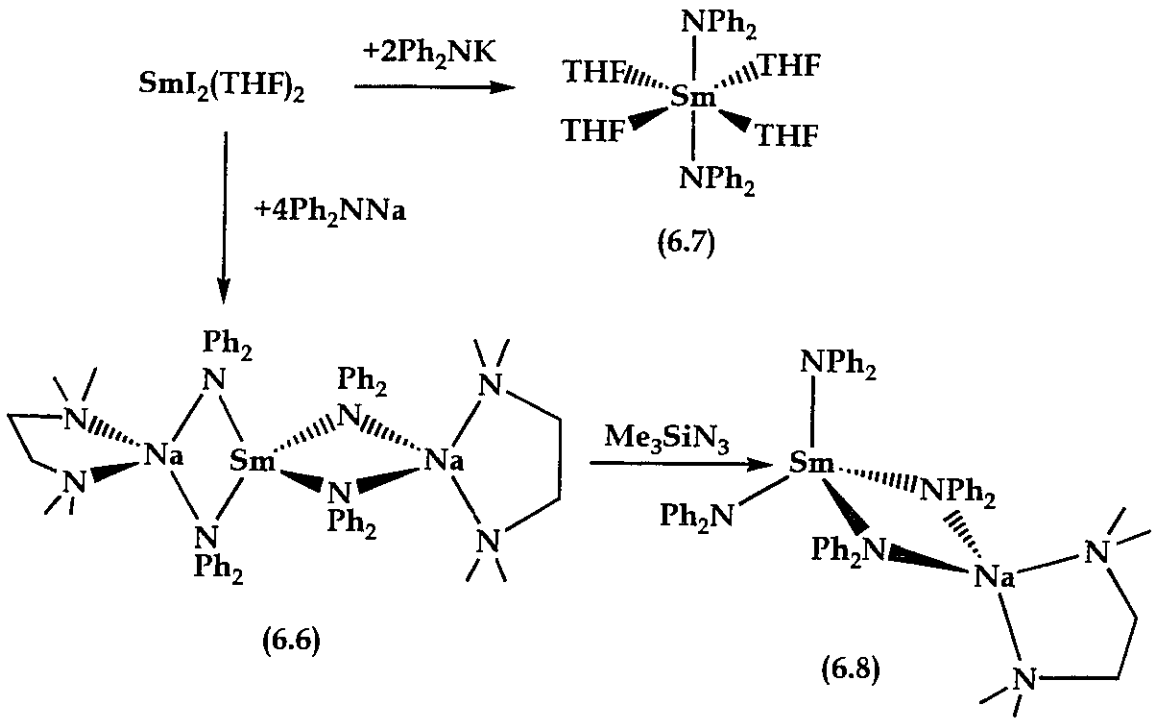
formed *via* C-H σ-bond metathesis.

In order to test these hypotheses, the reaction of $SmI_2(TMEDA)_2$ with R_2NNa having no α -H (e.g. Ph_2NNa) was examined. The reaction using a 1:4 stoichiometry of reagents yielded a four-coordinate metallate Sm(II) amide $(Ph_2N)_4SmNa_2(TMEDA)_2$ **(6.6).** This complex showed the characteristic resonances of the aromatic groups in the IR spectra. Combustion analysis data were consistent with the proposed formulation. The high magnetic moment of **6.6** (μ_{eff} = 3.61μ_B) falls in the expected range observed for other mononuclear Sm(II) metal centers.[23]

The tetrahedral coordination geometry of the Sm atom in complex **6.6** indicates that the steric hindrance is probably responsible for the stabilization of the divalent oxidation state. In order to test this second possibility, the synthesis of a neutral Sm(II) compound was attempted. **(Scheme 6.3)** The reaction of $SmI_2(THF)_2$ with Ph_2NK in a 1:2 ratio at room temperature and in THF gave a high yield of analytically pure $[(Ph_2N)_2Sm(THF)_4](THF)$ **(6.7).** The formulation was indicated by combustion analysis while the absence of iodine was clearly shown by X-ray fluorescence. The magnetic moment calculated on the basis of the proposed formulation (μ_{eff} = 3.80 μ_B) was also as expected for the f^6 electronic configuration of a Sm(II) metal center. The formulation was confirmed by an X-ray crystal structure.

The deviation of the complex **(6.7)** from the regular octahedral geometry is rather

bizarre and might be caused by the steric repulsion between the two amides which are roughly *cis* positioned. This phenomenon cannot be easily interpreted exclusively on the basis of steric consideration since a simple *trans* arrangement, with the two amides aligned and four equatorial THF, should in principle release the steric compression in the molecule and afford a regular octahedral structure. Therefore, the possibility that this distortion might be caused by electronic rather than by steric factors cannot be conclusively excluded at this stage. The fact that both the complexes **6.6** and **6.7** are stable in solution as well as solid state, showing no tendency to dimerize or disproportionate, indicates that the ligand steric bulk is not a prerequisite for the stabilization of the Sm(II) metal center. In fact, the complex **6.7** has four THF molecules which in principle can be dissociated. Another possible reason for the stability of these two samarium complexes is that the corresponding $(Ph_2N)_3Sm(THF)$ or $(Ph_2N)_4SmNa$ species, formed as a result of the disproportionation reaction, may possess some intrinsic instability. To test this final possibility, we have attempted the preparation of Sm(III) complexes. While the direct synthesis from $SmCl_3(THF)_3$ with 3 or 4 equivalents of Ph_2NNa failed, the Sm(III) anionic metallate $(Ph_2N)_4SmNa(TMEDA)$ **(6.8)** was obtained *via* reaction of the Sm(II) derivative **6.6** with Me_3SiN_3 *via* a rather complicated reaction, which obviously required decomposition of the azide and possible elimination of NaN_3. The reaction afforded an orange colored solution which yielded orange crystals of **6.8.** The complex was characterized on the exclusive basis of microanalytical and



Scheme 6.3

infrared data.

In conclusion, the results reported in this chapter have underlined an intrinsic instability of Sm(II) amide where the ligand steric hindrance alone is not sufficient to stabilize the +2 oxidation state. By contrast, the absence of α -hydrogen in the ligand is certainly beneficial for the stabilization of the divalent oxidation state. However, it is also possible that electronic factors are of importance in determining the stability of these species.

VI. 4 : X-Ray Crystallography

Data were collected at temperatures in the range -140 to -160°C using the ω-2θ

scan technique to a maximum 2θ value of 50.0° for suitable air-sensitive crystals mounted on glass fibres. Cell constants and orientation matrices were obtained from the least-squares refinement of 25 carefully centered high-angle reflections. Redundant reflections were removed from the data set. The intensities of three representative reflections were measured after every 150 reflections to monitor crystal and instrument stability. Data were corrected for Lorentz and polarization effects. Absorption corrections (DIFABS) were applied to the data in the case of high residual. The structures were solved by direct methods. The non-hydrogen atoms positions were refined anisotropically. Hydrogen atom positions were located in the difference Fourier maps but not refined. The final cycle of full-matrix least-squares refinement was based on the number of observed reflections with [$I > 2.5\sigma$ (I)]. Neutral atomic scattering factors were taken from Cromer and Waber.[24] Anomalous dispersion effects were included in Fcalc. All calculations were performed using the TEXSAN package on a Digital VAX station. Details on crystal data, selected bond distances and bond angles are given in **Appendix E.**

Complex **6.1** is dimeric with two $Sm(Cy_2N)_2(THF)$ units bridged by two chlorine atoms **(Fig. 6.1).** Each Sm has a distorted trigonal bipyramidal geometry. The equatorial plane is bound by two N atoms of two amides and one bridging chlorine atom [Cl1-Sm1-Cl2 = 78.9(1)°, Cl1-Sm1-O2 = 80.9(2)°, Cl1-Sm1-N1 = 115.8(3)°, Cl1-Sm1-N2 = 124.4(4)°, Cl2-Sm1-O2 = 159.8(2)°, Cl2-Sm1-N1 = 100.6(4)°, N1-Sm1-N2 = 119.1(5)°] while the oxygen atom of one THF molecule and one of the

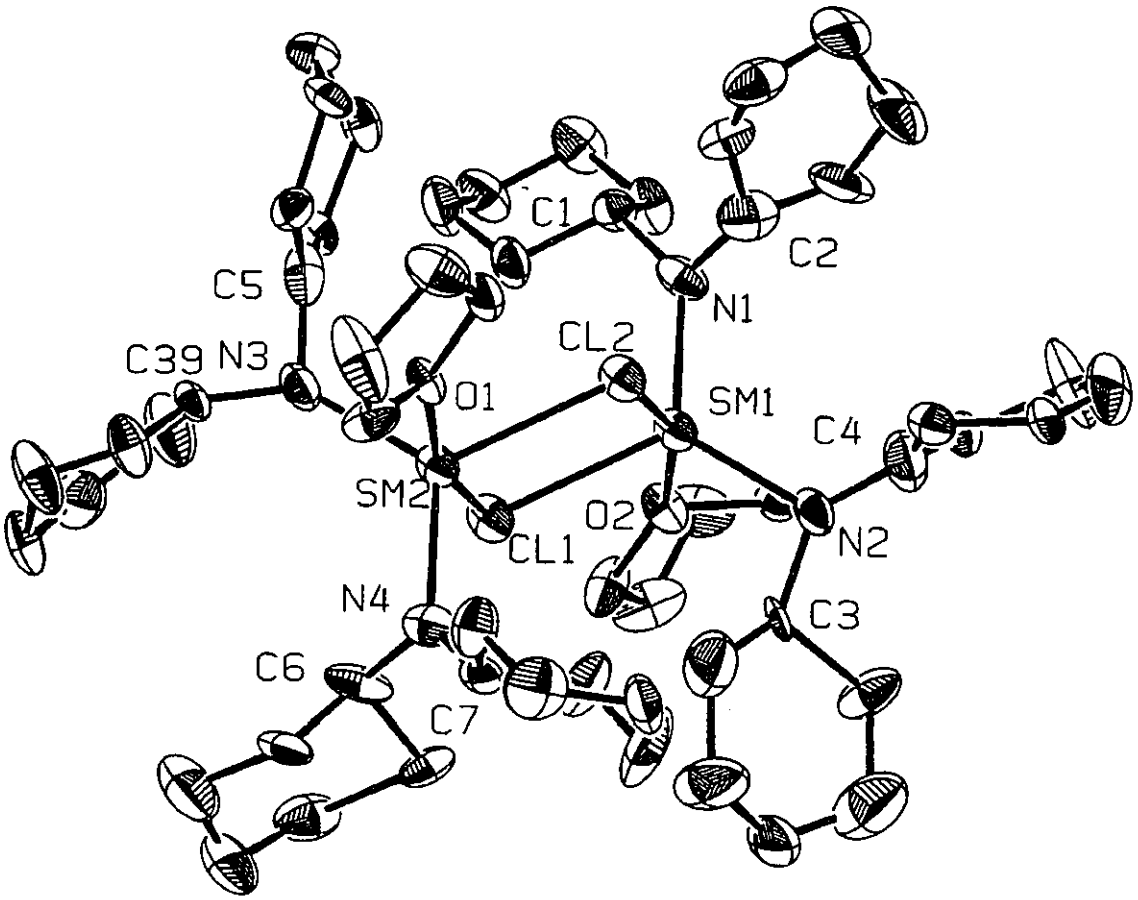


Fig. 6.1. X-Ray Structure of 6.1, $[(Cy_2N)_2Sm(\mu\text{-}Cl)(THF)]_2$

Selected Bond Distances (Å) and Bond Angles (deg): Sm1-Cl1 = 2.782(4), Sm1-Cl2 = 2.819(5), Sm1-N1 = 2.19(1), Sm1-N2 = 2.23(1), Sm1-O2 = 2.573(8), Cl1-Sm1-Cl2 = 78.9(1), Cl1-Sm1-O2 = 80.9(2), Cl1-Sm1-N1 = 115.8(3), Cl1-Sm1-N2 = 124.4(4).

two bridging chlorine are placed on the axis. The geometry around the N atoms of the amides [Sm1-N1 = 2.19(1)Å, Sm1-N2 = 2.23(1)Å] is almost trigonal planar [Sm1-N1-C1 = 136.5(9)°, Sm1-N1-C2 = 107.4(9)°, C1-N1-C2 = 112(1)°]. The Sm_2Cl_2 core is perfectly planar [torsion angle Cl1-Sm1-Cl2-Sm2 = 0.0(1)°] with slightly different

Sm-Cl and Sm-N bond distances [Sm1-Cl1 = 2.782(4)Å, Sm1-Cl2 = 2.819(5)Å, Sm2-Cl1 = 2.819(5) Å, Sm2-Cl2 = 2.782(4) Å].

The complex **6.2** is monomeric with a Sm atom placed in the center of a distorted trigonal bipyramid **(Fig. 6.2)** bound by two N atoms of two amide groups and three chloride atoms [Cl1-Sm1-Cl2 = 155.69(5)°, Cl3-Sm1-N1 = 119.9(1)°, Cl3-Sm1-N2 = 121.7(1)°, N1-Sm1-N2 = 118.3(2)°] (Fig. 2). Two N atoms from two amides [Sm1-N1 = 2.218(5)Å, Sm1-N2 = 2.202(5)Å] and one chlorine [Sm1-Cl3 = 2.888(2)Å]. define the equatorial plane while two other chlorides [Sm1-Cl13 = 2.764(2)Å, Sm1-Cl2 = 2.754(2)Å] are placed on the axial positions forming somewhat shorter Sm-Cl distances. The three chlorine atoms also bridge two Li atoms, significantly narrowing the Cl-Sm-Cl angle [Cl1-Sm1-Cl3 = 78.08(5)°]. The equatorial chlorine atom bridges the two lithium cations forming an almost linear Li-Cl-Li array [Li1-Cl3-Li2 = 175.5(4)°]. Each Li atom bears a molecule of TMEDA which completes the pentacoordination of the alkali cation. The geometry around the N atoms of the amides significantly deviates from the trigonal planar configuration [Sm1-N1-C1 = 112.1(4)°, Sm1-N1-C4 = 130.6(4)°, C1-N1-C4 = 116.9(5)°] expected from the sp^2 hybridization of the amide nitrogen atom.

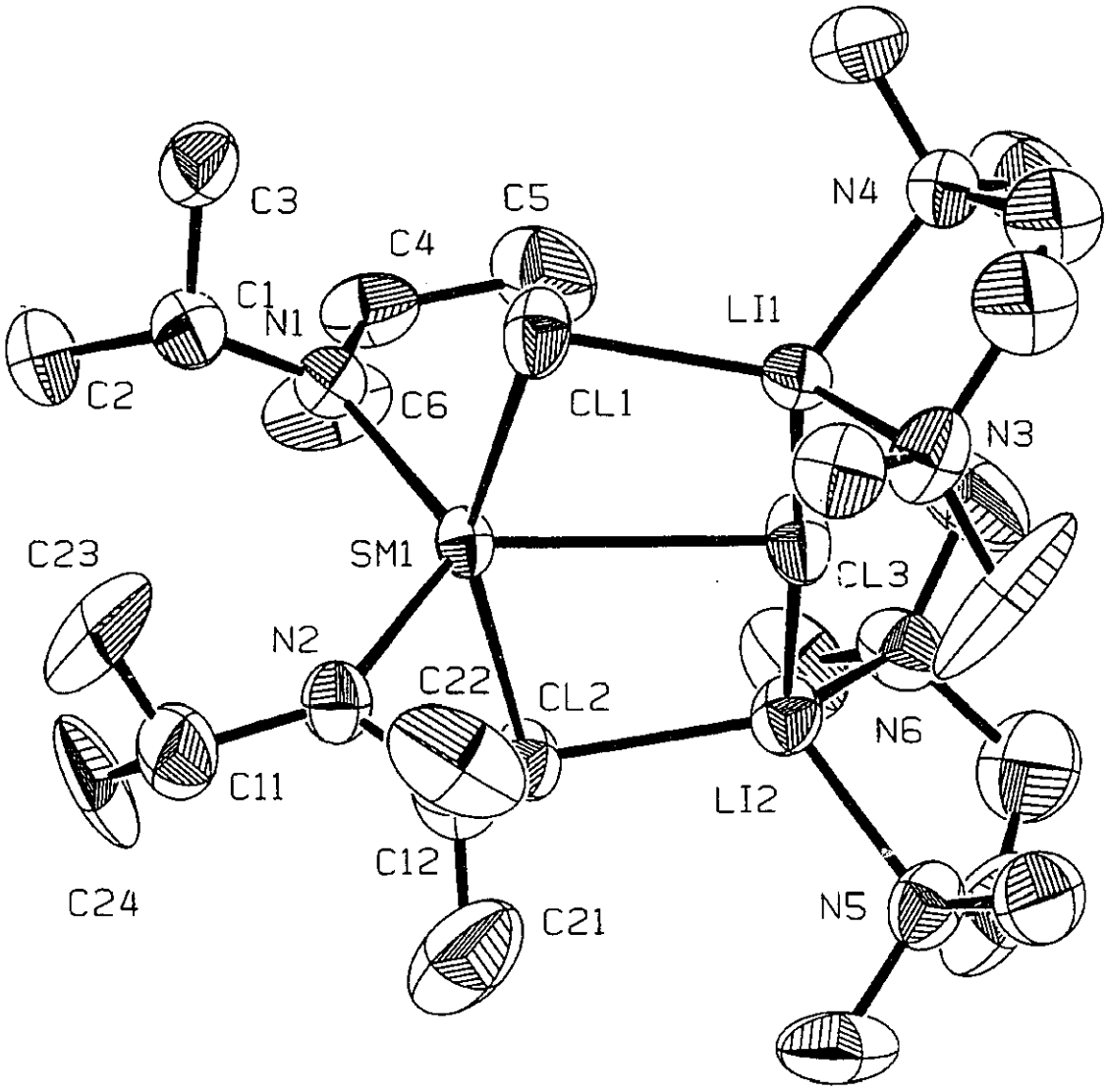


Fig. 6.2. X-Ray Structure of 6.2, $[(i\text{-}Pr_2N)_2SmCl_3(LiTMEDA)_2]$

Selected Bond Distances (Å) and Bond Angles (deg): Sm1-Cl1 = 2.764(2), Sm1-Cl2 = 2.754(2), Sm1-Cl3 = 2.888(2), Sm1-N1 = 2.218(5), Sm1-N2 = 2.202(5), Cl1-Sm1-Cl2 = 155.69(5), Cl1-Sm1-Cl3 = 78.08(5), Cl1-Sm1-N1 = 97.0(1), Cl1-Sm1-N2 = 95.7(1).

Complex **6.3** possesses a tetranuclear core **(Fig. 6.3)** with four Sm atoms being

part of the eight membered ring formed with three bridging chlorides [Sm1-Cl5 = 2.839(5)Å, Sm4-Cl4 = 2.782(5) Å, Sm4-Cl5 = 2.814(6) Å, Sm3-Cl3 = 2.836(5) Å, Sm2-Cl3 = 2.709(5) Å] and one amide [Sm1-N1 = 2.43(1)Å, Sm2-N1 = 2.56(1)Å]. The eight membered ring surrounds three μ^3- chlorines which define a plane perpendicular to

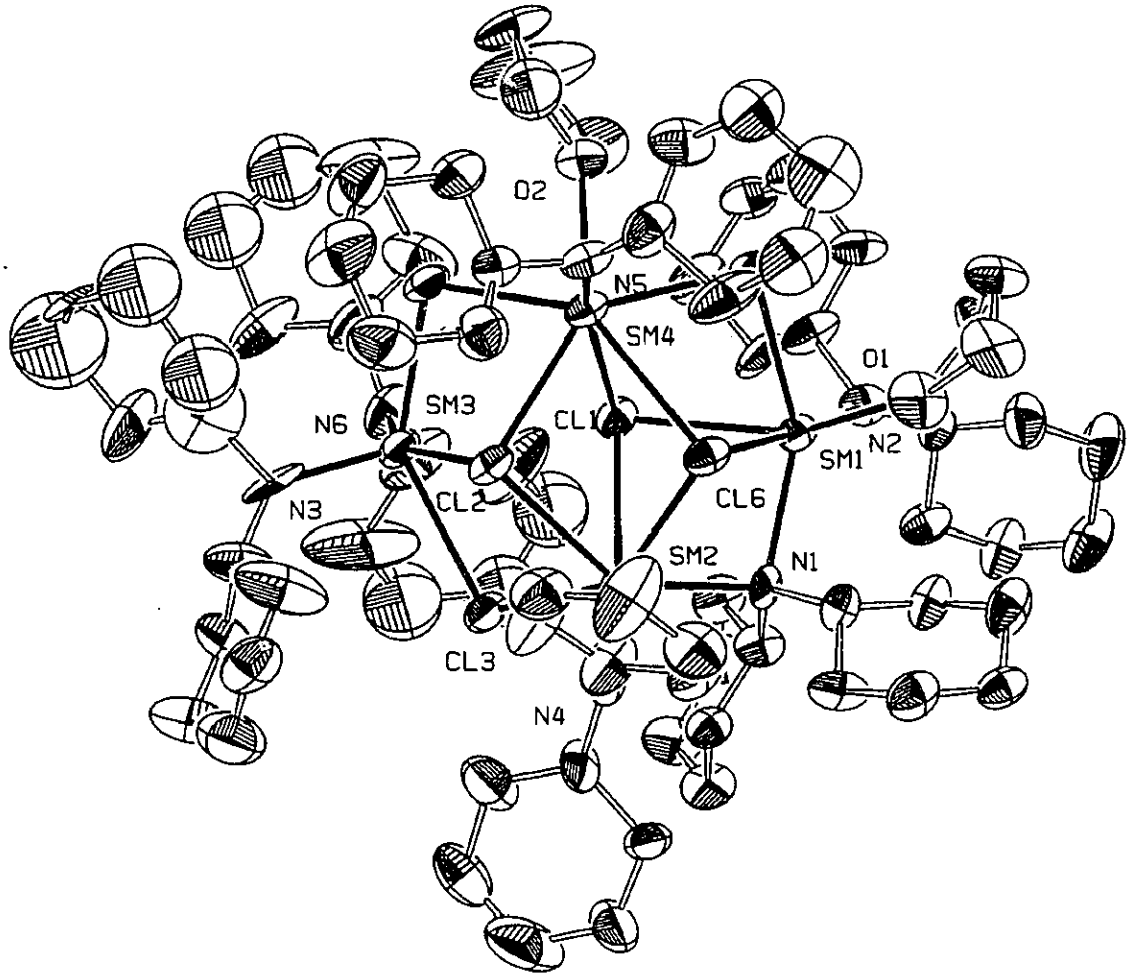


Fig. 6.3. X-Ray Structure of 6.3 ,$(Cy_2N)_6Sm_4Cl_6(THF)_2$

Selected Bond Distances (Å) and Bond Angles (deg): Sm1-Sm2 = 3.862(2), Sm1-Cl1 = 2.852(5), Sm1-Cl5 = 2.839(5), Sm1-Cl6 = 3.017(5), Sm1-O1 = 2.46(1), Sm1-N1 =

2.43(1), Sm1-N2 = 2.20(2), Sm2-Sm1-Cl1 = 52.2(1), Sm2-Sm1-Cl5 = 103.7(1), N1-Sm1-C1 = 125.0(5), N2-Sm1-C1 = 29.8(5), Sm1-Sm2-Cl1 = 46.83(9), Sm1-Sm2-Cl2 = 103.4(1), Sm1-Sm2-Cl3 = 115.9(1), Sm1-Sm2-Cl6 = 51.0(1), Sm1-Sm2-N1 =38.0(3), Sm1-Sm2-N4 = 136.6(4).

that of the Sm4Cl3N ring, and bridge the four unequivalent Sm atoms [Sm1-Cl1 = 2.852(5)Å, Sm2-Cl1 = 3.092(5)Å, Sm4-Cl1 = 3.015(5)Å]. The first Sm atom is six-coordinated, the distorted octahedral geometry being defined by one μ^2- bridging amide, three bridging chlorides [Sm1-Cl1 = 2.852(5)Å, Sm1-Cl5 = 2.839(5)Å, Sm1-Cl6 = 3.017(5)Å], one terminal amide [Sm1-N2 = 2.20(2)Å] and a molecule of THF [Sm1-O1 = 2.46(1)Å]. The second Sm atom is also six-coordinated with four bridging chlorides, one bridging amide [Sm2-N1 = 2.56(1)Å] and one terminal amide [Sm2-N4 = 2.11(2) Å]. The third Sm is five-coordinated with three bridging chlorides and two terminal amides [Sm3-N3 = 2.13(2)Å, Sm3-N6 = 2.22(2)Å] while the fourth metal atom is seven-coordinated and is bound to five bridging chlorides, one terminal amide and a molecule of THF.

The crystal structure of **6.4** revealed the molecule to be mononuclear **(Fig. 6.4)** consisting of a distorted tetrahedral Sm atom surrounded by four Cy_2N groups [N1-Sm1-N2 = 126.6(6)°, N1-Sm1-N3 = 87.4(6)°, N1-Sm1-N4 = 107.5(7)°, N2-Sm1-N3 = 105.6(5)]. Two of the four amides bridge a lithium cation, forming an almost planar SmN2Li core [Torsion angle N1-Sm1-N3-Li1 = 3°]. The geometry around the N

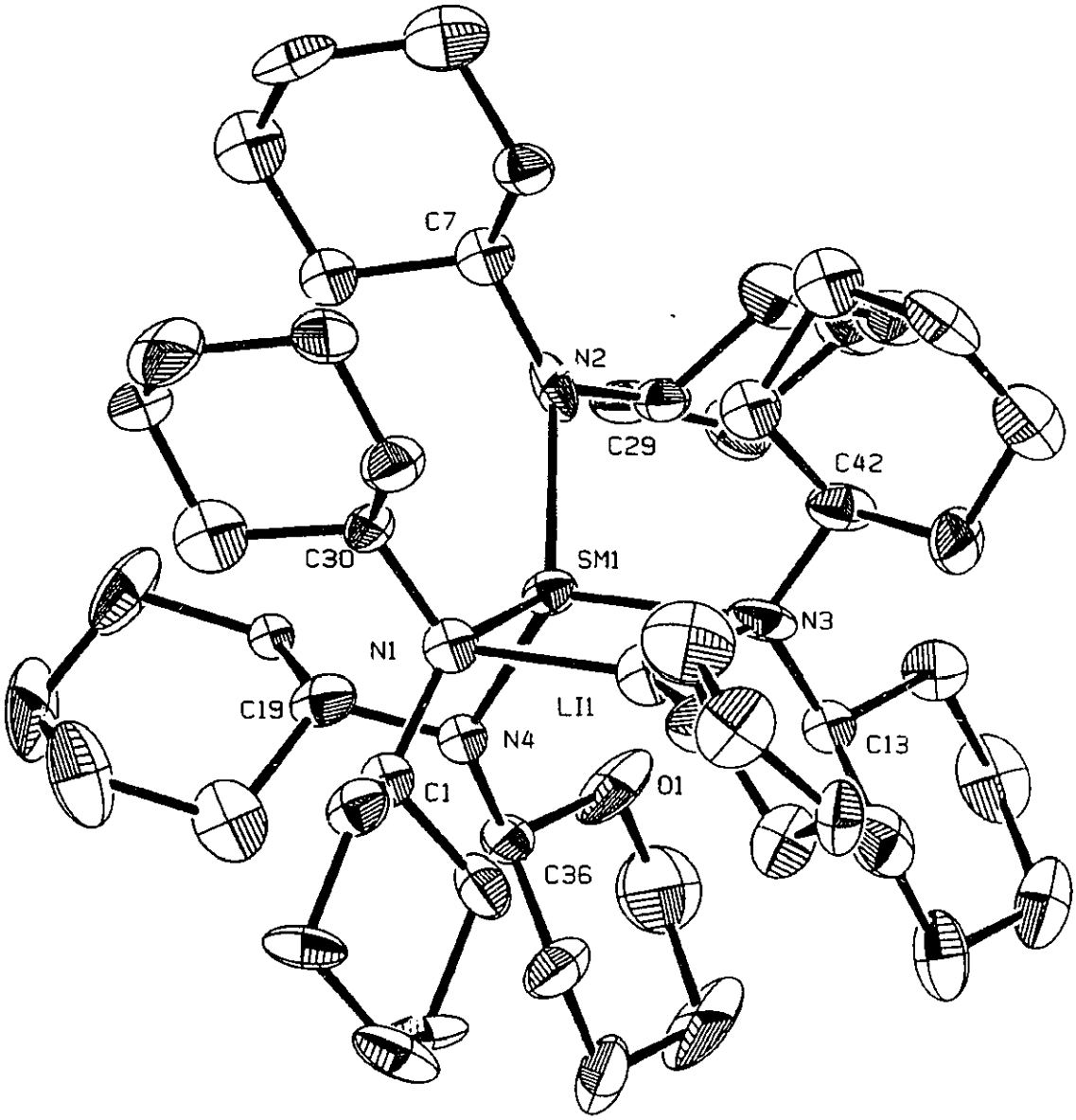


Fig. 6.4. X-Ray Structure of 6.4, $[(Cy_2N)_4SmLi(THF)].THF$

Selected Bond Distances (Å) and Bond Angles (deg): Sm1-N1 = 2.36(2), Sm1-N2 = 2.29(2), Sm1-N3 = 2.38(2), Sm1-N4 = 2.33(2), Sm1-Li1 = 3.02(4), N1-Sm1-N2 = 126.6(6), N1-Sm1-N3 = 87.4(6), N1-Sm1-N4 = 107.5(7), N1-Sm1-Li1 = 43.2(8), N2-Sm1-N3 = 105.6(5).

atoms of two terminal amides is trigonal planar with rather distorted angles [Sm1-N2-C7 = 142(1)°, Sm1-N2-C24 = 103(1)°, C7-N2-C24 = 115(2)°] whereas the other two bridging amides possess a distorted tetrahedral geometry [Sm1-N1-C1 = 125(1)°, Sm1-N1-C30 = 103(1)°, Sm1-N1-Li1 = 86(1)°, C1-N1-C30 = 116(2)°, C1-N1-Li1 = 102(2)°]. The Sm-N bond distances with the bridging tetrahedral nitrogen atoms are only slightly longer [Sm1-N1 = 2.36(2)Å, Sm1-N3 = 2.38(2)Å] than those formed by the terminal trigonal planar nitrogen atoms [Sm1-N2 = 2.29(2)Å, Sm1-N4 = 2.33(2)Å]. The trigonal coordination geometry of the Li cation is completed by one molecule of THF forming an almost perfectly linear Sm-Li-O vector [Sm1-Li1-O1 = 179(2)°].

Complex **6.5** is monomeric with Sm having a distorted tetrahedral geometry defined by three nitrogen atoms of three Cy_2N groups and one oxygen atom from a THF molecule [O1-Sm1-N1 = 128.0(4)°, O1-Sm1-N2 = 93.8(4)°, O1-Sm1-N3 = 95.1(4)°, N1-Sm1-N2 = 108.4(5)°, N2-Sm1-N3 = 123.3(5)°, N1-Sm1-N3 = 109.1(5)°] **(Fig. 6.5).** The distortion is likely to be due to the steric bulk of the amide groups which forces the amide groups apart and towards the THF molecule, thus widening the angles between amides and reducing the angle between the amide groups and THF. The Sm-N bond distances are comparable to those of the other complexes reported above [Sm1-N1 = 2.26(1)Å, Sm1-N2 = 2.28(1)Å, Sm1-N3 = 2.28(1)Å].

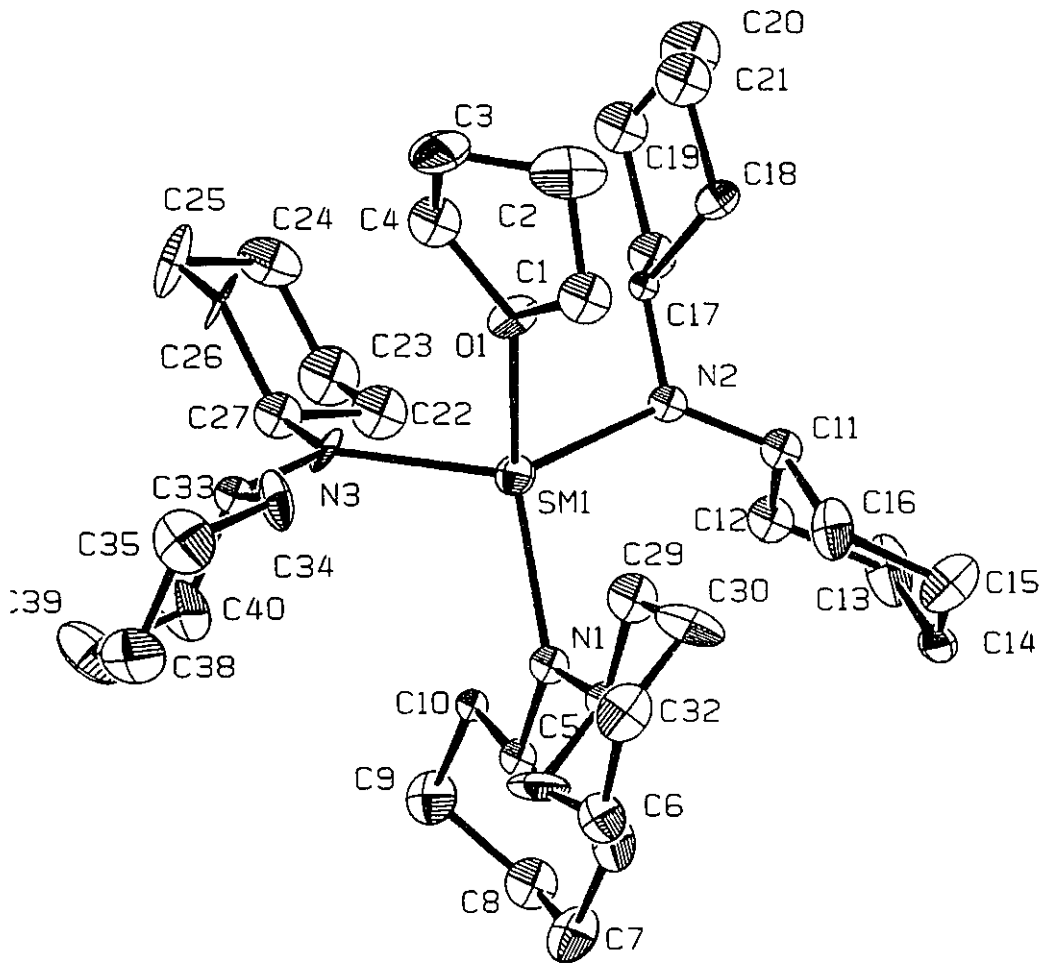


Fig. 6.5. X-Ray Structure of 6.5, [Sm(Cy$_2$N)$_3$THF].toluene

Selected Bond Distances (Å) and Bond Angles (deg): Sm1-N1 = 2.26(1), Sm1-N2 = 2.28(1), Sm1-N3 = 2.28(1), Sm1-O1 = 2.51(1), O1-Sm1-N1 = 128.0(4), O1-Sm1-N2 = 93.8(4), O1-Sm1-N3 = 95.1(4), N1-Sm1-N2 = 108.4(5), N1-Sm1-N3 = 109.1(5), N2-Sm1-N3 = 123.3(5).

The structure of complex **6.6** consists of a discrete mononuclear species with the Sm atom lying in the centre of a symmetrically distorted tetrahedron [N1-Sm1-N1b

= 152.4(1)°] defined by the nitrogen atoms of four amides groups [N1-Sm1-N1a = 86.9(1)°, N1-Sm1-N1b = 99.7(1)°] **(Fig. 6.6)**. Each pair of amides bridges the Sm to one peripheral sodium atom [Na1-N1 = 2.482(3)Å] pointing the aromatic rings above and below the SmN2Na plane [Torsion angle Sm1-N1-Na1-N1a = 0.0(1)°]. The geometry around nitrogen atoms of the amides is therefore a distorted

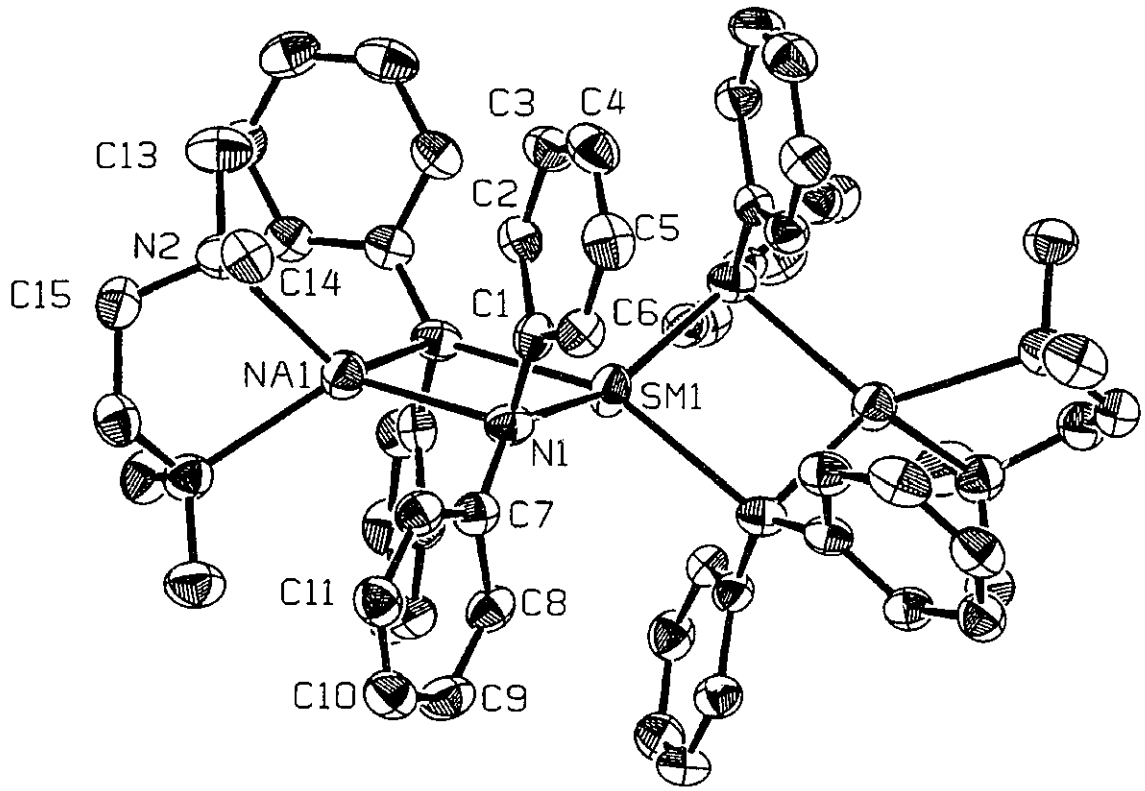


Fig. 6.6. X-Ray Structure of 6.6, $(Ph_2N)_4Sm[Na(TMEDA)]_2$

Selected Bond Distances (Å) and Bond Angles (deg): Sm1-N1 = 2.574(3), Sm1-N1a = 2.574(3), Sm1-Na1 = 3.609(2), N1-Na1 = 2.482(3), Na1-Sm1-Na1a = 180.00, Na1-Sm1-N1 = 43.44(6), Na1-Sm1-N1a = 136.56(6), N1-Sm1-N1a = 152.4(1).

tetrahedron [Sm1-N1-C1 = 99.6(2)°, Sm1-N1-C7 = 134.6(2)°, Na1-N1-C1 = 102.1(2)°, Na1-N1-C7 = 99.4(2)°, C1-N1-C7 = 120.6(3)°]. All the amides are equidistant from Sm forming Sm-N bond distances [Sm1-N1 = 2.574(3)Å] which are slightly lengthened with respect to the other Sm(III) amide complexes reported in this chapter probably as a result of the difference in ionic radius. One molecule of TMEDA completes the tetrahedral coordination sphere of each Na cation [Na1-N2 = 2.411(3)Å, N1-Na1-N1a = 91.(1)°, N1-Na1-N2 = 123.9(1)°].

The coordination geometry of the samarium atom in complex **6.7** shows that the samarium center is bound by two nitrogen atoms of the amide groups (**Fig. 6.7**) and the oxygen atoms of four THF molecules [O1-Sm1-O1a = 145.6(2)°, O1-Sm1-O2 = 73.1(1)°, O1-Sm1-O2a = 139.6(1)°, O1-Sm1-N1 = 80.4(1)°, O1-Sm1-N1a = 83.1(1)°, N1-Sm1-N1a = 121.7(2)°] and may be considered as a trigonal prismatic. Similar arrangement was found in the structure of $(Cbz)_2Sm(THF)_2$. The Sm-N [Sm1-N1 = 2.550(4)Å] and Sm-O distances [ranging from 2.608 to 2.631 Å] are rather normal and compare well with those of the other complexes reported in this chapter. The nitrogen atoms of two amides are having slightly distorted trigonal planar geometry [Sm1-N1-C1 = 104.8(3)°, Sm1-N1-C11 = 132.8(3)°, C1-N1-C11 = 120.8(4)°].

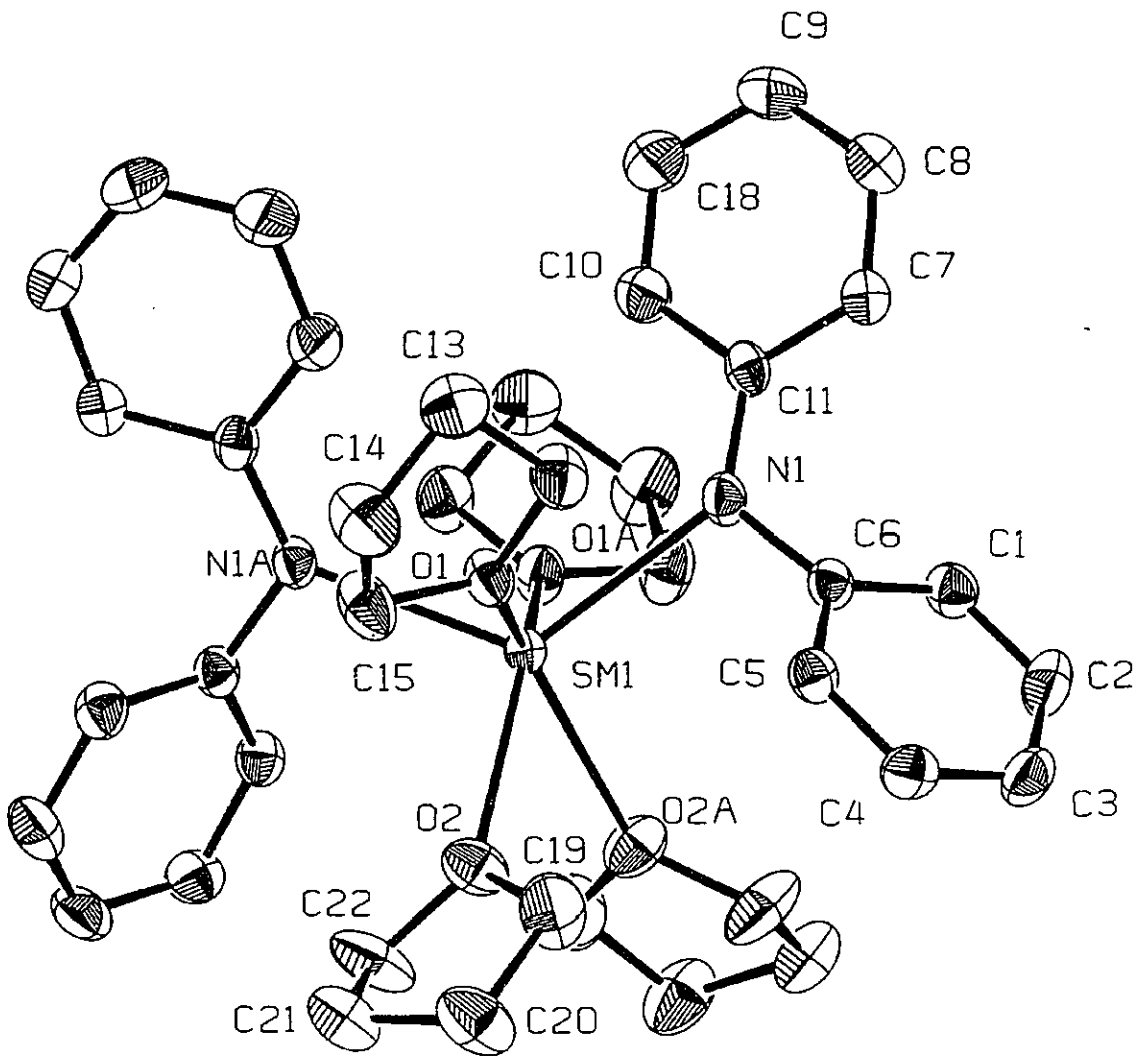


Fig. 6.7. X-Ray Structure of 6.7 , $[(Ph_2N)_2Sm(THF)_4]\cdot THF$

Selected Bond Distances (Å) and Bond Angles (deg): Sm1-O1 = 2.608(3), Sm1-O2 = 2.631(3), Sm1-N1 = 2.550(4), O1-Sm1-O1a = 145.6(2), O1-Sm1-O2 = 73.1(1), O1-Sm1-N1 = 80.4(1), O1-Sm1-N1a = 83.1(1), O1-Sm1-O2a = 139.6(1).

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Chapter VII

Conclusions

This thesis deals with the synthesis, characterization and reactivity studies of a novel series of V(II), V(III), Ti(III), Ti(IV), Sm(II) and Sm(III) complexes.

The main goal in our research on the chemistry of low-valent vanadium and titanium was to model and to attempt the understanding of the catalytic transformation of dinitrogen into ammonia and hydrazine as reported for other systems by Shilov and Schrauzer. To our surprise, we found that low-valent titanium and vanadium alkoxides / aryloxides did not give any appreciable interaction with dinitrogen. Even using dinitrogen complexes as the starting material, dinitrogen was liberated during the reaction. The final oxidation state of the metal and the nuclearity in most of these complexes seemed to be determined mainly by the steric bulk of the ligands used.

The employment of nitrogen-donor based ligands (such as amides and bidentate amidinate ligands) has allowed the isolation of a series of compounds, both on vanadium and titanium. The comparison of the crystal structures of these compounds again emphasized the role of steric hindrance of the ligands in determining:

(a) the stability of the lower oxidation states,

(b) the formation of M-M bonds, and

(c) the occurrence of dinitrogen fixation.

By using very bulky benzamidinate ligands, the steric bulk around the metal atom prevented both the formation of dinuclear species and disproportionation and allowed the isolation of end-on bridging dinitrogen complex. Conversely, with less bulky formamidinates, it was possible to isolate a diamagnetic, dimeric complex with a formal V-V triple bond. The use of other types of nitrogen-donor based ligands, i.e. anionic amides, provided quite encouraging and interesting results, such as the isolation of exceedingly stable dinitrogen complexes, C-H σ-bond metathesis, and formation of metallacycles.

The use of the anionic amides as ligands for Ti(III) and Ti(IV) alkyl complexes proved to be quite a versatile choice in stabilizing these very reactive complexes. The formation of Ti(III) alkyls as well as disproportionation of Ti(III) to Ti(IV) alkyls and carbenes was observed, presumably as a result of steric bulk of the alkyl substituents. Alkyl groups lacking β-hydrogens (e.g. CH_2CMe_3, CH_2SiMe_3, CH_2CMe_2Ph) were especially susceptible to disproportionation and gave Ti(IV) complexes. Yields of Ti(IV) alkyls could be improved by using Ti(IV) precursors as the starting materials. No trivalent titanium dinitrogen complexes have been found

by using the amides as supporting ligands.

Using the same anionic amides, a variety of Sm(III) amide derivatives was prepared. Stable Sm(II) amides were obtained only in the case where the ligands possessed no α -hydrogen atoms. Even in this case, we did not find any evidence of the ability of these species to interact with N_2.

APPENDICES

Appendix A

Table I. Crystal Data and Structural Analysis Results of 2.1 and 2.2

Complex	2.1	2.2
Empirical Formula	$C_{66}H_{77}N_4O_9Ti_3$	$C_{68}H_{70}O_4N_4Cl_2Ti_2$
Formula weight	1214.04	1173.99
Crystal System	Monoclinic	Monoclinic
Space group	C2/c	$P2_1/a$
a (Å)	14.758(5)	10.781(7)
b (Å)	21.920(17)	25.053(9)
c (Å)	19.855(13)	14.141(1)
α (deg)		
β(deg)	102.339(4)	104.08(6)
γ (deg)		
V (Å^3)	6274(7)	3705(4)
Z	4	4
Radiation:		
λ(Mo Kα) (Å)	0.70930	0.70930
T°C	25	25
D_{calcd}(g cm^{-3})	1.285	
μ_{calcd}(cm^{-1})	4.0	

R, R_w	0.058, 0.024	0.118, 0.082

Table II. Crystal Data and Structural Analysis Results of 2.3b and 2.4

Complex	2.3b	2.4
Empirical Formula	$C_{44}H_{74}N_3O_2Cl_2Ti$	$C_{18}H_{54}Si_6N_3Ti$
Formula weight	798.88	529.06
Crystal Color	Orange	Blue
Crystal System	Triclinic	Trigonal
Space group	P-1	P3/c
a (Å)	12.877(2)	16.260(3)
b (Å)	16.850(3)	
c (Å)	12.605(2)	8.4986(8)
α (deg)	106.65(1)	
β (deg)	100.65(1)	
γ (deg)	68.63(1)	
V (Å^3)	2430.4(7)	1945.8(5)
Z	2	2
Radiation:		
λ(Mo Kα) (Å)	0.70930	0.71069
T°C	25	-40
D_{calcd}(g cm^{-3})	1.078	0.903
μ_{calcd}(cm^{-1})	3.1	4.07
R, R_w	0.080, 0.081	0.076, 0.089

Table III. Crystal Data and Structural Analysis Results of 2.5 and 2.6

Complex	2.5	2.6
Empirical Formula	$C_{24}H_{27}O_3Ti$	$C_{48}H_{68}O_4Ti$
Formula weight	411.38	756.96
Crystal Color	Green	Yellow
Crystal System	Triclinic	Monoclinic
Space group	P-1	C2/c
a (Å)	11.373(3)	24.88(2)
b (Å)	11.458(3)	11.152(6)
c (Å)	10.859(4)	20.82(2)
α (deg)	117.04(2)	
β (deg)	115.29(3)	129.50(5)
γ (deg)	93.56(4)	
V (Å^3)	1080.1(9)	4458
Z	2	4
Radiation:		
λ(Mo Kα) (Å)	0.71069	0.70930
T°C	-158	-156
D_{calcd}(g cm^{-3})	1.265	1.086
μ_{calcd}(cm^{-1})	4.10	1.8
R, R_w	0.036, 0.051	0.051, 0.075

Table IV. Crystal Data and Structural Analysis Results of 2.7 and 2.8

Complex	2.7	2.8
Empirical Formula	$C_{67}H_{108}O_4N_4TiLi$	$C_{20}O_4N_2TiCl$
Formula weight	1088.44	445.82
Crystal Color	Orange	Yellow
Crystal System	Orthorhombic	Monoclinic
Space group	P_{bca}	$P2_1/c$
a (Å)	23.223(8)	7.880(1)
b (Å)	25.298(5)	12.544(4)
c (Å)	22.670(3)	22.683(4)
α (deg)		
β (deg)	96.57(2)	
γ (deg)		
V (Å^3)	13319(5)	2227.4(9)
Z	8	4
Radiation:		
λ(Mo Kα) (Å)	0.70930	0.71069
T°C	23	25
D_{calcd}(g cm^{-3})	1.086	1.329
μ_{calcd}(cm^{-1})	1.8 ?	5.25
R, Rw	0.074, 0.085	0.045, 0.037

Table V. Bond Distances (Å) And Bond Angles (deg) for 2.1 and 2.2

2.1	2.2
Ti1 - O1 = 2.067(7)	Ti - Cl = 2.435(7)
Ti1 - O2 = 2.030(7)	Ti - O1 = 1.853(14)
Ti1 - O5 = 1.802(11)	Ti - O2 = 2.067(15)
Ti2 - O3 = 1.902(8)	Ti - O2a = 2.073(14)
Ti2 - O1 = 2.089(7)	Cl - Ti - O1 = 167.8(5)
Ti1 - Ti2 = 3.264(2)	Cl - Ti - O2 = 90.0(5)
Ti2 - Ti1 - Ti1a = 151.92(6)	Cl - Ti - O2a = 92.0(4)
O1 - Ti2 - O2 = 72.8(3)	O1 - Ti - O2 = 98.7(6)
O3 - Ti2 - O4 = 170.1(4)	O1 - Ti - O2a = 98.5(6)
O3 - Ti2 - N1 = 88.7(1)	O2 - Ti - O2a = 74.5(6)
N1 - Ti2 - O2 = 104.6(1)	Ti - O2 - Tia = 105.5(6)
N1 - Ti2 - N2 = 78.6(2)	Ti - O1 - C1 = 171.9(11)
O1 - Ti1 - O1a = 154.8(3)	
O2 - Ti1 - O2a = 129.3(3)	
O1 - Ti1 - O5 = 102.6(2)	
O2 - Ti1 - O5 = 115.3(2)	

Table VI. Bond Distances (Å) And Bond Angles (deg) for 2.3b and 2.4

2.3b	2.4
Ti1 - O1 = 1.899(4)	Ti1 - N1 = 1.945(8)
Ti1 - Cl1 = 2.492(2)	Si1 - N1 = 1.69(2)
Ti1 - N1 = 2.288(6)	Si2 - N1 = 1.82(2)
Cl1...N3 = 3.080(6)	Si1 - C4 = 1.86(3)
O1 - Ti1 - O2 = 176.2(2)	Si2 - C1 = 1.89(3)
N1 - Ti1 - N2 = 79.99(2)	N1 - Ti1 - N1 = 119.89(9)
Cl1 - Ti1 - Cl2 = 96.09(8)	N1 - Si1 - C4 = 111(1)
Cl1 - Ti1 - N1 = 172.6(2)	N1 - Si1 - C6 = 120(1)
Cl1 - Ti1 - O1 = 90.3(2)	Ti1 - N1 - Si1 = 122(1)
	Ti1 - N1 - Si2 = 118(1)
	Si1 - N1 - Si2 = 120.2(5)

Table VII. Bond Distances (Å) And Bond Angles (deg) for 2.5

2.5
Ti1 - Ti1a = 3.085(2)
Ti1 - O1 = 1.830(2)
Ti1 - O3 = 2.009(2)
O1 - Ti1 - O2 = 119.26(9)
O1 - Ti1 - O3 = 113.88(9)
O2 - Ti1 - O3 = 108.32(8)
Ti1 - O1 - C9 = 146.1(2)
Ti1 - O2 - C1 = 154.6(2)
Ti1 - O3 - Ti1a = 100.55(8)
O3 - Ti1 - O3a = 79.45(8)

Table VIII. Bond Distances (Å) And Bond Angles (deg) for 2.7 and 2.8

2.7	2.8
Ti1 - O1 = 1.917(6)	Ti1 - Cl1 = 2.402(2)
Ti1 - O2 = 1.900(6)	Ti1 - O1 = 1.955(3)
Ti1 - O3 = 1.905(6)	Ti1 - O2 = 2.255(4)
Ti1 - O4 = 1.909(5)	Ti1 - O3 = 1.870(3)
N1 - Li1 = 2.096(16)	Ti1 - N1 = 2.316(4)
N2 - Li1 = 2.115(17)	Ti1 - N2 = 2.211(4)
N3 - Li1 = 2.110(16)	Cl1 - Ti1 - O1 = 92.3(1)
N4 - Li1 = 2.126(17)	Cl1 - Ti1 - O2 = 94.7(1)
O1 - Ti1 - O2 = 105.07(25)	Cl1 - Ti1 - O3 = 92.9(1)
O1 - Ti1 - O3 = 104.5(3)	Cl1 - Ti1 - N1 =174.8(1)
O1 - Ti1 - O4 = 125.3(3)	Cl1 - Ti1 - N2 = 94.2(1)
O2 - Ti1 - O3 = 118.75(25)	O1 - Ti1 - O2 = 74.2(1)
O2 - Ti1 - O4 = 102.63(24)	O1 - Ti1 - O3 = 164.7(2)
O3 - Ti1 - O4 = 101.9(3)	O1 - Ti1 - N1 = 87.2(1)
N1 - Li1 - N2 = 88.4(6)	O1 - Ti1 - N2 = 97.1(2)
N1 - Li1 - N3 = 123.6(7)	O2 - Ti1 - O3 = 91.1(1)
N1 - Li1 - N4 = 115.3(7)	O2 - Ti1 - N1 = 88.8(2)

Appendix B

Table I. Crystal Data and Structural Analysis Results of 3.10 and 3.12

Complex	3.10	3.12
Empirical Formula	$C_{34}H_{56}N_2Ti$	$C_{38}H_{82}N_6Si_4TiLi$
Formula weight	540.73	790.29
Crystal System	triclinic	Monoclinic
Space group	$P1^-$	$P2_1/c$
a (Å)	10.318(1)	13.757(2)
b (Å)	15.5144(9)	17.329(7)
c (Å)	10.241(1)	22.151(4)
α (deg)	98.909(9)	
β (deg)	99.40(1)	104.31(1)
γ (deg)	86.106(9)	
V (Å^3)	1596.2(5)	5117(2)
Z	2	4
Radiation:		
λ(Mo Kα) (Å)	0.71069	0.71069
T°C	-144	23
D_{calcd}(g cm^{-3})	1.125	0.875
μ_{calcd}(cm^{-1})	2.86	2.76

R, Rw	0.036, 0.047	0.074, 0.065

Table II. Crystal Data and Structural Analysis Results of 3.13 and 3.14

Complex	3.13	3.14
Empirical Formula	$C_{26}H_{50}Si_4N_2Ti$	$C_{48}H_{88}N_4Ti_2Cl_2O$
Formula weight	550.94	903.96
Crystal Color	red, prism	orange, cube
Crystal System	Triclinic	Monoclinic
Space group	$P\bar{1}$	C2/c
a (Å)	11.639(2)	16.205(4)
b (Å)	17.188(2)	14.804(3)
c (Å)	8.935(2)	20.748(5)
α (deg)	90.35(1)	
β (deg)	109.24(1)	96.11(2)
γ (deg)	102.16(1)	
V (Å^3)	1644.2(4)	4949(4)
Z	2	4
Radiation:		
λ(Mo Kα) (Å)	0.71069	0.71069
T°C	23	-161
D_{calcd}(g cm^{-3})	1.113	1.213
μ_{calcd}(cm^{-1})	4.15	4.64
R, Rw	0.046, 0.067	0.075, 0.087

Table III. Selected Bond Distances (Å) and Angles (deg) for 3.10 and 3.12

3.10	3.12
Ti1 - N1 = 1.896(2)	Ti1 - N1 = 2.036(8)
Ti1 - N2 = 1.879(2)	Ti1 - N2 = 2.027(8)
Ti1 - C25 = 2.121(2)	Ti1 - C7 = 2.18(1)
Ti1 - C30 = 2.089(2)	Ti1 - C14 = 2.18(1)
N1 - Ti1 - N2 = 120.93(8)	N3 - Li1 = 2.10(2)
N1 - Ti1 - C25 = 111.98(8)	N4 - Li1 =2.12(2)
N1 - Ti1 - C30 = 110.26(8)	N5 - Li1 = 2.17(2)
N2 - Ti1 - C25 = 110.81(8)	N6 - Li1 = 2.12(2)
N2 - Ti1 - C30 = 112.26(8)	N1 - Ti1 - N2 = 127.4(3)
C25 - Ti1 - C30 = 84.92(9)	N1 - Ti1 - C7 = 108.1(3)
Ti1 - N1 - C1 = 141.3(1)	N1 - Ti1 -C14 = 100.0(4)
Ti1 - N1 - C7 = 103.2(1)	N2 - Ti1 - C7 = 99.9(4)
C1 - N1 - C7 = 115.5(2)	N2 - Ti1 - C14 =119.7(4)
	C7 - Ti1 - C14 = 97.4(4)
	Ti1 - N1 - Si1 = 16.5(4)
	Ti1 - N1 - Si2 = 21.9(4)
	Si1 - N1 - Si2 = 21.6(5)

Table IV. Selected Bond Distances (Å) and Angles (deg) for 3.13 and 3.14

3.13	3.14
Ti2 - N1 = 1.931(3)	Ti1 - Cl2 = 2.296(2)
Ti2 - N2 = 1.939(3)	Ti1 - O1 = 1.828(2)
Ti2 - C13 = 2.092(5)	Ti1 - N1 = 1.910(6)
Ti2 - C20 = 2.109(4)	Ti1 - N2 = 1.876(6)
N1 - Ti2 - N2 = 120.6(1)	Cl2 - Ti1 - O1 = 109.3(2)
N1 - Ti2 - C13 = 108.4(2)	Cl2 - Ti1 - N1 = 109.2(2)
N1 - Ti2 - C20 = 108.1(2)	Cl2 - Ti1 - N2 = 109.9(2)
N2 - Ti2 - C13 = 109.1(2)	O1 - Ti1 - N1 = 113.5(2)
N2 - Ti2 - C20 =110.0(2)	O1 - Ti1 - N2 = 108.5(2)
C13 - Ti2 - C20 = 98.4(2)	N1 - Ti1 - N2 = 106.3(2)
Ti2 - C13 - C14 = 120.7(3)	Ti1 - O1 - Ti1 = 154.9(4)
Ti2 - C20 - C21 = 119.2(3)	Ti1 - N1 - C1 = 120.6(5)
Ti2 - N1 - Si1 = 124.8(2)	Ti1 - N1 - C7 = 123.5(4)
Ti2 - N1 - Si2 = 117.5(2)	C1 - N1 - C7 = 115.7(5)
Si1 - N1 - Si2 = 117.5(2)	

APPENDIX C

Table I. Crystal Data and Structural Analysis Results of 4.4 and 4.5

Complex	4.4	4.5
Empirical formula	$C_{54}H_{72}O_2N_2V$	$C_{42}H_{42}O_2N_2V$
Formula weight	832.12	657.74
Crystal system	triclinic	monoclinic
Space Group	P-1	$P2_1/a$
a (Å)	9.701(2)	16.373(1)
b (Å)	15.303(3)	11.1624(9)
c (Å))	9.000(2)	19.536(3)
α (deg)	101.99(2)	
β (deg)	112.59(2)	97.35(1)
γ (deg)	74.20(2)	
V (Å^3)	1179.0(4)	3541.3(7)
Z	1	4
Radiation		
λ(MoKα Å)	0.71069	0.71069
T°(C)	-158	25
D_{calcd}(g cm^{-3})	1.172	1.234
μ_{calcd} (cm^{-1})	2.42	5.7

R, R_v	0.053, 0.068	0.044, 0.017

Table II. Crystal Data and Structural Analysis Results of 4.6 and 4.7

Complex	4.6	4.7
Empirical formula	$C_{51}H_{41}O_2N_3V$	$C_{20}H_{30}O_4N_2V$
Formula weight	778.85	413.41
Crystal color	red	orange
Crystal system	monoclinic	orthorhombic
Space Group	C2/c	$Pna2_1$
a (Å)	20.65(2)	13.519(5)
b (Å)	14.28(1)	13.846(4)
c (Å)	16.08(1)	11.196(2)
α (deg)		
β (deg)	119.89(7)	
γ (deg)		
V (Å^3)	4113(7)	2096(1)
Z	4	4
Radiation		
λ(MoKα Å)	0.71069	0.71069
T°(C)	25	-158
D_{calcd}(g cm^{-3})	1.258	1.310
μ_{calcd}(cm^{-1})	2.74	4.82
R, R_w	0.053, 0.049	0.037, 0.047

Table III. Crystal Data and Structural Analysis Results of 4.14

Complex	4.14
Empirical formula	$C_{39}H_{45}O_{10}V_2N_2Si$
Formula weight	831.76
Crystal color	orange
Crystal system	triclinic
Space Group	P-1
a (Å)	14.443(6)
b (Å)	15.039(6)
c (Å)	10.679(3)
α (deg)	100.66(3)
β (deg)	97.46(3)
γ (deg)	113.84(3)
V (Å^3)	2030(1)
Z	2
Radiation	
λ(MoKα Å)	0.71069
T°(C)	-162
D_{calcd}(g cm^{-3})	1.360
μ_{calcd}(cm^{-1})	5.28
R, R_w	0.045, 0.060

Table IV. Selected Bond Distances (Å) and Angles (deg) for 4.4 and 4.5

4.4	4.5
V(1)-O(1) = 1.916(2)	V(1)-O(1) = 2.000(3)
V(1)-N(1) = 2.235(2)	V(1)-O(2) = 2.038(3)
O(1)-C(6) = 1.351(3)	V(1)-N(1) = 2.256(3)
O(1)-V(1)-N(1) =93.39(8)	V(1)-N(2) = 2.202(4)
N(1)-V(1)-N(1a) = 180.00	O(1)-V(1)-O(2) = 173.41(13)
O(1)-V(1)-O(1a) = 180.00	O(1)-V(1)-N(1) = 92.23(15)
	O(1)-V(1)-N(2) = 95.70(15)
	N(1)-V(1)-N(2) = 82.41(13)
	V(1)..H(118) = 2.504
	V(1)..H(218) = 2.544

Table V. Selected Bond Distances (Å) and Angles (deg) for 4.6 and 4.7

4.6	4.7
V(1)-N(1) = 2.103(8)	V(1)-O(1) = 2.068(4)
V(1)-N(2) = 2.198(5)	V(1)-O(2) = 2.105(3)
V(1)-O(1) = 2.025(4)	V(i)-O(3) = 2.172(4)
N(1)-V(1)-N(2) = 94.7(1)	V(1)-O(4) = 2.163(4)
N(1)-V(1)-O(1) = 101.9(1)	V(1)-N(1) = 2.245(4)
O(1)-V(1)-O(1a) = 156.3(2)	V(1)-N(2) = 2.208(4)
N(2)-V(1)-N(2a) = 170.5(3)	O(1)-V(1)-O(3) = 95.1(1)
O(1)-V(1)-N(2) = 93.0(2)	O(1)-V(1)-O(2) = 168.7(1)
	O(1)-V(1)-O(4) = 77.3(1)
	O(1)-V(1)-N(1) = 97.1(1)
	O(1)-V(1)-N(2) = 94.7(1)

Table VI. Selected Bond Distances (Å) and Angles (deg) for 4.14

4.14
V2-V2a = 2.498(1)
V2-N1 = 1.847(3)
N1-N2 = 1.377(4)
V2-O7 = 1.894(3)
V2-O8 = 2.264(2)
V1-O3 = 2.177(2)
V1-O4 = 1.920(2)
V1-V1a = 3.089(2)
V1-O1 = 1.974(2)
N1-V2-N1a = 94.9(1)
O9-V2-O10 = 75.9(1)
O7-V2-O8 = 74.90(9)
O3-V1-O4 = 77.00(9)
V1-O1-V1a = 102.1(1)
O1-V1-O1 = 77.8(1)
N1-N2-C36 = 117.6(3)

APPENDIX D

Table I. Crystal Data and Structural Analysis Results of 5.5 and 5.6

Complex	5.5	5.6
Empirical formula	$C_{28}H_{50}ClVN_4$	$C_{42}H_{75}N_6V$
Formula weight	529.12	715.04
Crystal system	triclinic	monoclinic
Space Group	P-1	$P2_1/c$
a (Å)	11.132(4)	17.35(1)
b (Å)	13.630(4)	10.854(2)
c (Å)	10.276(2)	22.777(4)
α (deg)	95.92(2)	
β (deg)	98.38(2)	103.04(2)
γ (deg)	109.29(3)	
V (Å^3)	1437(2)	4178(2)
Z	2	4
Radiation		
λ(MoKα Å)	0.71069	0.71069
T°C	-160	-160
D_{calcd}(g cm^{-3})	1.223	1.137
μ_{calcd} (cm^{-1})	4.49	2.62

R, Rw	0.047, 0.063	0.057, 0.075

Table II. Crystal Data and Structural Analysis Results of 5.9 and 5.11

Complex	5.9	5.11
Empirical formula	$C_{34}H_{62}N_4Si_4O_2V$	$C_{26}H_{46}Si_4VN_4Cl$
Formula weight	722.17	613.41
Crystal system	orthorhombic	triclinic
Space Group	Pbcn	P-1
a (Å)	18.133(7)	12.781(5)
b (Å)	12.504(6)	13.128(4)
c (Å))	17.428(4)	12.126(5)
α (deg)	104.85(3)	
β (deg)	113.19(4)	
γ (deg)	66.80(4)	
V (Å^3)	3951(4)	1705(3)
Z	4	2
Radiation		
λ(MoKα Å)	0.71069	0.71069
T °C	-161	-151
D_{calcd}(g cm^{-3})	1.214	1.194
μ_{calcd} (cm^{-1})	3.94	5.18
R, Rw	0.046, 0.059	0.030, 0.044

Table III. Crystal Data and Structural Analysis Results of 5.12

Complex	5.12
Empirical formula	$C_{52}H_{92}Si_8V_2N_{10}$
Formula weight	1183.93
Crystal system	triclinic
Space Group	P-1
a (Å)	14.181(2)
b (Å)	18.713(2)
c (Å))	13.257(2)
α (deg)	99.48(1)
β (deg)	94.13(2)
γ (deg)	91.87(2)
V (Å^3)	3458(2)
Z	2
Radiation	
λ(MoKα Å)	0.71069
T°C	-157
D_{calcd}(g cm^{-3})	1.137
μ_{calcd} (cm^{-1})	4.34
R, Rw	0.050, 0.056

Table IV. Selected Bond Distances (Å) and Angles (deg) for 5.5 and 5.6

5.5	5.6
V1-Cl1 = 2.300(1)	V1-N1 = 2.099(3)
V1-N1 = 1.944(2)	V1-N2 = 2.091(3)
V1-N2 = 2.158(2)	V1-N3 = 2.075(3)
V1-N3 = 1.960(2)	V1-N4 = 2.091(4)
V1-N4 = 2.147(2)	V1-N5 = 2.1:0(4)
Cl1-V1-N1 = 123.00(8)	V1-N6 = 2.091(4)
Cl1-V1-N2 = 95.47(7)	N1-V1-N2 = 63.7(1)
Cl1-V1-N3 = 123.57(7)	N3-V1-N4 = 63.5(1)
Cl1-V1-N4 = 96.50(7)	N5-V1-N6 = 63.6(1)
N1-V1-N3 = 113.4(1)	N1-V1-N5 = 91.9(1)
N1-V1-N2 = 64.84(9)	N1-C1-N2 = 112.1(3)
N3-V1-N4 = 64.60(9)	N3-C2-N4 = 112.2(4)
N2-V1-N4 = 167.77(8)	N5-C29-N6 = 112.5(4)
N1-C15-N2 = 11.6(2)	C5-N1-C1 = 123.3(3)
N3-C7-N4 = 123.0(2)	C17-N2-C1 = 122.9(3)
C1-N3-C7 = 123.8(2)	
C7-N4-C9 = 122.9(2)	
C15-N1-C17 = 123.7(2)	
C15-N2-C23 = 122.3(2)	

Table V. Selected Bond Distances (Å) and Angles (deg) for 5.9 and 5.11

5.9	5.11
V1-N1 = 2.221(4)	V1-Cl1 = 2.306(2)
V1-N2 = 2.232(3)	V1-N1 = 2.005(3)
V1-O1 = 2.174(4)	V1-N3 = 1.969(3)
V1-O2 = 2.147(4)	V1-N2 = 2.111(2)
Si1-N1 = 1.729(4)	V1-N4 = 2.114(2)
O1-V1-O2 = 180.0	N1-V1-N3 = 106.9(1)
N1-V1-N2 =61.4(1)	Cl1-V1-N1 = 139.71(8)
N1-V1-O1 = 86.01(9)	Cl1-V1-N3 = 113.40(9)
N1-V1-N1 = 172.0(2)	Cl1-V1-N4 = 91.82(8)
N1-C10-N2 = 118.1(4)	Cl1-V1-N2 = 95.69(8)
Si1-N1-C10 = 130.8(3)	N1-C7-N2 = 114.4(3)
Si2-N2-C10 = 128.1(3)	N3-C8-N4 = 114.1(3)
	Si1-N3-C8 = 132.2(2)
	Si4-N4-C8 = 130.8(2)
	Si2-N2-C7 = 132.7(2)
	Si3-N1-C7 = 129.0(2)

Table VI. Selected Bond Distances (Å) and Angles (deg) for 5.12

5.12
V1-N1 = 1.756(5)
V2-N2 = 1.757(5)
N1-N2 = 1.235(6)
V1-N7 = 2.074(5)
V1-N8 = 2.137(5)
V1-N9 = 2.051(5)
V1-N10 = 2.137(5)
N7-V1-N9 = 116.0(2)
N7-V1-N1 = 129.2(2)
N1-V1-N9 = 114.7(2)
N1-V1-N8 = 97.4(2)
N1-V1-N10 = 97.7(2)
N8-V1-N10 = 164.9(2)
N7-V1-N8 = 64.9(2)
N9-V1-N10 = 65.3(2)
V1-N1-N2 = 173.7(4)
V2-N2-N1 = 179.3(4)
N7-C27-N8 = 116.5(5)
N9-C38-N10 = 116.2(5)

APPENDIX E

Table I. Crystal Data and Structural Analysis Results of 6.1 and 6.2

Complex	6.1	6.2
Empirical Formula	$C_{56}H_{105}O_2Sm_2N_4Cl_2$	$C_{24}H_{60}N_6Li_2Cl_3Sm$
Formula weight	1238.18	703.42
Crystal System	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	14.344(1)	11.552(1)
b (Å)	23.897(2)	15.483(1)
c (Å)	10.2031(9)	11.330(1)
α (deg)	88.479(9)	101.69(1)
β (deg)	121.83(1)	106.13(1)
γ (deg)	93.73(1)	88.89(2)
V (Å^3)	2965(1)	1904.8(6)
Z	2	2
Radiation:		
λ(Mo Kα) (Å)	0.71069	0.71069
T°C	-156	-145
D_{calcd}(g cm^{-3})	1.387	1.226
μ_{calcd}(cm^{-1})	20.99	17.78

R, R_w	0.031, 0.042	0.035, 0.047

Table II. Crystal Data and Structural Analysis Results of 6.3 and 6.4

Complex	6.3	6.4
Empirical Formula	$C_{80}H_{148}Cl_6N_6Sm_4O_2$	$C_{56}H_{106}N_4O_2LiSm$
Formula weight	2040.41	1024.82
Crystal Color	orange, plates	yellow, prism
Crystal System	triclinic	orthorhombic
Space group	$P\bar{1}$	$Pna2_1$
a (Å)	16.508(1)	16.6145(9)
b (Å)	16.7795(9)	17.5858(9)
c (Å)	16.4030(8)	19.7754(9)
α (deg)	89.794(1)	
β (deg)	88.688(2)	
γ (deg)	79.531(1)	
V (Å^3)	4466.8(7)	5778(9)
Z	2	4
Radiation:		
λ(Mo Kα) (Å)	0.71069	0.71069
T°C	-140	-157
D_{calcd}(g cm^{-3})	1.517	1.178
μ_{calcd}(cm^{-1})	28.26	10.57
R, R_w	0.062, 0.078	0.069, 0.083

Table III. Crystal Data and Structural Analysis Results of 6.5 and 6.6

Complex	6.5	6.6
Empirical Formula	$C_{47}H_{82}N_3SmO$	$C_{60}H_{72}N_8Na_2Sm$
Formula weight	855.58	1101.66
Crystal Color	red, prism	green, prism
Crystal System	monoclinic	tetragonal
Space group	$P2_1/c$	$I4_1/acd$
a (Å)	10.250(2)	18.0004(9)
b (Å)	23.305(2)	
c (Å)	19.088(1)	34.106(1)
α (deg)		
β (deg)	100.90(1)	
γ (deg)		
V (Å^3)	4477(2)	11051(1)
Z	4	8
Radiation:		
λ(Mo Kα) (Å)	0.71069	0.71069
T°C	-153	-143
D_{calcd}(g cm^{-3})	1.269	1.324
μ_{calcd}(cm^{-1})	13.50	11.24
R, R_w	0.071, 0.091	0.028, 0.037

Table IV. Crystal Data and Structural Analysis Results of 6.7

Complex	6.7
Empirical Formula	$C_{44}H_{60}O_5SmN_2$
Formula weight	847.37
Crystal Color	black cube
Crystal System	monoclinic
Space group	C2
a (Å)	19.066(1)
b (Å)	11.932(1)
c (Å)	9.200(1)
α (deg)	
β (deg)	93.89(1)
γ (deg)	
V (Å^3)	2088.1(6)
Z	2
Radiation:	
λ(Mo Kα) (Å)	0.71069
T°C	-147
D_{calcd}(g cm^{-3})	1.348
μ_{calcd}(cm^{-1})	14.53
R, R_w	0.021, 0.027

Table V. Bond Distances (Å) And Bond Angles (deg) for 6.1 and 6.2

6.1	6.2
Sm1 - Cl1 = 2.782(4)	Sm1 - Cl1 = 2.764(2)
Sm1 - Cl2 = 2.819(5)	Sm1 - Cl2 = 2.754(2)
Sm1 - O2 = 2.573(8)	Sm1 - Cl3 = 2.888(2)
Sm1 - N1 = 2.19(1)	Sm1 - N1 = 2.218(5)
Sm1 - N2 = 2.23(1)	Sm1 - N2 = 2.202(5)
Cl1 - Sm1 - Cl2 = 78.9(1)	Cl1 - Sm1 - Cl2 = 155.69(5)
Cl1 - Sm1 - O2 = 80.9(2)	Cl1 - Sm1 - Cl3 = 78.08(5)
Cl1 - Sm1 - N1 = 115.8(3)	Cl1 - Sm1 - N1 = 97.0(1)
Cl1 - Sm1 - N2 = 124.4(4)	Cl1 - Sm1 - N2 = 95.7(1)
Cl2 - Sm1 - O2 = 159.8(2)	Cl2 - Sm1 - Cl3 = 77.74(4)
Sm1 - Cl1 - Sm2 = 101.1(1)	Sm1 - N1 - C1 = 112.1(4)
Sm1 - N1 - C1 = 136.5(9)	Sm1 - N1 - C4 = 130.6(4)
Sm1 - N1 - C2 = 107.4(9)	C1 - N1 - C4 = 116.9(5)
C1 - N1 - C2 = 112(1)	Sm1 - Cl1 - Li1 = 92.2(2)
N1 - Sm1 - N2 = 119.1(5)	Sm1 - Cl2 - Li2 = 93.1(3)
	Li1 - Cl3 - Li2 = 175.5(4)

Table VI. Bond Distances (Å) And Bond Angles (deg) for 6.3 and 6.4

6.3	6.4
Sm1 - Sm2 = 3.862(2)	Sm1 - N1 = 2.36(2)
Sm1 - Cl1 = 2.852(5)	Sm1 - N2 = 2.29(2)
Sm1 - Cl5 = 2.839(5)	Sm1 - N3 = 2.38(2)
Sm1 - Cl6 = 3.017(5)	Sm1 - N4 = 2.33(2)
Sm1 - O1 = 2.46(1)	Sm1 - Li1 = 3.02(4)
Sm1 - N1 = 2.4391)	N1 - Sm1 - N2 = 126.6(6)
Sm1 - N2 = 2.20(2)	N1 - Sm1 - N3 = 87.4(6)
Sm4 - Cl1 = 3.015(5)	N1 - Sm1 - N4 = 107.5(7)
Sm4 - Cl2 = 2.850(5)	N1 -- Sm1 - Li1 = 43.2(8)
Sm4 - Cl4 = 2.782(5)	N2 - Sm1 - N3 = 105.6(5)
Sm4 - Cl6 = 2.998(5)	N2 - Sm1 - N4 = 106.4(6)
Sm4 - N5 = 2.17(2)	N2 - Sm1 - Li1 = 128.8(8)
Sm4 - O2 = 2.45(1)	Sm1 - N1 - C1 = 125(1)
Sm2 - Sm1 - Cl1 = 52.2(1)	Sm1 - N1 - C30 = 103(1)
Sm2 - Sm1 -Cl5 = 103.7(1)	C1 - N1 - C30 = 116(2)
Sm2 - Sm1 - Cl6 = 45.15(9)	Sm1 - N1 - Li1 = 86(1)

Table VII. Bond Distances (Å) And Bond Angles (deg) for 6.5 and 6.6

6.5	6.6
Sm1 - O1 = 2.51(1)	Sm1 - Na1 = 3.609(2)
Sm1 - N1 = 2.26(1)	Sm1 -Na1a = 3.609(2)
Sm1 - N2 = 2.28(1)	Sm1 - N1 = 2.574(3)
Sm1 - N3 = 2.28(1)	Sm1 - N1a = 2.574(3)
O1 - Sm1 - N1 = 128.0(4)	Na1 - N1 = 2.482(3)
O1 - Sm1 - N2 = 93.8(4)	Na1 - N1a = 2.482(3)
O1 - Sm1 - N3 = 95.1(4)	Na1 - N2 = 2.411(3)
N1 - Sm1 - N2 = 108.4(5)	Na1 - Sm1 - Na1a = 180.00
N1 - Sm1 - N3 = 109.1(5)	Na1 - Sm1 - N1 = 43.44(6)
N2 - Sm1 - N3 = 123.3(5)	Na1 - Sm1 - N1a = 136.56(6)
Sm1 - N1 - C5 = 127(1)	N1 - Sm1 - N1 = 152.4(1)
Sm1 - N1 - C28 = 120(1)	N1 - Sm1 - N1a = 86.9(1)
C5 - N1 - C28 = 114(1)	N1a - Sm1 - N1a = 99.7(1)
	Sm1 - N1 - Na1 = 91.08(9)
	Sm1 - N1 - C7 = 134.6(2)
	Sm1 - N1 - C1 = 99.6(2)

Table VIII. Bond Distances (Å) And Bond Angles (deg) for 6.7

6.7
Sm1 - O1 = 2.608(3)
Sm1 - O2 = 2.631(3)
Sm1 - N1 = 2.550(4)
Sm1 - N2 = 2.550(4)
O1 - Sm1 - O1a = 145.6(2)
O1 - Sm1 - O2 = 73.1(1)
O1 -Sm1 - O2a = 139.6(1)
O1 - Sm1 - N1 = 80.4(1)
O1 - Sm1 - N1a = 83.1(1)
O2 - Sm1 - N1 = 126.5(1)
O2 - Sm1 - N1a = 100.3(1)
N1 - Sm1 - N1a = 121.7(2)
O2 - Sm1 - O2a = 74.7(2)