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Abstract

Reaction of $[NbCl_3(TMEDA)]_2$ with LDA in a stoichiometric ratio of 1:3 Nb/Lithium amide, resulted in a new diamagnetic niobium (II) cluster $(TMEDA)_3Nb_2Cl_5Li$ **(2.1)** with a very short $Nb\equiv Nb$ bond. Similarly, reaction of $NbCl_4(THF)_2$ with 2 equiv. of Cy_2NLi caused the reduction of the metal center to produce a diamagnetic and tetranuclear cluster, $[Nb_4Cl_{12}Li_2(THF)_8]$ **(2.2)**. Further reaction of $[NbCl_3(TMEDA)]_2$ or $(TMEDA)_3Nb_2Cl_5Li$ **(2.1)** with $(3,5\text{-}Me_2Ph)(Ad)NLi$ in THF yielded the tetravalent, dinuclear and diamagnetic $\{[(3,5\text{-}Me_2Ph)(Ad)N]Nb(3,5\text{-}Me_2Ph)\}_2(\mu\text{-}NAd)_2.2(ether)$ **(2.3)**. In the reaction of $Nb_2Cl_6(TMEDA)_2$ with azobenzene cleavage of the N=N bond results in the formation of the niobium imido complex, $NbCl_3(C_6H_5N)(TMEDA)$ **(2.4)**.

The reaction of $Nb_2Cl_6(TMEDA)_2$ with the potassium salt of tripyrrolylmethane in a 1:1 ratio afforded two products which have been isolated and characterized. The first compound is the dinuclear $\{[H\text{-}C(C_4H_3N)_3]Nb(THF)\}_2 \cdot 2THF$ **(3.1)** with two trivalent and diamagnetic metals bridged by two tripyrrolyl trianions. The second product of the reaction is $\{([H\text{-}C(C_4H_3N)_3]_2NbK)_2\}\{Nb_4Cl_{11}[K(THF)_2]_2\}\cdot 2THF$ **(3.2)** which displays some unusual features. The complex is ionic with the cationic $\{Nb_4Cl_{11}[K(THF)_2]_2\}^{2+}$ unit containing the metal in a mixed valence state and the cationic moiety are balanced by two identical anionic $\{([H\text{-}C(C_4H_3N)_3]_2NbK)_2\}^-$ units each containing Nb in the tetravalent state. A similar reaction carried out with the lithium salt of the tripyrrolide anion led instead to a monomeric tetravalent $\{[H\text{-}C(C_4H_3N)_3]_2Nb\}\{Li(THF)_4\}_2$ **(3.3)** complex.

Reaction of $Nb_2Cl_5Li(TMEDA)_3$ with Ph_2NK in THF afforded a complex reaction from which three complex were isolated and characterized. The first compound $Cl_2Nb_2(\mu\text{-}Cl)_3(TMEDA)_2$ **(4.1)** was obtained in analytically pure form as dark purple, paramagnetic and moderately air-sensitive crystals. The second compound is a trivalent and dinuclear $\{[(Ph_2N)_2Nb]_2[\mu\text{-}NPh(\mu\text{-}\eta^1{:}\eta^2\text{-}C_6H_4)](\mu\text{-}H)\}\{Li\ (TMEDA)_2\}$.toluene **(4.2)** which was formed *via* oxidative addition of the two Nb(II) centers to the C-H σ-bond of one aromatic ring. This species thermally rearranges into the dinuclear and diamagnetic $(Ph_2N)_2Nb\{[\mu\text{-}NPh(\eta^6\text{-}C_6H_5)]_2Nb\}$.ether **(4.3)**.

A nitride-bridged mixed-valence Nb(IV)/Nb(V) species $\{[(Cy_2N)_2Nb]_2(\mu\text{-}N)\}(\mu^3\text{-}N)Li(TMEDA)$ **(5.1)** was produced through reaction of the diamagnetic cluster $Nb_2Cl_5Li(TMEDA)_3$ with Cy_2NLi. Potassium or lithium salts of bis-pyridylamine $[(C_5H_4N)_2N^-]$ react with $Nb_2Cl_5Li(TMEDA)_3$ in THF to afford $[(py_2N)_2Nb]_2(\mu\text{-}C_5H_4N)(\mu\text{-}Npy)[Li(THF)_2](THF)_2[Li_2Cl_2(THF)_4]$ **(5.2)**. Both compound are arising from the cooperative oxidative addition of the two metal centers on either the N-N or the C-N bond of the amide ligand respectively.

A nitrogen atom was abstracted from a pyrrolyl ring to afford the dinuclear and ionic $\{[(2,5\text{-}Me_2C_4H_2N)_2Nb][(\eta^5\text{-}2,5\text{-}Me_2C_4H_2N)(2,5\text{-}Me_2C_4H_2N)Nb](\mu\text{-}N)(\mu,\eta'{:}\eta'{:}\eta^4\text{-}1,4\text{-}Me_2C_4\ H_2)\}\{[(TMEDA)NbCl]_2(\mu\text{-}Cl)_3Li(TMEDA)\}$.2(toluene) **(6.1)** and the neutral unprecedented amido/carbene/hydride complex $[(\eta^5\text{-}2,5\text{-}Me_2C_4H_2N)Nb][(2,5\text{-}Me_2C_4H_2N)(Me_2NCH_2CH_2NMe)Nb](\mu\text{-}H)(\mu\text{-}CH_2)(\mu,\eta^1{:}\eta^4\text{-}2,5\text{-}Me_2C_4\ H_2N)$ **(6.2)** during the reaction of $Nb_2Cl_5Li(TMEDA)_3$ with $2,5\text{-}Me_2C_4H_2NLi$.

The reactions of $Nb_2Cl_5Li(TMEDA)_3$ with the pyrrolyl and indolyl lithium salts gave monomeric paramagnetic and anionic niobium (IV) complexes with $[Li(THF)_4]_2$ as a counter cation $[(C_4H_4N)_6Nb[Li(thf)_4]_2.thf$ **(7.1)** and $(C_8H_6N)_6Nb[Li(thf)_4]_2$ **(7.2)**]. Similarly, the reaction of diphenylmethane dipyrrolyl lithium salt with $Nb_2Cl_6(TMEDA)_2$ in 2:1 ratio resulted $[Ph_2C(C_4H_4N)_2]_3Nb[K(thf)_2]_2$ **(7.3)** complex through a disproportionation reaction.

A novel paramagnetic Nb (II) complex with a very short M-M distance, (7-azaindolyl)$_4$Nb$_2$[(μ-Cl)Li(THF)$_3$]$_2\cdot$ 2THF **(8.1)** was produced from reaction of $Nb_2Cl_5Li(TMEDA)_3$ with 7-azaindolyl lithium salt. Conversely, reaction with the potassium salt of the same ligand resulted in formation of the diamagnetic (7-azaindolyl)$_4$Nb$_2$ **(8.2)** complex with a similar paddle-wheel configuration and a short M-M bond distance as complex **8.1**.

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To my husband, Ali; my daughter, Sameen;

and my parents

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List of Abbreviations

TEEDA	N, N, N', N'-tetraethylethylenediamine
TMEDA	N, N, N', N'-tetramethylethylenediamine
THT	tetrahydrothiophene
Me_2S	dimethylthio
THF	tetrahydrofuran
DME	dimethoxyethane
depe	(diethylphosphino)ethane
dmpe	(dimethylphosphino)ethane
dppe	(diphenylphosphino)ethane
dmpm	(dimethylphosphino)methane
.DPpTP	diphenyl(p-tolyl)phosphine)
DPP	diphenylpropylphosphine
TpTP	tri-p-tolylphosphine
DPVP	diphenylvinylphosphine
EDPP	ethyldiphenylphospine
TPP	tripropylphosphine
Et_3P	triethylphosphine
PMe_3	trimethylphosphine
Py′	4-dimehylaminopyridine
Py	Pyridine
Py_2N	bis-pyridilamide
LDA	lithium isopropylamide

hpp	1,3,4,6,7,8 hexahydropyrimido[1,2-a]pyrimidine
Ad	adamantyl
azin	7-azaindolyl
Cp	cyclopentadienyl
Cy	cyclohexyl
Me	methyl
Et	ethyl
i-Pr	isopropyl
Ph	phenyl
t-Bu	tert-butyl
R	alkyl group
X	halogen
Å	angstroms
δ	chemical shift
μ_{eff}	effective magnetic moment in Bohr magnetons
χ_g	magnetic susceptibility
cm^{-1}	wave number
MHz	frequency in megahertz
NMR	nuclear magnetic resonance
El. Anal	Elemental Analyses
g	gram
ml	milliliter
mmol	millimole

ppm	part per million
d	doublet
br	broad (IR, NMR)
IR	infra red
m	multiplet (NMR), medium (IR)
q	quintet
qu	quartet
s	singlet (NMR), strong (IR)
t	triplet
w	weak
C	carbon
H	hydrogen
N	nitrogen

CHAPTER I

Introduction

Niobium General Characteristics

Niobium is a group V transition metal belonging to the second transition period. This element was formerly known in the American continent as Columbium until more recently when the name of Niobium, used in the European nomenclature, was internationally adopted. The name Niobium was given in honor of the mythological figure of Niobes, daughter of Tantalus and wife of Amphion king of Thebes and whose children were slain by Artemis and Apollo when she compared herself to their mother Leto. The weeping Niobes was changed by Zeus into a stone from which tears continue to flow. In this thesis we will show that never a name was more appropriate for an element displaying such a uniquely high reactivity which, although very rewarding, in too many instances made chemical reactions unpredictable, often intractable and always particularly difficult to handle. An extreme reactivity is the *leit-motif* of this thesis. Tears, however, were more likely to flow from the eyes of this candidate and of her thesis supervisor rather than from Niobium itself.

The earliest references to organo-niobium chemistry date back to the literature of 1928,[1] when $NbCl_5$ was reported to react with arenes to give HCl and metal aryl species for which the formulation $[NbCl_4(C_{10}H_7)]$ (subsequently retracted in 1959[2]) was proposed. The first well characterized organometallic compound of niobium was a cyclopentadienyl compound, Cp_2NbBr_3, reported by Wilkinson and Birmingham in

1954.[3] The first structurally characterized molecular Nb^{III} derivatives was reported in 1970,[4] while an entire class of Nb^{III} halide adducts was discovered only in 1973.[5] When we started this thesis work, the oxidation state +2 was virtually unknown.

While in the metallic state, niobium displays an unusually high resistance to corrosion and can be dissolved only by treatment with *aqua regia*. By contrast, low- and zerovalent complexes of this metal are characterized by high instability which of course preludes to a very high chemical reactivity. Thus, the most established oxidation states for this metal are in fact the most stable ones. Namely they are the +4 and +5. Yet their reactivity presents unique features which make niobium one of the most fascinating elements to use for chemical studies. The pentavalent state is the most frequently encountered oxidation state in the chemistry of niobium. These complexes are characterized by a very high Lewis acidity which characterizes the majority of the transformations reported to date. Tetravalent complexes are also established but are more chemically inert, often dinuclear and sometimes diamagnetic, while mononuclear species display magnetic moments as expected for the d^1 electronic configuration.[6]

By enriching the electronic configuration and lowering the oxidation states Nb derivatives display an enhanced tendency to perform oxidative addition reactions. The tendency to reach the more stable higher oxidation states is the driving force for these transformations. As mentioned briefly above, low- and medium valent niobium complexes are basically unknown. Nevertheless, their chemistry has been rather extensively investigated by generating *in situ* highly reactive low-valent complexes.[7] This strategy has afforded the discovery of a wealth of desirable transformations arising from molecular activation processes (C-X bond cleavage). One of the goals of this thesis was an attempt to develop the chemistry of low-valent niobium complexes and to better elucidate their ability to perform molecular activation processes.

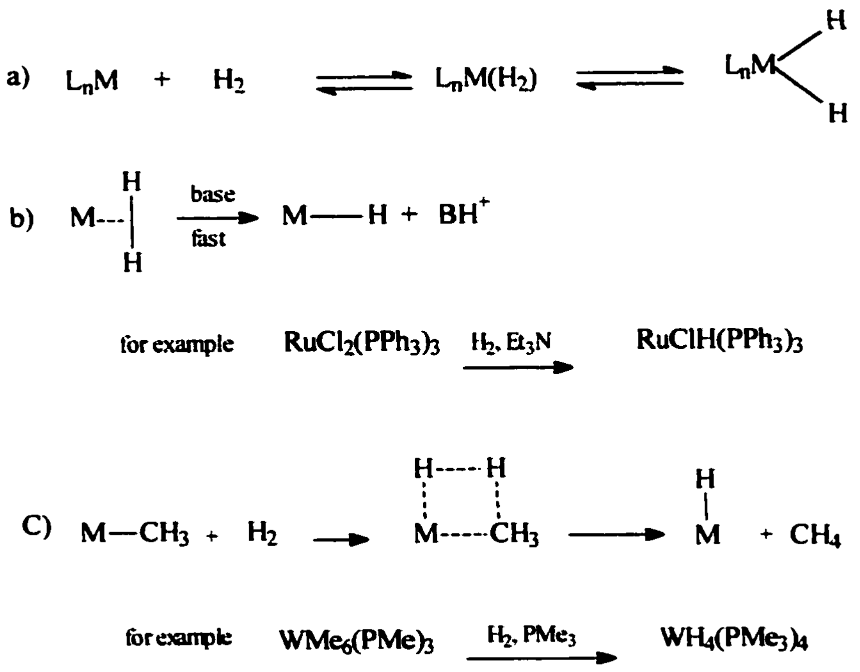
Interest in the Synthesis of Low Valent Transition Metals

Electron-rich and strongly reducing transition metal complexes are capable of performing oxidative additions into a variety of chemical bonds. These processes, which are central to catalytic transformations, may be performed by one metal or via cooperative attack of two or more metals on the same substrate. The most frequently encountered examples of these processes are related to the so-called activation of small molecules and which, again, are pivotal part of many catalytic transformations, some of them widely exploited for the commercial manufacturing of commodity chemicals. Among the transition elements, low valent early metals display a particularly enhanced reactivity which is also typically uncontrollable and responsible for a larger variety of serendipitous transformations.

The following sections offer some background about the most primacy transformation where low-valent Nb and Ta have displayed a particular versatility. Namely they are: H-H bond cleavage and formation of hydride, C-H and C-N bond activation and M-M bond formation.

H-H Bond Cleavage

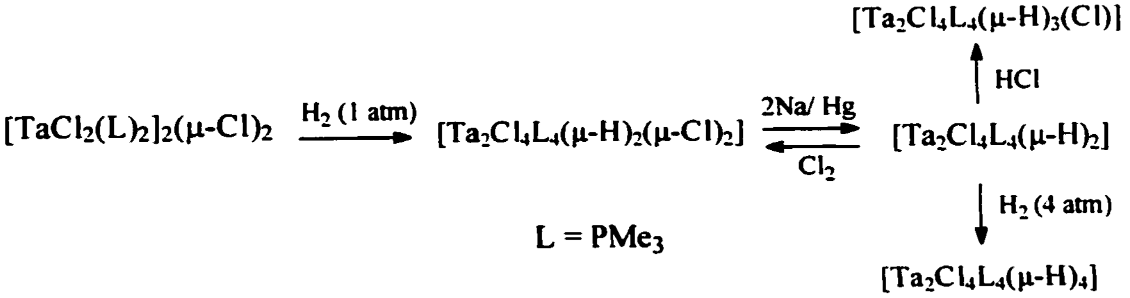
The addition of hydrogen to a low-valent transition metal complex is an important step in catalytic cycles such as olefin, alkyne or arene hydrogenation, hydroformylation reactions, reductive oligomerization of CO (the "Fischer-Tropsch reaction"), etc..[8] The interaction of elemental hydrogen with a transition metal complex can be categorized into three main reaction pathways. The first consists of the oxidative addition reaction of molecular hydrogen as for example performed by metal complexes such as $IrCl(CO)(PPh_3)_2$ (Scheme 1.1).



Scheme 1.1

This kind of reaction implies a preliminary coordination of H_2 to the metal atom before cleavage of the H-H bond occurs to form two new M-H bonds.[9] However, the involvement of η^2-H_2 complexes (see for example the case of $Os(H)_4(PPh_3)_3$)[10] is not a necessary prerequisite. The second reaction pathway involves formation of stable or metastable η^2-H_2 complexes. This curious type of coordination is evidently favored by low π basicity and strong σ acidity of the ML_n system (Scheme 1.1a). The third reaction pathway involves the formation of a four-center transition state (Scheme 1.1c). [11]

As an example of the versatility of low-valent Nb and Ta complexes in terms of molecular activation, tantalum trichloride adducts reacts with H_2 to form hydride complexes (Scheme 1.2):[12]



Scheme 1.2

These hydrides have been successfully employed in a variety of transformations which include hydrogenation of a variety of arene substrates. The formation of saturated hydrocarbons starting from the mixture of H_2 and CO as produced by the water-gas shift reaction, involves an impressive series of molecular activation processes assisted by low-valent metals. The CO triple bond is cleaved during the process as well as the H-H bond while carbon-carbon and C-H bonds are formed as partner transformations. During the 70's and 80's and under the pressure of energy production soaring prices, interest was revitalized for understanding and modeling this remarkable process. The original Fisher-

Tropsch process uses a form of Fe or Ru oxide as a catalyst.[13] However early transition metals such as Zr and Ta complexes were widely used by Bercaw and Wolczanski for their modeling studies which marked a milestone towards the understanding of this process and of other related catalytic transformations.[14]

While elemental oxygen can be obviously reduced by *in situ* generated low-valent Nb and Ta complexes,[15] the reactivity of these species is so high that it is not limited to the activation of a reactive molecule such as CO but it makes also possible the interaction with the far-more stable isoelectronic N_2. Just to exemplify the versatility of heavier group V metals towards N_2 it is sufficient here to remind that activation of N_2 under mild conditions (25°C, 1 atm) was observed during the reduction of $NbCl_5$ by magnesium under N_2 atmosphere.[16] A large variety of complexes able to perform different extent of dinitrogen reduction fixation and even partial hydrogenation is today available in the literature of Nb and Ta.[17]

C-H Bond Cleavage

The selective activation and subsequent functionalization of C-H bonds under ordinary laboratory conditions has been of interest to organometallic chemists for more than 20 years.[18] The ambitious goal of activating methane and using this largely available feedstock for sophisticated chemical transformations other than combustion, was always a challenging drive for studies in this field. The main types of reactions involving C-H bond cleavage can be categorized as follows:

1. *Oxidative addition to acidic or weakly acidic C-H bonds:*

Weakly acidic C-H bonds such as those of RC≡CH, $HC(CN)_3$, CH_3NO_2, CH_3CN, or cyclopentadiene can undergo oxidative addition leading to cleavage and formation of the corresponding organometallic species (Scheme 1.3).[19]

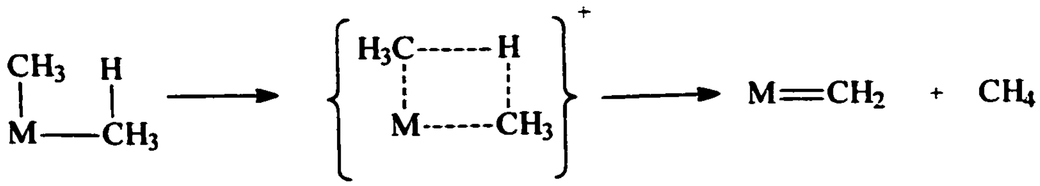
$$Ir(dmpe)_2Cl_2 + CH_3CN \longrightarrow IrCl_2H(CH_2CN)(dmpe)$$

Scheme 1.3

The more basic the metal, the more facile the addition and thus there is no surprise that low-valent late metals such as Rh and Ir in the oxidation state +1 are the most versatile. The high affinity of these metals for both hydrogen and carbon donor atoms does in fact provide the thermodynamic driving force for the oxidative additions.

2. *Hydrogen transfer from alkyl groups to give M-H and M-C bonds;*

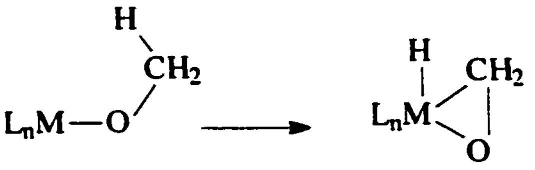
α-hydride transfer: Methyl compounds such as $TaMe_5$ or WMe_6 decompose thermally to give CH_4 and polymeric material. Since the metal is in its maximum oxidation state there is no possibility for an intramolecular oxidative-addition. Hence the decomposition occurs via a four-center transition state (Scheme 1.4).[20]



$$(ArO)_2TaMe_3 \xrightarrow{h\nu} (ArO)_2Ta(=CH_2)Me$$

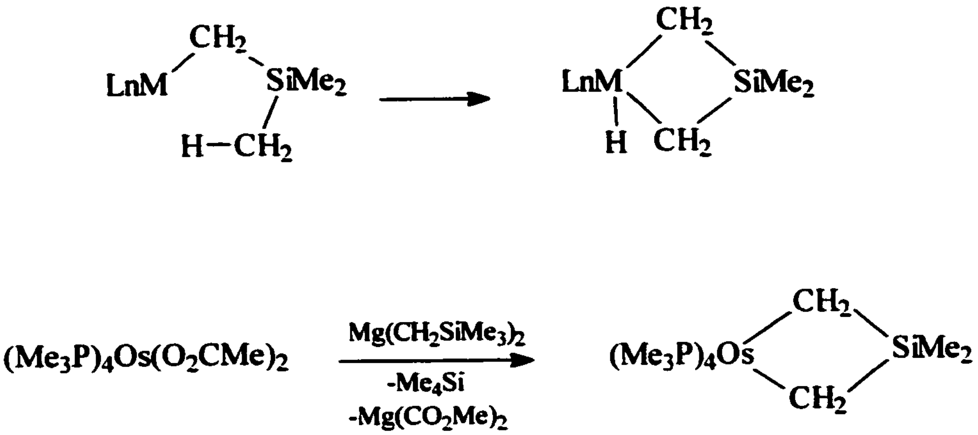
Scheme 1.4

β-hydride transfer: The β-hydride transfer is the most important transfer reaction, occurring not only with alkyls, but also with acyl derivatives and, depending on the nature of the metal even for alkoxides (Scheme 1.5). Among the plethora of metal complexes which have been discovered, especially those of platinum(II) such as $(R_3P)_2PtR'_2$ display a particular versatility.[21]



Scheme 1.5

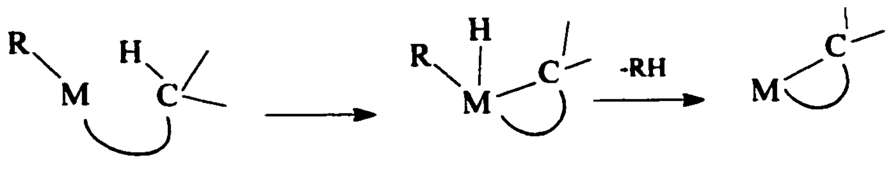
γ-hydride transfer: Gamma transfer leads to the formation of a metallacyclic derivative either stable or as simple intermediates. In this type of hydride transfer, when more than one alkyl group is present on the metal, elimination of alkane can also easily occur (Scheme 1.6):[22]



Scheme 1.6

3. Hydrogen transfers from hydrogen atoms on aryl rings in cyclometallation reactions

In these reactions the genesis of the alkylidene function involve intramolecular C-H cleavage reactions that can be considered as oxidative-additions sometimes resulting in intermediate M-H and M-C bonds formation (Scheme 1.7):[23]



Scheme 1.7

4. Oxidative-addition of aromatic C-H bonds.

C-H bonds of arenes are more reactive than those of saturated hydrocarbons. Nevertheless, elevated temperatures or photochemical irradiation are required for this type of reaction to occur (Scheme 1.8):[24]

$$Cp_2TaH + C_6H_6 \longrightarrow Cp_2Ta(H)_2Ph$$

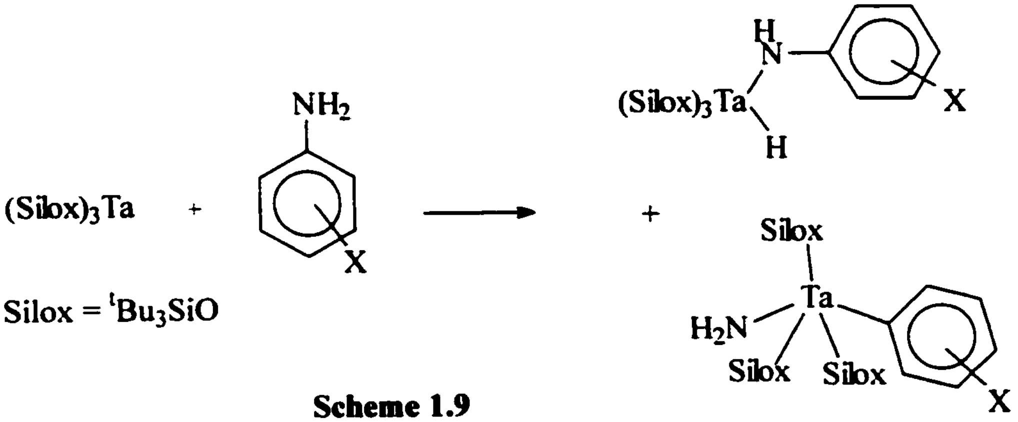
$$Cp_2WH_2 \xrightarrow[-H_2]{h\nu} [Cp_2W] \xrightarrow{C_6H_6} Cp_2WHPh$$

Scheme 1.8

Examples of intramolecular attack on aromatic C-H bonds by in situ generated low-valent metal complexes are rather common in the literature.

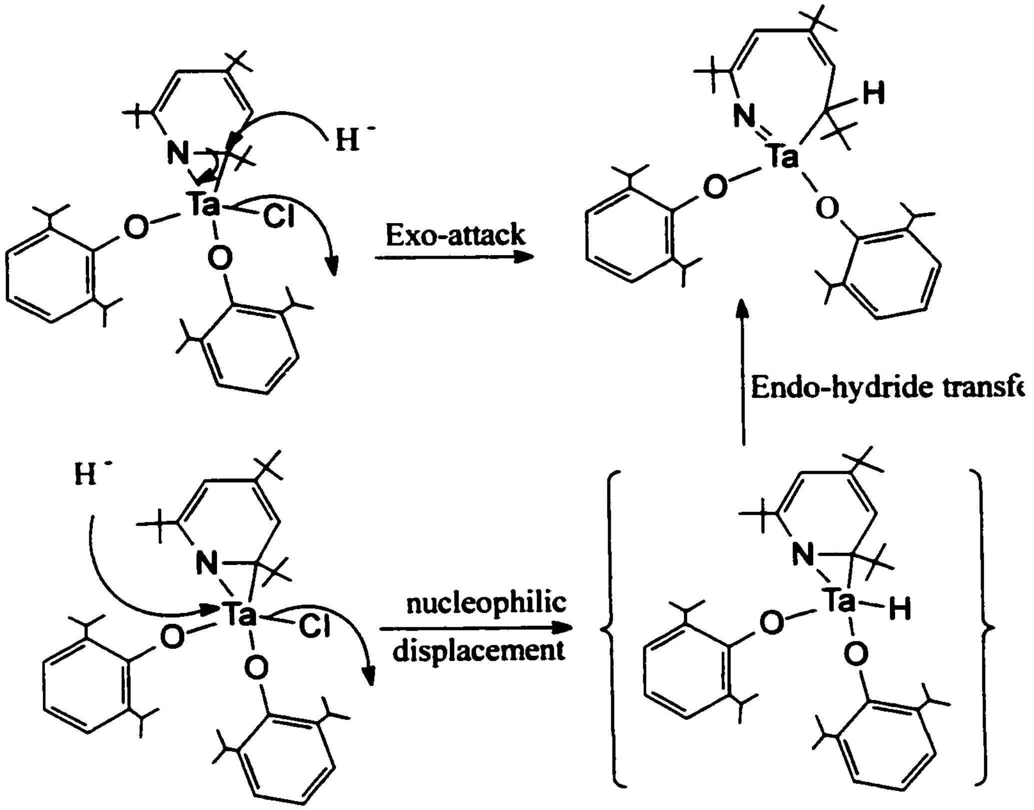
C-N bond cleavage

Although more polarized and in principle more reactive that C-H or C-C bonds, C-N and C-O bond cleavage pose in fact a challenge, especially if these transformations have to be found in a catalytic fashion. Oxidative addition into carbon-nitrogen and carbon-oxygen single bonds are critical transformations for hydrodenitrogenation (HDN)[25] and hydrodeoxygenation (HDO)[26] of crude oil.[27] There are only a few examples of catalysts capable of performing these remarkable transformations.[28] Again, group V metals seem to provide promising substrates for this type of reactivity. For example, the C-N bond of aniline has been cleaved in the reaction with $(Silox)_3Ta$ (Scheme 1.9):[29]



Scheme 1.9

In spite of higher multiplicity and allegedly higher stability, cleavage of C=N multiple bonds seems to be easier to be achieved than C-N single bond judging from the amount of examples available in the literature.[30,28c-d] Mechanistic considerations about C-N bond cleavage as promoted by nucleophilic metal hydride have been described by Wigley in the reaction of a Ta(V) complex with $LiBEt_3H$ (Scheme 1.10) leading to a spectacular case of pyridine ring opening.[25d]



Scheme 1.10

The mechanism of the reaction involves a direct, *exo*-hydride attack on the carbon-nitrogen bond of the pyridine ring. Nucleophilic attack of the hydride at the metal to form an unstable hydride complex, followed by an *endo* hydride transfer from the metal to the pyridine ligand also represents a viable pathway for C-N bond scission.

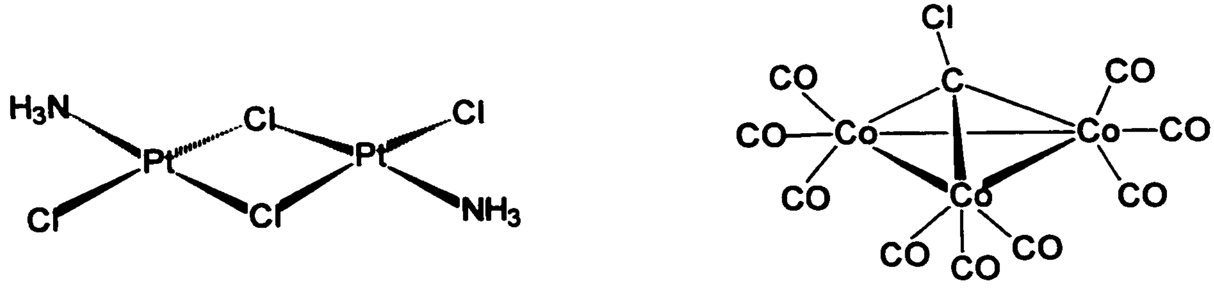
Formation of Metal-Metal Multiple Bonds

In the classical concept of coordination chemistry as formulated in the original coordination theory by Werner, the formation of M-M bonds cannot be explained.[31] Nevertheless, today this attractive and unique functionality is very well established and is responsible for a formation of an entire family of compounds, the clusters,[32] which, in turn, are responsible for many important aspects of modern chemistry.

Cluster compounds are characterized by the presence of two or more metals in the same molecular aggregate. Additional ligands may or may not be present and the existence of direct M-M bonds is the driving force for holding together the molecular aggregate. The chemical behavior of a metal center in a certain oxidation state is distinctively different from the corresponding mononuclear species. Metal-metal bonds in polynuclear compounds can be regarded as authentic electronic reservoirs and, as such, may make possible unusual transformations requiring the intervention of several electrons. One of the most spectacular cases is the six-electron reduction of dinitrogen as achieved by the nitrogenase cofactor. This species consists of a simple cubane-type tetranuclear cluster of Fe and sulfur where electrons can be stored in a large series of M-M centered molecular orbitals.[33] Clusters can be also used for trapping exotic functions (a range of hydrocarbon fragments, down to bare carbon atoms), to enforce unusual coordination geometries, and to promote transformations in catalytic fashion.[32]

Favorable conditions for the occurrence of M-M bonds include a low formal oxidation state and a high atomic number since under these circumstances widely protruding *d* orbitals with good overlap properties are present. Group V metals display some interesting anomalies in this particular field. The lighter congener of the family, vanadium, presents all ranges of M-M distances (from supershort range to non-bonding distances depending on the nature of the bridging ligands.[34] On the basis of this behavior, the magnetic properties and the reactivity of these derivatives, it was argued that V-V short and very short distances may be better regarded as ligand artifact.[35] Although the existence of unsupported M-M bonded was never conclusively established for any of the group V metals, there are indications that Nb and Ta species may form significant and robust M-M single and multiple bonds. Compounds of niobium with single bonds were obtained by reduction of niobium pentachloride with 1 equiv of reducing agent or by reacting monomeric $NbCl_4L_2$ (L= THF, CH_3CN) with ligands such as MeOH[6h] or PMe_3.[6a,f] The existence of double M-M bonds has been claimed in $Nb_2Cl_6(THT)_3$[7j] with face-sharing bioctahedral geometry or $Nb_2Cl_6(PMe_3)_4$[6g] with edge–sharing bioctahedral arrangement. However, the paramagnetism of these complexes makes doubtful that these bonds may be a factor responsible for holding together the dimetallic structure.

Dinuclear complexes of niobium and tantalum in the (+II) oxidation state are very rare[36,7q] due to both lack of suitable starting materials containing the metal in the low oxidation state, and the fact that dinuclear complexes of niobium or tantalum in higher oxidation states are often not reducible by common reducing agents. For example, while $W_2Cl_6(PMe_3)_4$ can be reduced to form $W_2Cl_4(PMe_3)_4$, the tantalum analogue does not form the divalent species under the same reduction conditions.[6g] The only divalent Ta and Nb compounds available when we start this work contain very long M-M distances and



Classic Werner Complex

Metal Atom Cluster

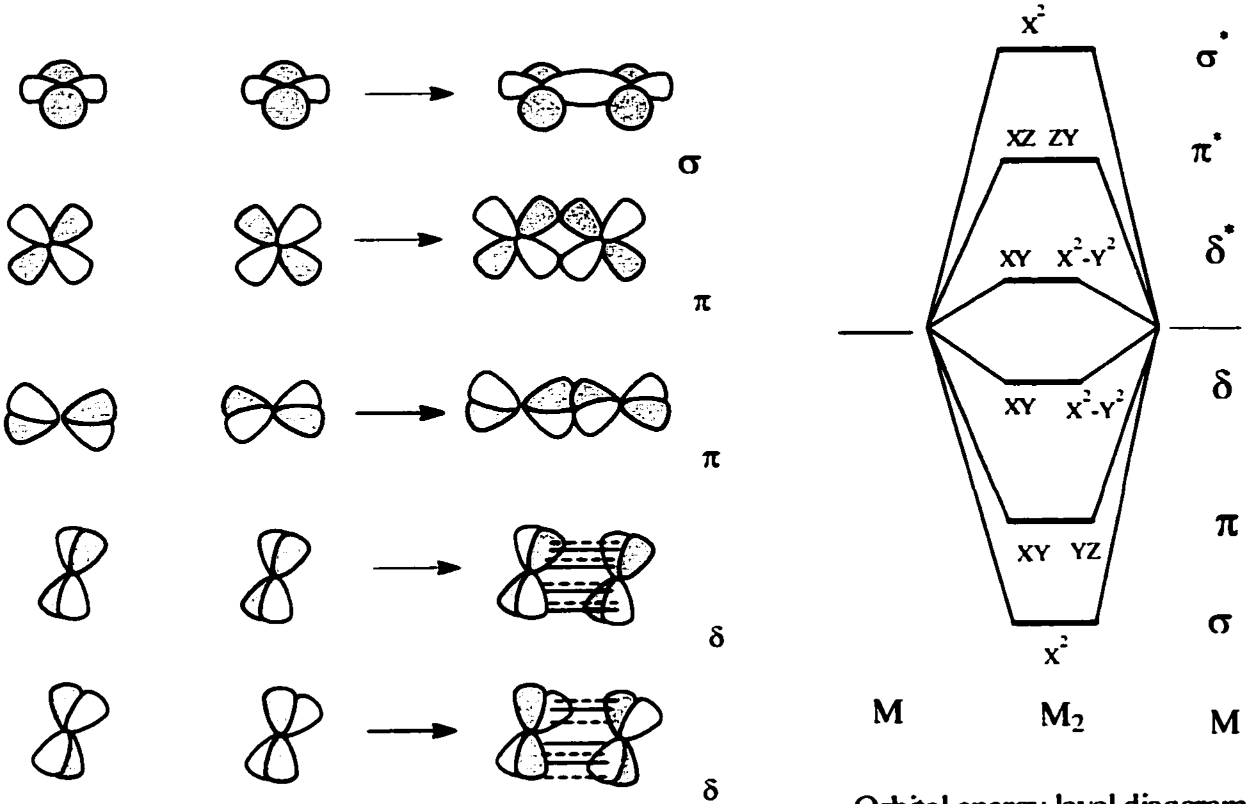
Scheme 1.11

are paramagnetic.[7p-q]

Magnetism as well as bond distances are usually used as tools to evaluate the existence of M-M bonds between these metals and to establish their multiplicity. By comparing the Nb-Nb distances in $Nb_2(hpp)_4$ (hpp = 1,3,4,6,7,8-hexahydropyrimido[1,2-a]pyrimidinate) [2.2035(9) Å][35d], $[Na(THF)_3]_2[Nb_2Cl_5(\mu\text{-}THT)_3]_2$ [2.610(3) Å][7q] and the diamagnetic Nb(II) d^3-d^3 dimer in $[(C_5H_4Me)Nb(\mu\text{-}Cl)(CO)_2]_2$ with a surprisingly long Nb-Nb distance [Nb-Nb = 3.0567(1) Å],[37] it appears evident that the nature of the ligands plays a very significant role in determining the distance between the two metal centers.

The M-M interactions between two metal centers are realized via the direct overlap of their outermost *d* orbitals. These *d* orbitals can combine to form σ, π and δ orbitals as shown in scheme 1.12. If the *z* axis is selected as internuclear axis, the strongest interaction (involving greatest overlap) is the sigma interaction between the d orbitals. Next in effectiveness of overlap are the d_{xz} and d_{yz} orbitals, which form π orbital. The last, and weakest, of these interactions are originated by the d_{xy} and $d_{x2\text{-}y2}$ orbitals which are forming δ molecular orbitals.

The relative energies of the resulting molecular orbitals are shown in scheme 1.12. In the absence of ligands, an M_2 fragment would have five bonding orbitals resulting from *d-d* interactions, with molecular orbitals increasing in energy in the order σ, π, δ, δ^*, π^*, σ^*.



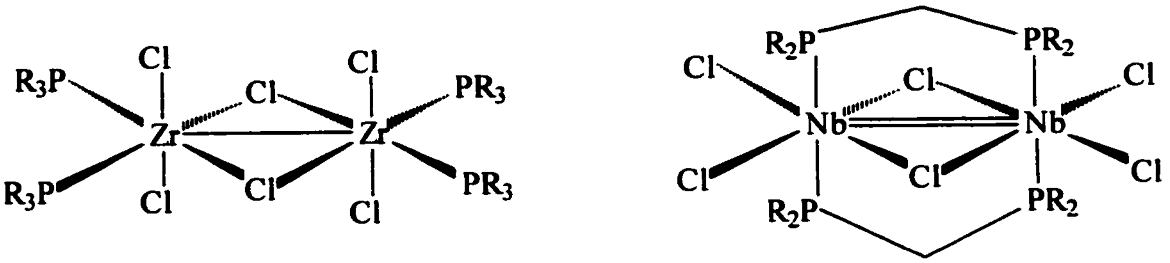
Orbital energy level diaqgram

Scheme 1.12

Major Structural Types

The most common structural contexts for complexes with M-M multiple bonds can be summarized as follows:

1. *Edge-Sharing Bioctahedral*: Complexes with this type of structure are abundant, and may in principle exhibit M-M bond orders ranging from single to triple. The M-M bonds are believed to be formed from the overlap of pairs of *d* orbitals. Examples of single (σ^2) and double ($\sigma^2\pi^2$) bonds are provided by molecules such as **1.1** and **1.2** respectively (Scheme 1.13):[38]



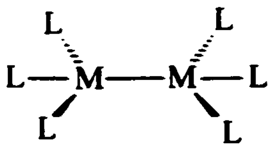
1. 1

1. 2

Scheme 1.13

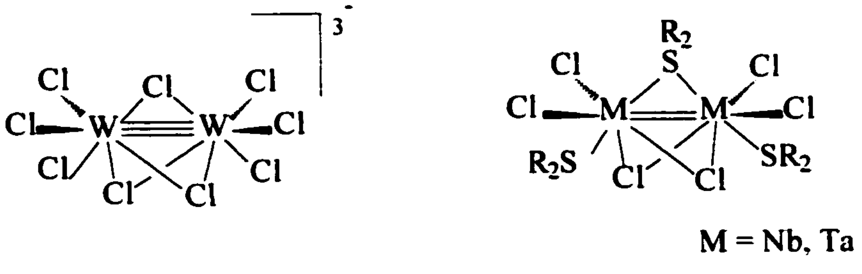
The majority of structurally characterized edge-sharing bioctahedra of niobium and tantalum of the type $M_2Cl_6L_4$ and $M_2Cl_6(L\text{-}L)_2$ [L for monodentate and L-L for bidentate donor ligand] contain phosphine donor ligands. The M-M distance in the edge-sharing bioctahedra depends on the type of the metal and the basicity of donor ligands. For example in the $M_2Cl_6(dene)_2$ complexes, the Nb-Nb distance is shorter (by 0.014 Å) than the Ta-Ta distance which is in contrary of the trend seen in Nb/Ta compounds of the edge-sharing bioctahedral type (see for example the $M_2Cl_6(dmpm)_2$ compounds).[7c]

The coordination of six ligands in the manner shown in Scheme 1.14 causes all the δ and δ* orbitals to shift their energies, and leaves three M-M bonding type orbitals, σ and (doubly degenerate) π. Thus, this particular structural architecture is especially favorable for the formation of triple bonds with $\sigma^2\pi^4$ configuration.



Scheme 1.14

2. *Face-Sharing Bioctahedra*: The interpretation of bonding in face sharing bioctahedral complexes is complicated by the presence of three bridging atoms. The first example of M-M triple bond was discovered within this structural context for tungsten (Scheme 1.15a). Still this type of geometrical arrangement is believed to support M-M multiple bonds. For example in the case of Nb and Ta complexes, double and triple bonds are believed to exist in the complexes of formula of $M_2X_6(SR_2)_3$ and $M_2X_6(THT)_3^{2-}$ respectively (Scheme 1.15b).[7q]



(a) (b)

Scheme 1.15

Magnetic Properties

As it was mentioned earlier magnetism is one of the tools which is used to evaluate the existence of M-M bonds between transition metals in one compound and to determine their multiplicity. The magnetic properties of a transition metal complex are related to the number of unpaired electrons present per unit weight and hence per mole. In particular, the major contributors to the observed paramagnetism of a substance containing unpaired electrons are the orbital motions of the unpaired electrons as well of the spins. However, there are numerous cases where the spin contribution is so predominant that magnetic susceptibility values can be interpreted in terms of the number of unpaired electrons. This correlation is best expressed by using a quantity called magnetic moment (μ_{eff}) which may be calculated from the measured molar susceptibility χ_M. For mononuclear complexes of metal ions of the first transition series, the orbital splitting pattern derived from ligand field theory provide a reliable first order interpretation (most importantly, in understanding the number of unpaired electrons) of measured magnetic susceptibilities. However, there are two areas in which such a simple approach is inadequate: (1) for mononuclear complexes of the heavier transition elements, where spin-orbit coupling is larger, and (2) in all bi- and polynuclear complexes where spin-spin coupling takes place either by direct orbital overlap or by pathways involving bridging ligands.

In cases where direct orbital overlap between metal atoms is strong, we are dealing with M-M bonds (single or multiple) and no special problems are expected. There are, however, many cases in which the interaction is relatively weak and the energy separation between states with different numbers of unpaired electrons is small. In such compounds magnetic moments show a marked dependence on temperature and the interpretation of the magnetic behavior is anything but straightfoward.[38]

Scope of the thesis

The indication emerging from the selection of literature presented above is that low-valent niobium complexes may be provided of a very high reactivity which may be promising for a number of transformations and features spanning from M-M bond formation to molecular activation processes. The aim of this thesis was to embark on a systematic study to explore the chemistry of the divalent state. While the utilization of in situ generated complexes may be occasionally useful, however, it is hampered and occasionally confused by possible involvement of the ligands in the reactivity of the reducing agent. Thus the starting point of this thesis was the search for a suitable low-valent starting material providing accessibility to classes of compounds via mild-condition ligand replacement reactions. It was hoped that in this way a better control on the chemical reactivity of these species, expected to be very high, could be achieved.

Before describing our results perhaps it is better to briefly summarize and outline the literature background about niobium compounds.

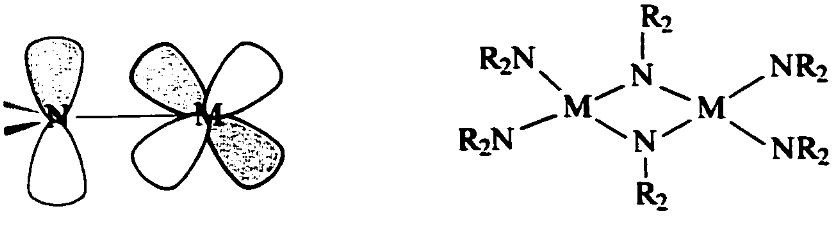
Halide Complexes

The most convenient starting material to access the chemistry of niobium are the highly reactive pentahalides.[39] The lower valent niobium halides are prepared by reduction of niobium pentahalide. Among the most convenient tetravalent complexes which can be used as starting materials $[NbCl_4(THF)_2]$, $[NbCl_4(MeCN)_2].MeCN$, $[Nb_2Cl_8(L)_4]$ (L = Me_3P, Me_2PhP), $[NbCl_4(Me_3P)_3]$, $[NbCl_4(L)_2]$ (L = Et_3P, $EtPh_2P$) and $[NbCl_4(dmpe)_2]$[6] should be mentioned. Conversely, for the trivalent state only trichlorides of the formula $[Nb_2Cl_6(L)_2]$ (L = dppm, dmpm, dppe, depe, TEEDA), $[Nb_2Cl_6(L)_4]$ (L = PMe_3, $PhPMe_2$), $[Nb_2Cl_6(THF)_2(THT)]$, $[Nb_2Cl_6(L)_3]$ (L = THT, Me_2S, TPP, C_5H_5N, 4-MeC_5H_4N, 3,5-$Me_2C_5H_3N$), $[NbCl_3(DME)]$, are available. The species have been obtained by reduction of $NbCl_5$ with sodium amalgam, sodium-potassium alloy, tributyl tin hydride or magnesium in the presence of the appropriate ligands.[7a-o] Divalent niobium halides are limited to: [$NbCl_2(dmpe)_2$], [$NbCl_2(PMe_3)_4$], [$Nb_2Cl_6(THT)_3(NEt_4)_2CH_3CN$], [$Nb_4Cl_{10}Na_2(THT)_6(THF)_6$] and [$NbCl_2(Py)_4$].[7p-r] While coordinated phosphine derivatives may be not particularly useful due to the great stability of the M-P bond, the other complexes described above contain ligands (pyridine or even worse THT) which can be expected to be the primary target of the reactivity of the low-valent Nb complex we want to generate.

Complexes of Niobium with Nitrogen Donor Ligands

Anionic organic amides as obtained from the deprotonation of secondary amines are versatile ligands for the stabilization of low oxidation states. Their versatility can be ascribed to:

- the electronic flexibility as provided by the availability of the nitrogen lone pair and which can be made available for further donation depending on the need of the transition metal (Scheme 1.16a);
- possibility of tuning steric bulk via the appropriate selection of organic substituents;
- ability to act as bridging ligand (Scheme 1.16b). This is also a particularly attractive feature for assembling di- and polynuclear structures containing highly reactive metal centers hopefully able to perform cooperative attack on the same substrate. The ability of



(a) (b)

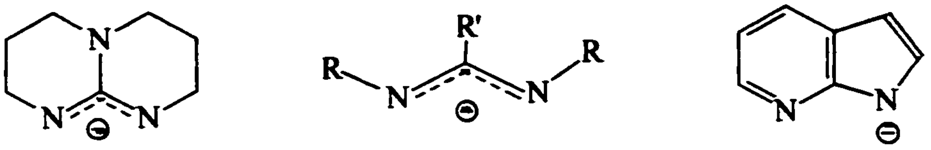
Scheme 1.16

ability of bridging amides to favor the occurrence of short intermetallic contacts makes possible formation of M-M bonds which may contribute to the stabilization of highly reactive units.[40]

Niobium and tantalum amide complexes can easily undergo substitution, as well as C-H bond activation or C-N bond cleavage.[41,30f] For example, upon reaction of $[\eta^2$-(N,C)-2,4,6-$NC_5{}^tBu_3H_2]Ta(OAr)_2Cl$ (**1.3**) with 1 equiv of $LiBEt_3H$, the C-N bond of the η^2(N,C)-pyridine ligand is cleaved due to addition of hydride on the metal-bound carbon of η^2(N,C)-pyridine (Scheme 1.10).[25d] The methylated complex of 1.3, $[\eta^2$-(N,C)-2,4,6-$NC_5{}^tBu_3H_2]Ta(OAr)_2Me$, through thermolysis, can give the same type of C-N bond cleavage after migration of methyl group from metal to the metal-bound carbon of η^2(N,C)-pyridine.[41] The Nb-N bond is also surprisingly reactive since it is susceptible of insertion reactions, for example by CO_2, CS_2 and COS in $[Nb(NR_2)_5]$.[42]

Pentavalent niobium forms important complexes of formula $Nb(NR_2)_xX_{5-x}$ through reaction of $NbCl_5$ with $LiNR_2$.[43] The coordination of the dialkylamides and the nuclearity is largely determined by the steric bulk of the NR_2 groups and by their ability to form σ and π bonds.[44] The homoleptic niobium amide complexes are generally synthesized by reacting $LiNR_2$ with niobium pentachloride while the heteroleptic derivatives are more conveniently prepared by transamination reactions.[45] Until 1971, the only known Nb(IV) homoleptic amide complex was $Nb(NR_2)_4$ [R= n-Bu, n-Pr, Et, Me, Ph] while only two heteroleptic derivatives, $Nb(NEt_2)_2(NC_5H_{10})_2$ and $Nb(NMe_2)(NEt_2)_3$, were reported by Bradley.[40,46] In the large family of tetravalent niobium cyclopentadienyl derivatives, the complex $CpNb(NMe_2)_3$, was also reported in 1971.[47] Starting from this original work only a few more compounds have been reported to date.[48] Namely they consist of Pc_2Nb (Pc = Phthalocyanine)[49] and a number of imido compounds containing Nb=NR units and the metal in the (+V) and (+IV) oxidation state.[50] Particularly interesting derivatives in this category of compounds are the binuclear dinitrogen complexes where the M=N multiple bonds may be regarded as imido functions.[51a,b]

Imido ligands display a unique capability to stabilize complexes in high-oxidation states[51d,e] and display direct involvement of the metal-nitrogen multiple bond in the reactivity of the metal center.[50] For niobium in oxidation state (+III), there is a limited number of non-halide complexes known, for example complexes of niobium with cyclopentadienyl and alkyne[52], calix[4]arene tetraanion[49f], and with alkyl isocyanide ligands.[53] For complexes of Nb in the (+II) oxidation state only $Nb_2(hpp)_4$[36d] and $Nb_2(azine)_4.2LiCl.4THF$ (azin = the anion of 7-azaindole)[36e] are known and they have been obtained through reduction of higher oxidation state niobium by strong reducing agents. In contrast to hpp and azin ligands, formamidinates are not good candidates for synthesis of $M_2(formamidinato)_4$ complexes [M = Nb, Ta] as it was obtained in the case of vanadium (Scheme 1.17). Reaction of the heavier metals of the group V with this ligand so far gave dinuclear complexes containing doubly bonded M_2^{6+} units which typically reacted with formamidinate anion by performing an oxidative addition which resulted into a cleavage of the ligand C-N.[30e] The resulting products products contain either M^{III} or M^{IV} and fragments such as ArN and ArNC.



hpp ligand   Amidinate ligand   7-azaindole ligand

Scheme 1.17

Given these premises, saturated N-donor based ligands were selected to attempt the synthesis of unprecedented low-valent niobium amide complexes which may offer the ground for further discovery of unusual reactivity patterns.

Niobium Cluster Complexes

While in their lower oxidation states, niobium and tantalum show tendency to aggregate and forming cluster compounds. The cluster complexes reported so far have been obtained by reduction of the penta-halides by elemental niobium or tantalum, or in the presence of sodium chloride at elevated temperatures (Scheme 1.18).

$$14NbCl_5 + 16Nb + 20NaCl \xrightarrow{12h,\ 850^{\circ}C} 5Na_4Nb_6Cl_{18}$$

Scheme 1.18

The M_6X_{12} units are usually found in di-cationic form and with each metal bearing a terminally bound additional ligand (X^-, H_2O, etc.) on the external coordination site.[55] Within the M_6 octahedron there is a series of M-M bonds with an overall fractional order. For example, assuming that the 16 electrons present in the $[Nb_6Cl_{12}]^{2+}$ unit and available for M-M bonding are equally distributed over the twelve M-M edges, an overall M-M bond order of 2/3 results which nicely agrees with the experimental bond distance of ~2.80 Å. Other examples of Nb_6 clusters are provided by Nb_6I_{11}, $CsNb_6I_{11}$, $Nb_6I_{11}H$ and $CsNb_6I_{11}H$. These species contain octahedral clusters and display eight face-bridging (i.e., μ_3) iodine atoms.[55] A very few Nb_3 and Nb_4 clusters have been also reported in the literature.[56]

Thesis Summary

The aim of this research was to explore the reactivity of niobium in medium and low oxidation states and to better clarify the enormous potential of these species for molecular activation processes involving C-N, N-H bond cleavages, C-H bond activation and N_2 activation. Possible reason for the paucity in the literature of low-valent niobium chemistry is the absence of suitable starting materials. Thus a major effort was carried out in the initial part of this work for the preparation of low-valent salts containing the metal in the final desired oxidation state which may enable the preparation of low-valent complexes via mild-condition ligand replacement reactions. Anionic amides, whose versatility is well established in terms of electronic flexibility in addition to their inherent ability to stabilize low-valent states of transition metals have been explored as possible stabilizing ligand systems.

Given the above rationale, we have initially explored the chemistry of established Nb(III) salts. This has required to improve their synthesis and to make them available on large scale. The reactivity has been probed with the largest possible number of amide ligands (aliphatic, aromatic, mixed aliphatic aromatic, bidentates and macrocyclic). To our disappointment these reactions mainly led to intractable materials. Conversely, one of these reactions provided accessibility to the large-scale preparation of a molecular divalent niobium salt (see Chapter II) which in turn gave the key for a wide investigation of the chemistry of divalent niobium. As a result of a variety of C-X bond oxidative addition processes promoted by this potent reductant, a number of trivalent complexes (Chapter IV and V), otherwise not accessible have been prepared and their properties fully elucidated. Chapter VI reports a unique case of denitrogenation of a pyrrole ring while Chapters III and VII show the preference of disproportionation pathway versus molecular activation described in chapter VI by using ligands from the same family. Finally, Chapter VIII tackle the M-M interaction in some of these dinuclear low-valent compounds.

It should be mentioned that the thesis is primarily focused on those reactions that were successful in providing a coherent and logic development of a chapter of novel science. No mention is given in this thesis of the large amount of exploratory work carried out to define the chemistry of low-valent niobium. For example, a number of reactions with both NbII and NbIII salts have been carried out with diversified reagents including different aliphatic anionic amides [$(CH_3)_2N^-$, $(TMS)_2N^-$, $(TMS)N(C_2H_4)_2((TMS)N)_2^{2-}$, 1,2-$C_6H_{10}N_2H_2^{2-}$, 1,2-$C_6H_{10}N_2(^iPr)_2^{2-}$. 2,2,6,6-$(CH_3)_4C_5H_6N^-$, $C_4H_8N^-$], a few macrocyclic ligands (octamethylcalixtetrapyrrole, octaethyl calixtetrapyrrole, octapropylcalixtetrapyrrole , tetracyclohexylcalixtetrapyrrole) as well as some aryloxides [2,6-$(CH_3)_2C_6H_3O^-$, 2,4,6-$(CH_3)_3C_6H_2O^-$, $C_{10}H_7O^-$, 2,6-$(C_4H_{12})_2$,4-$(CH_3)C_6H_2O^-$] only resulting in the formation of intractable materials.

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CHAPTER II

Reactivity of tri- and tetravalent niobium halides with anionic amide ligands: metal reduction, C-N and N-N bond Cleavage

II. 1: Introduction

As shown in the previous chapter, the chemistry of medium-valent Nb and Ta is poorly known and nearly exclusively limited to the family of the cyclopentadienyl derivatives. The initial target of the present study was to develop the chemistry of niobium in the +3 oxidation state. The very simple idea at the basis of this work was to test the possibility of taking advantage of the availability of low-valent salts such as $Nb_2Cl_6(TMEDA)_2$ and to use them as starting material for ligand replacement reactions. It was hoped that by using mild reaction conditions new series of low-valent complexes could be prepared in this way, thus significantly contributing to the development of the chemistry of virtually unknown oxidation states. The task appeared to be rather arduous, given the simplicity of the idea. However, we felt that by selecting the appropriate ligand system the stabilization of trivalent complexes could be achieved. The preparation of trivalent complexes was regarded as a particularly promising task since a very high level of reactivity was expected for these species able to span the most different and disparate types of molecular activation processes.

The idea of using anionic organic amides[1] as stabilizing ligands is not new. It was pioneered by Lappert and Bradley who independently covered a large section of the periodic table by building up classes of amide compounds. The main features of anionic organic amide as ligands are summarized in the previous chapter. It is worth reiterating here that the electronic flexibility of these moieties, able to engage up to four electrons for bonding the transition metal, was regarded as particularly promising for the stabilization of alleged highly reactive species. The little information available about low valent complexes of niobium amides is exclusively resulting from the reduction of the corresponding complexes in higher oxidation states.[2] Thus, since low-valent Nb amides were unknown when we started this study, to carry out an exploration on the reaction of trivalent salts with largely available Li amide was regarded as the most obvious series of experiments to be attempted. Also the established ability of anionic amide to bridge two transition metals and to assemble polymetallic structures was regarded as especially promising given that the possible formation of M-M bonds may add stability to the low-valent species. Finally, in the enormous selection of possible amide ligands available, priority was given to those provided of high or medium steric bulk. This idea was advised by the recent findings in the chemistry of Mo where bulky amide afforded the discovery of an unusual type of reactivity in the dinitrogen activation field[3].

In this chapter we describe the results obtained by reacting tri- and tetravalent niobium salts with anionic amides. In one case, one of these reactions led to a selective reduction of the metal center enabling the preparation of an unprecedented divalent Nb salt which in turn provided another interesting starting material to explore the chemistry of low-valent Nb. Herein we describe our findings.

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). $^{i}Pr_2NH$,

Cy_2NH (Aldrich) were distilled prior to use over molten potassium under N_2. The lithium salts of the corresponding amines ($^iPr_2NLi$ and Cy_2NLi) were prepared by treating a hexane solution of the amine with stoichiometric amounts of n-BuLi. $NbCl_4(THF)_2$,[3,5-$Me_2PhN(Ad)$]Li.Et_2O (Ad = adamantyl) and $Nb_2Cl_6(TMEDA)_2$ were prepared according to published procedures.[4,5] Azobenzene was deaerated under vacuum at 25°C. Infrared spectra were recorded on a Mattson 9000 FTIR instrument from Nujol mulls prepared in a drybox. Elemental analyses were carried out with a Perkin Elmer 2400 CHN analyzer. NMR Spectra were recorded with a Bruker AMX 500 MHz spectrometer.

Preparation of $Nb_2Cl_5Li(TMEDA)_3$ (2.1):

Method A: Solid $Nb_2Cl_6(TMEDA)_2$ (1.0 g, 1.6 mmol) was added to a solution of LDA ($^iPr_2NLi$) (1.0 g, 9.0 mmol) in THF (70 mL). The slurry was stirred at room temperature for two hours during which time the pink starting material disappeared to give a dark brown solution. Stirring was continued overnight and the solvent evaporated *in vacuo*. The residual oil was redissolved in ether (60 mL) and the resulting solution filtered to remove LiCl. The resulting solution was concentrated to small volume and allowed to stand undisturbed for two days at -30°C. Dark brown air-sensitive crystals of **2.1** separated (0.15 g, 0.17 mmol, 11%).

Method B: Neat TMEDA (0.95 ml, 6 mmol) was added to a suspension of $Nb_2Cl_6(TMEDA)_2$ (1.0 g, 1.6 mmol) in ether (70 mL). The mixture was cooled to -78°C for 20 min. and then treated with a solution of n-BuLi in hexane (1.34 ml, 2.5 M, 3.17 mmol). The mixture was stirred and allowed to warm up to room temperature and stirred for one additional hour. The mixture was evaporated to dryness *in vacuo* and the residue redissolved in toluene (100 mL). A small amount of light colored solid was eliminated by filtration. The solution was then evaporated to dryness and the residual solid redissolved in ether. Brown crystalline **2.1** (0.39 g, 0.54 mmol, yield 34%) separated upon allowing the solution to stand at room temperature overnight. I.R. and NMR spectra were identical to those of the complex prepared according to the procedure described in method A. El. Anal. Calcd (found) for $C_{18}H_{48}N_6Cl_5Nb_2Li$: C 30.08(29.84), H 6.73(6.64), N 11.69(11.51). I.R. (Nujol mull, cm^{-1}) ν: 2780(m), 1370(w), 1286(m), 1260(m), 1124(m), 1067(m), 1021(s), 951(s), 918(w), 791(vs). ^1H-NMR (C_6D_6, 200MHz, 25°C) δ: 2.67 (s, 12H, CH_3), 2.62 (s, 12H, CH_3), 2.57(s, 12H, CH_3), 2.30(s, 4H, CH_2), 1.89 (m, 4H, CH_2), 1.40(m, 4H, CH_2). ^9Li-NMR (C_6D_6, 500MHz, 25°C) δ: 0.3.

Preparation of [$Nb_4Cl_{12}Li_2(THF)_8$] (2.2):

A solution of Cy_2NLi (2.0 g, 11.1 mmol) in THF (100mL) was treated with $NbCl_4(THF)_2$ (2.1 g, 5.5 mmol). The resulting greenish slurry was stirred for one hour during which it turned into a reddish brown solution. The reaction mixture was allowed to stir for other 3 hours. After centrifugation, the volume of the solution was reduced to about 70 mL. Layering with diethyl ether (30 mL) and standing at room temperature for a few days afforded diamagnetic dark-red crystals of **2.2** (0.15 g, 0.11 mmol, 10%). El. Anal. Calcd (found) for $C_{32}H_{64}Cl_{12}Li_2O_8Nb_4$: C 27.7(27.19), H 4.65(4.62). I.R. (Nujol, KBr plates, cm^{-1}) ν: 1343(s), 1318(w), 1293(m), 1247(m), 1178(s), 1140(w), 1044(s), 1025(s), 1012(s), 964(w), 915(m), 858(m), 679(s).

Preparation of {(3,5-Me_2Ph)(Ad)N]Nb(3,5-Me_2Ph)}$_2$(μ-NAd)$_2$.ether (2.3):

Method A: A suspension of $Nb_2Cl_6(TMEDA)_2$ (1.0 g, 1.6 mmol) in THF (70 mL) was treated with (3,5-Me_2Ph)(Ad)NLi (3.2 g, 9.5 mmol). The mixture was refluxed for 15 hours until complete disappearance of the insoluble starting material. The solvent was removed *in vacuo* and the residual solid residue suspended in Et_2O (100 mL). The suspension was filtered to eliminate LiCl and the resulting solution was concentrated to small volume and allowed to stand one day at room temperature upon which dark red crystals of **2.3** separated (0.27 g, 0.19 mmol, 13%). El. Anal. Calcd (found) for $C_{40}H_{58}N_2NbO$: C 71.09(70.84), H 8.65(8.64), N 4.15(4.09). I.R. (Nujol mull, cm^{-1}) ν: 1592(m), 1575(m), 1302(m), 1090(s), 1025(s), 950(m), 923(m), 801(s), 720(m), 684(m). ^1H-NMR (C_6D_6, 500MHz, 25°C) δ: 7.20(s, 2H, Ph_{ortho}), 6.77(s, 1H, Ph_{para}), 6.46(s, 2H, Ph_{ortho}), 6.35(s, 1H, Ph_{para}), 3.58 (q, 4H, CH_{2ether}), 2.47(s, 6H, CH_{2Ad}), 2.33(br.s, 3H, CH_{Ad}), 2.17(s, 6H, CH_3), 1.98(s, 6H, CH_3), 1.89(m, 6H, CH_{2Ad}), 1.51(m, 3H, CH_{Ad}), 1.30-1.14(dd, 6H, CH_{2Ad}), 1.24(br.s., 6H, CH_{2Ad}), 1.08(t, 6H, CH_{3ether}). ^{13}CNMR (C_6D_6, 125MHz, 25°C) δ: 139.8(quaternary Ph), 135.8(quaternary Ph), 133.9(quaternary Ph), 133.4 and 131.9(CH_{ortho} Ph), 130.6 and 127.7(CH_{para} Ph), 120.6(quaternary Ph), 67.4(CH_2, ether), 58.5 and 47.6(quaternary Ad), 48.77 and 46.0 (CH_2, Ad), 38.0 and 37.33(CH_2, Ad), 32.0 and 30.73(CH, Ad), 21.5 and 21.3(Me, Ph), 15.9(CH_3, ether).

Method B: A solution of $Nb_2Cl_5Li(TMEDA)_3$ (1.0 g 1.4 mmol) in THF (70 mL) was treated with (3,5-Me_2Ph)(Ad)NLi (1.8 g, 5.5 mmol). The mixture was stirred at room temperature overnight and then boiled for a few minutes. The solvent was removed *in vacuo* and the solid residue redissolved in ether (100 mL). A small amount of insoluble material was filtered off and the solution concentrated to small volume. Dark red crystals of **2.3** separated upon standing overnight at room temperature (0.60 g, 0.44 mmol, 32%).

Preparation of $NbCl_3(C_6H_5N)(TMEDA)$ (2.4):

To a suspension of $Nb_2Cl_6(TMEDA)_2$ (1.0 g, 1.6 mmol) in toluene (70 mL), azobenzene (0.57 g, 3.2 mmol) was added. The mixture was refluxed overnight. After filtration of a small amount of insoluble solid, orange crystals of **2.4** were isolated at room temperature (0.77 g, 1.95 mmol, 61%). El. Anal. Calcd (found) for $C_{12}H_{21}N_3NbCl_3$: C 35.41(35.01), H 5.16(4.78), N 10.33(9.88). I.R. (Nujol mull, cm^{-1}) ν: 1580(m), 1325(s), 1182(w), 1165(w), 1064(d), 1021(m), 983(s), 954(s), 916(s), 799(vs), 763(s), 688(s). ^1H-NMR (C_6D_6, 200MHz, 25°C) δ: 7.45(d, 2H, CH, Ph), 6.95(m, 2H, CH, Ph), 6.75(m, 1H, CH, Ph), 3.59(s, 6H, CH_3, TMEDA), 3.15(s, 6H, CH_3, TMEDA), 3.0(m, 2H, CH_2, TMEDA), 2.9(m, 2H, CH_2, TMEDA). ^{13}C-NMR (C_6D_6, 125MHz, 25°C) δ: 129.01(Ph), 128.58(Ph), 128.39(Ph), 128.19(Ph), 127.51(Ph), 125.91(Ph), 74.82(TMEDA), 72.59(TMEDA), 70.69(TMEDA), 67.74(TMEDA), 62.61(TMEDA).

II. 3: Results and Discussion

The reaction of LDA (lithium isopropylamide) with $Nb_2Cl_6(TMEDA)_2$ was completed in a few hours at room temperature. After suitable work-up, well-formed, dark brown air-sensitive crystals of a new diamagnetic product were isolated in poor yield. The I.R. and the NMR of the crystalline product clearly indicated that the complex contained two sets of non-equivalent TMEDA ligands. The presence of lithium, suggested by qualitative flame tests, was confirmed by Li-NMR spectroscopy. Combustion analysis data were in agreement with the formulation $(TMEDA)_3Nb_2Cl_5Li$ (**2.1**) (Scheme 2.2). An X-ray structure confirmed the formula and elucidated the molecular connectivity (Figure 2.1).

The crystal structure of **2.1** provides a rare example of a dinuclear Nb(II) complex. The diamagnetism and the very short Nb-Nb distance [Nb-Nb = 2.4008(7) Å] suggest the presence of a Nb-Nb triple bond.[6] Divalent halide complexes of Nb and Ta are particularly rare and limited to a few di- and polynuclear structures mainly bridged by tetrahydrothiophene ligands (THT).[7] The M-M triple bonds in these species are surprisingly long and thus to evaluate their properties it is important to prepare a variety of multiple bonded systems with the greatest possible diversity of ligand environments.

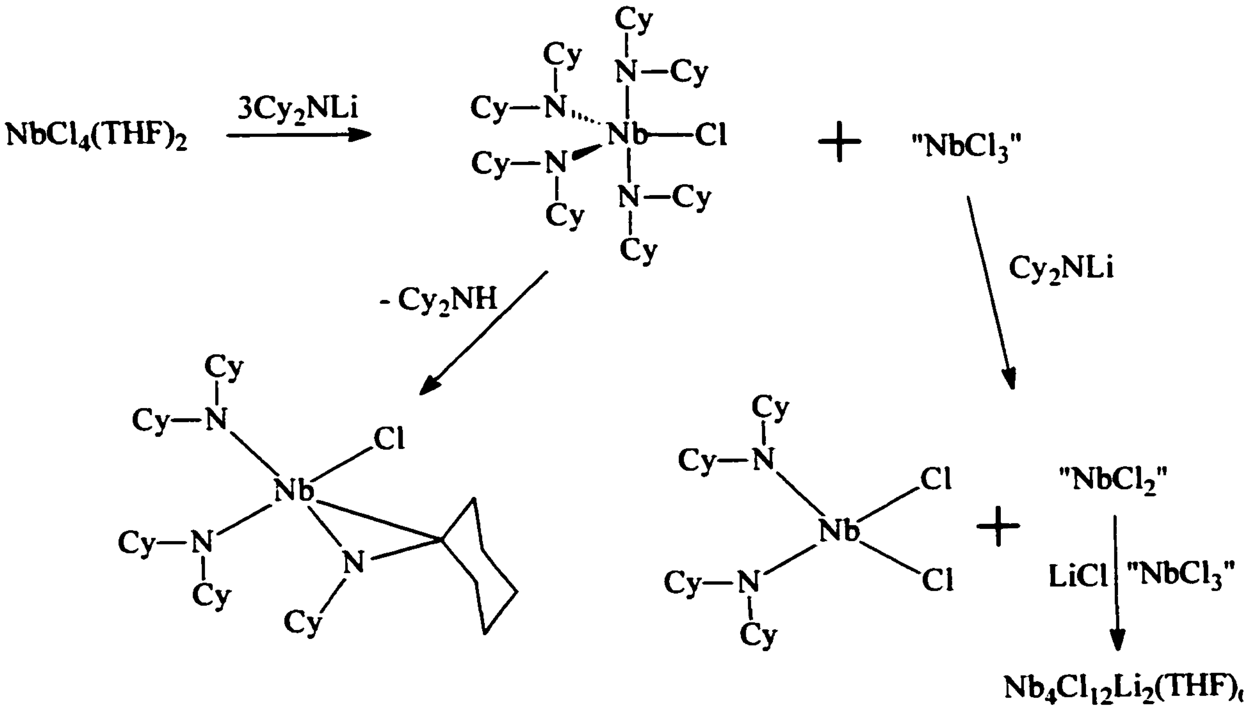
The shortness of the intermetallic distance contrasts with those of the few previously reported divalent diniobium or ditantalum THT bridged complexes,[7] whose unusually long M-M distances were ascribed to an intrinsic weakness of the metal-metal bonds.[7b] Thus in an attempt to elucidate the nature of the M-M interaction in this diamagnetic complex we have carried out ab initio theoretical calculations which clearly indicate the existence of a Nb-Nb triple bond. Details on the results are described in the dedicated section at the end of this chapter.

It was possible to prepare **2.1** in higher yield by simply reacting $Nb_2Cl_6(TMEDA)_2$ with two equivalents of n-BuLi in ether in the presence of a small excess of TMEDA. Even though the ability of amides to act as reductants is documented in the literature,[9] the fact that the same reaction with Ph_2NNa (instead of LDA) gave the tetravalent derivative $(Ph_2N)_4Nb$ (45%)[10] suggests that the reduction of the metal center during the formation of **2.1** might occur through the disproportionation of an unstable Nb(III) intermediate.

In an attempt to gain some insight into the reduction mechanism we have also carried out a similar reaction by using a higher valent Nb species.

The reaction of $NbCl_4(THF)_2$ with two equivalents of Cy_2NLi in THF gave, upon mixing, a rapid color change to green followed by a slow change to dark red. The diamagnetic tetranuclear niobium cluster $[Nb_4Cl_{12}Li_2(THF)_8]$ (**2.2**) (Scheme 2.1) was crystallized from THF/ether in modest but significant yield (10%). The IR spectrum and combustion analysis data clearly ruled out the presence of the amide ligand while the connectivity was elucidated by an X-ray crystal structure (Figure 2.2).

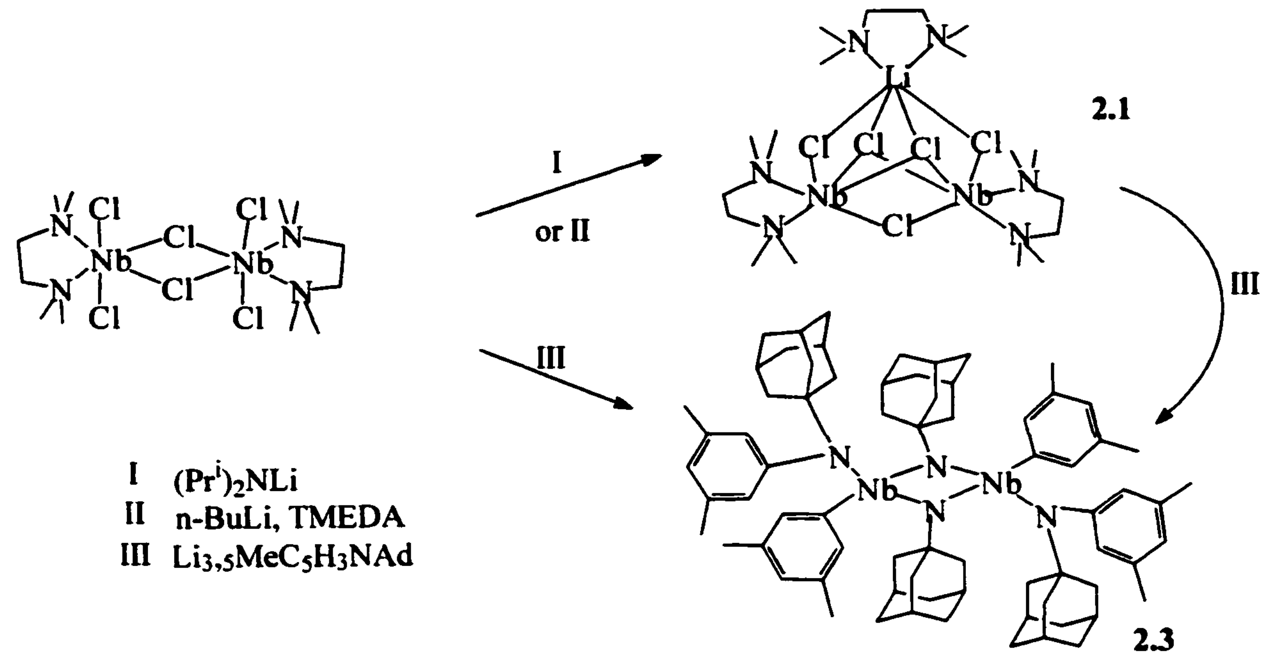
Thus two similar reductions carried out with two different amides on tri- and tetravalent Nb salts gave extensive reduction and formation of divalent niobium ions. The utilization of anionic organic amide as a reducing agent has a few precedents in the literature.[11] In this particular case, the formation of **2.2** is rather surprising given that highly reactive divalent niobium centers have been formed. Furthermore, it has been previously reported that the same reaction carried out in toluene and with a larger amount of amide afforded instead the nioba-aziridine derivative $(Cy_2N)_2Nb(CyNC_6H_{10})Cl$.[12] This particular reaction was accompanied by partial evolution of H_2 and no indication that other products may be formed. Conversely, the low yield of **2.2** suggests that another species may well be present in the reaction mixture. A possible suggestion for explaining the formation of **2.2** can be obtained from the behavior of $VCl_3(THF)_3$ with Cy_2NLi also in THF. Two different trivalent compounds the mononuclear $(Cy_2N)_2VCl(THF)$ and dinuclear $[(Cy_2N)_2V(\mu\text{-}Cl)]_2$ were formed from the expected replacement of two chlorine atoms by two amides.[13] However, when the reaction was carried out with a vanadium to amide stoichiometric ratio of 1:1, a disproportionation reaction took place instead with formation of $(Cy_2N)_2VCl_2$ and "VCl_2".[13] Thus if we assume that a similar disproportionative pathway takes place in the case of the reaction of $NbCl_4(THF)_2$, a mixture of pentavalent $(Cy_2N)_4NbCl$ (eventually evolving towards the previously reported nioba-aziridine derivative $(Cy_2N)_2Nb(CyNC_6H_{10})Cl$[12] and "$NbCl_3$" may be formed (Scheme 2.1). Similar to the case of VCl_3, "$NbCl_3$" may further give disproportionation towards "$NbCl_2$" and $(Cy_2N)_2NbCl_2$. As in the case of the TMEDA adducts[14] rapid aggregation of di- and trivalent niobium halides will afford the mixed di-/tri-valent species **2.2**. In agreement with this proposal, a reaction carried out in toluene and with the same stoichiometric ratio initially afforded the insoluble **2.2** which was isolated upon recrystallization in THF. The NMR spectrum of the residue obtained from



Scheme 2.1

the evaporation of the mother liquor clearly indicated the presence of the niobaaziridine derivative. Conversely, the presumably paramagnetic $(Cy_2N)_2NbCl_2$ complex could not conclusively be identified at this stage. Tetrametallic niobium clusters have a few precedents in the literature of the higher oxidation states and less than a handful of thiolates,[15] alkoxides[16] and carboxylates[17] has been reported. The present mixed-valence compound is formally composed by two trivalent and two divalent niobium atoms and it is reminiscent of the phosphine derivative $(Me_3P)_6Nb_4Cl_{10}$ prepared via Na/Hg reduction.[18] Unfortunately, the magnetic properties were not reported for that complex and thus the presence of five Nb-Nb single bonds was argued on the exclusive basis of the intermetallic distances.

The reaction of $Nb_2Cl_6(TMEDA_2$ with (3,5-Me_2Ph)(Ad)NLi yielded the tetravalent, dinuclear and diamagnetic [(3,5-Me_2Ph)(Ad)N]Nb(3,5-Me_2Ph)}$_2$(μ-NAd)$_2$.2(ether) [Ad = adamantyl] (**2.3**) (Figure 2.3). This product is likely to originate from the further reaction of **2.1** with the lithium amide (the reaction requires reflux in THF for several hours in this case) to form a transient [(3,5-Me_2Ph)(Ad)N]$_2$Nb species which generates **2.3** via oxidative addition into the C-N bond of the amide function (Scheme 2.2).[19] When the reaction is carried out at room temperature and worked up as usual, complex **2.3** was only the minor component of a mixture predominantly containing dark brown crystals of a new compound. When this crystalline mixture was redissolved in THF and boiled for a few minutes, only dark red crystals of **2.3** were obtained upon crystallization from ether. Unfortunately, efforts to characterize the brown compound were frustrated by several unfavorable factors such as poor crystal quality and unavoidable



I $(Pr^i)_2NLi$
II n-BuLi, TMEDA
III $Li_{3,5}MeC_5H_3NAd$

Scheme 2.2

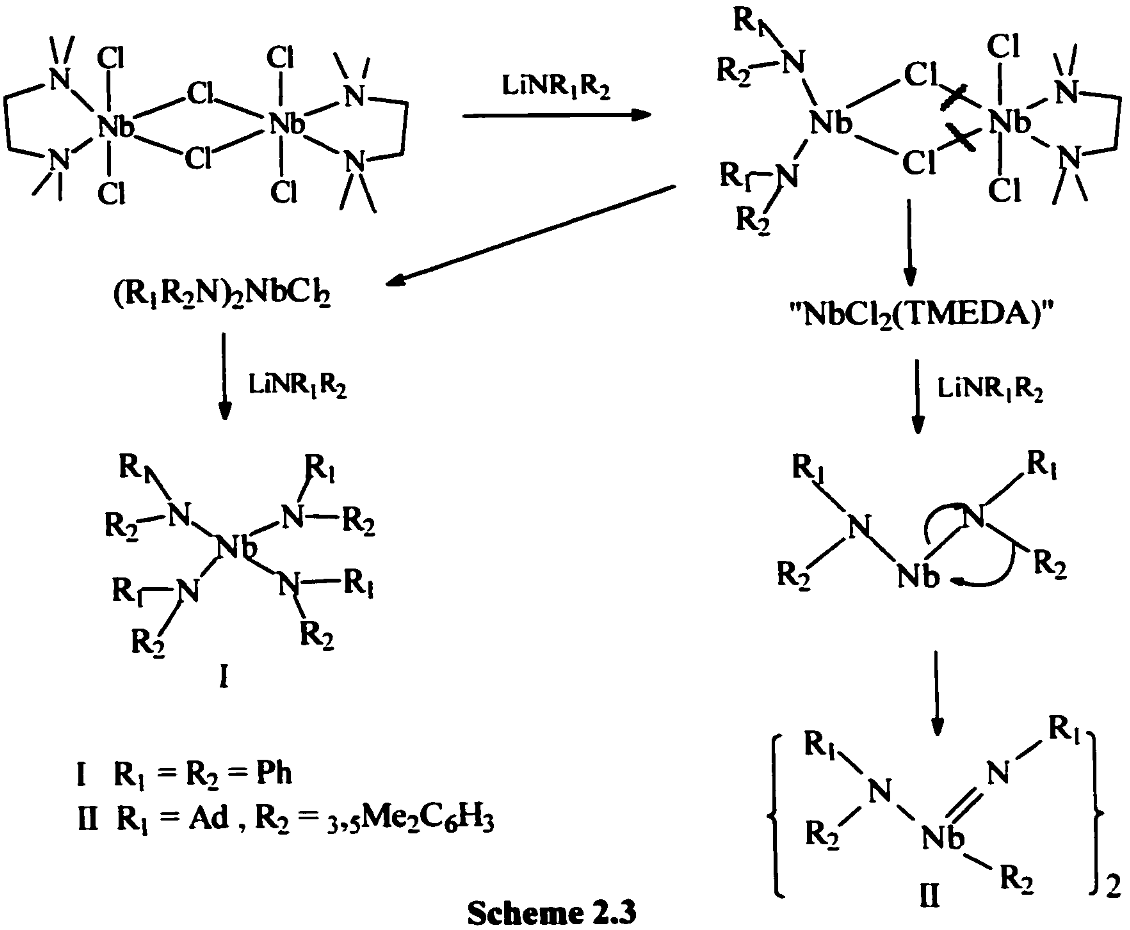
contamination of the product by substantial amount of the final orange product.

The ^{1}H-NMR spectrum of complex **2.3** clearly showed two different sets of phenyl ligands, one molecule of ether and the absence of TMEDA. Combustion analysis data indicated a formula with two amide ligands and one molecule of ether per niobium atom. The complex is non-fluxional and thermally stable. An interesting feature of the structure of complex **2.3** is the presence of a short Nb-Nb distance [Nb1-Nb1a = 2.6794(5) Å], which is even shorter than that observed in doubly bonded Nb(III) derivatives,[20] and is comparable to that of one triply bonded Nb(II) complex.[21] This relatively short distance, together with the diamagnetism, is perhaps indicative of the presence of a Nb-Nb single bond.

The structure of **2.3** shows that one C-N bond of one amide ligand (per Nb) was cleaved during the chlorine replacement reaction in the starting material by (3,5-Me_2Ph)(Ad)NLi. The complex is the result of an oxidation of the metal which provides the two electrons necessary to cleave the C-N bond and to form the aryl and imido moieties. Since the final complex contains niobium in the formal oxidation state +4, it is rather tempting to envision the process by assuming the formation of an intermediate "$(amide)_2Nb$" complex, perhaps dinuclear, which rearranges into the final tetravalent product by simply performing oxidative addition into the N-C bond (Scheme 2.3).

Metal-mediated atom and group transfer reactions are important fundamental processes because they provide a mean of utilizing a metal to cleave the very strong multiple bond. Imido derivatives contain a formal M-N double bond but which in fact may be better regarded as a triple bond. The imido function may work as a bridging ligand or may be more simply terminally bonded to the transition metal. Recent work by Bergmann has demonstrated that this function can be highly reactive and performing an impressive variety of molecular activation processes.

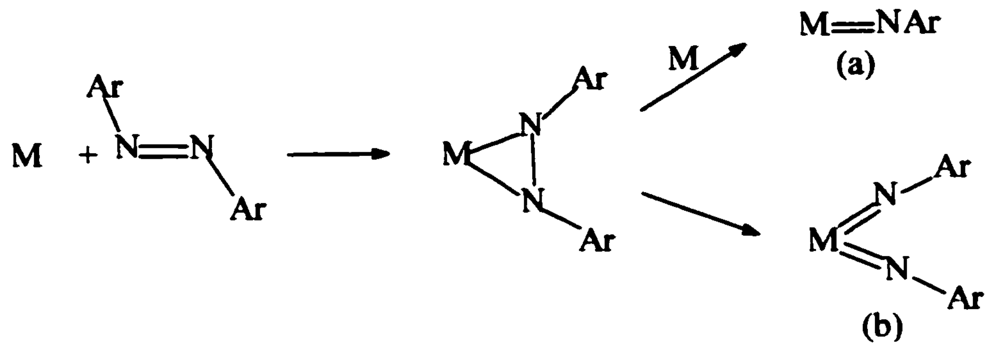
There are precedents in the literature of monomers and dimers of niobium imido complexes.[22,23] The early route to niobium imido compounds involved reduction of acetonitrile with $NbCl_4$ and zinc[24]. Somewhat later, alkylamines were used with $NbCl_5$ to



I $R_1 = R_2 = Ph$
II $R_1 = Ad$, $R_2 = 3{,}5Me_2C_6H_3$

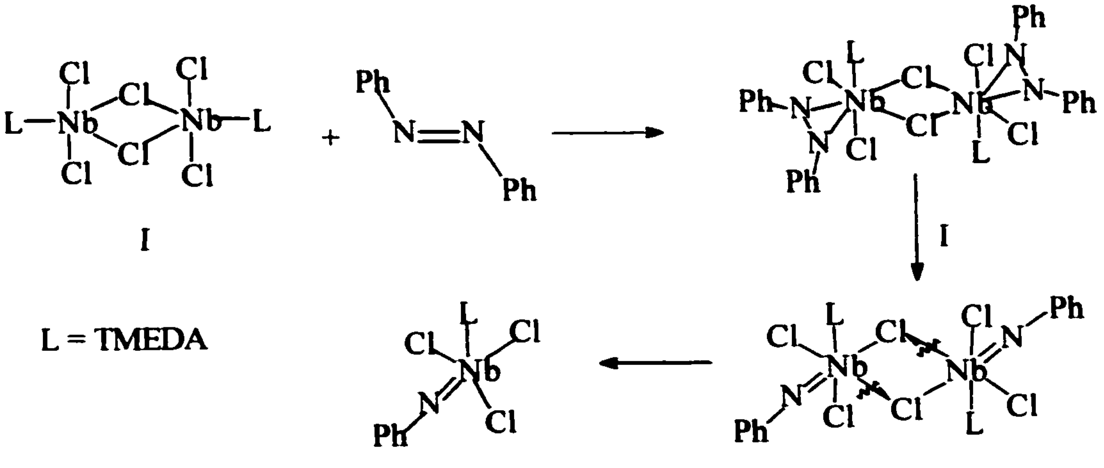
Scheme 2.3

give dimeric bridging imido-halides.[25] There are other routes for preparation of imido complexes by addition of diazenes to the metal halide complexes[26]. The mechanism below has been proposed by the authors who have observed this type of reaction. Formation of an η^2-diazene complex which activates the N=N bond by reducing its multiplicity, thus promoting its conversion to structure (b) in Scheme 2.4.[26] Based on these observations we became interested to investigate the reaction of low-valent Nb salts with azobenzene in order to generalize the ability of these species to perform oxidative addition. It was hoped that the reaction would stop at the level of a tetravalent complex. We have thus reacted $Nb_2Cl_6(TMEDA)_2$ with azobenzene (Scheme 2.4).



Scheme 2.4

During the reaction cleavage of the N=N bond indeed results in the formation of a niobium imido complex, $NbCl_3(C_6H_5N)(TMEDA)$ (**2.4**) (Figure 2.5). However, the formal pentavalent oxidation state was achieved. The result of the reaction is therefore rather similar to that of previously reported $Nb_2Cl_6(SMe_2)_3$ with azobenzene (Scheme 2.5).



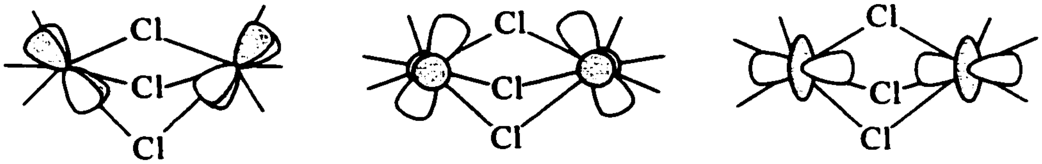
Scheme 2.5

In this particular case however a dimeric structure was obtained[27] while in the present case the complex is a monomeric one. The reason for this difference is likely to be found in the difference in steric hindrance between the SMe_2 and TMEDA ligands. Compound **2.4** is the result of oxidative addition of the N=N bound to the dinuclear niobium(III) compound and formation of the Nb(V) imido complex (Figure 2.4). The ^1H NMR spectrum of $NbCl_3(TMEDA)(NC_6H_5)$ has a very normal appearance, consistent with a diamagnetic Nb(d^0) species.

II. 4: Molecular Orbital Calculation

Theoretical calculations carried out on the atomic crystallographic coordinates of **2.1**[28] show that the three highest occupied molecular orbitals are mainly Nb-Nb centered with a metal atom contribution of predominantly *d*-orbital character and a minor but significant contribution from the *p* orbitals of the bridging chlorine atoms. The HOMO-LUMO gap (0.53 eV) is rather small yet sufficient to account for the observed diamagnetism in solution. The three MOs are formed by the overlap of hybrid atomic orbitals of the two niobium atoms. The shape of the HOMO is reminiscent of a M-M δ bond while the LUMO (-10.32 eV) is the corresponding out of phase combination.

The next occupied molecular orbital (HOMO-1), located at -11.24 eV is also M-M centered and has some π-bond character, while the next orbital (HOMO –2 = -12.17 eV) is a regular σ-bond lying symmetrically on the intermetallic vector (Chart 2.1). At this stage it is not clears which factor (electronic or steric) is responsible for the short Nb-Nb distance. Certainly, we cannot rule out the possibility that the lithium cation may ultimately determine the intermetallic distance by bringing together the two vertices of the two octahedral.



HOMO
(-10.85 eV)

HOMO-1
(-11.24 eV)

HOMO-2
(-12.17 eV)

Chart 2.1 Pictorial view of the frontier orbitals of **2.1**

DFT calculations were carried out on the atomic coordinates as obtained from the X-ray crystal structure for complex **2.2**. Given the diamagnetism, calculations were carried out on the singlet state. The HOMO-LUMO gap (0.45 eV) is rather small yet sufficient to account for the observed diamagnetism. The LUMO (-3.89 eV) is basically Nb-Cl centered MO. Conversely the next five frontier orbitals are mainly Nb-Nb bond centered. All these orbitals are formed by the overlap of complex hybrid combinations of several atomic orbitals of the four niobium atoms. The HOMO (-4.24 eV) shows two lobes along two parallel Nb-Nb vectors both closely reminiscent in shape of a Nb-Nb σ-bonds (Chart 2.2). The HOMO-1 (-4.34 eV) is also formed by hybrid combination and is very similar in shape to the HOMO. However, the two lobes are placed along the other two edges of the tetrametallic rhombus while a small lobe is present alongside the shortest diagonal. The next, (HOMO-2, -4.90 eV), presents four lobes each along one edge but with a nodal plane bisecting the two Nb atoms located on the longest diagonal.

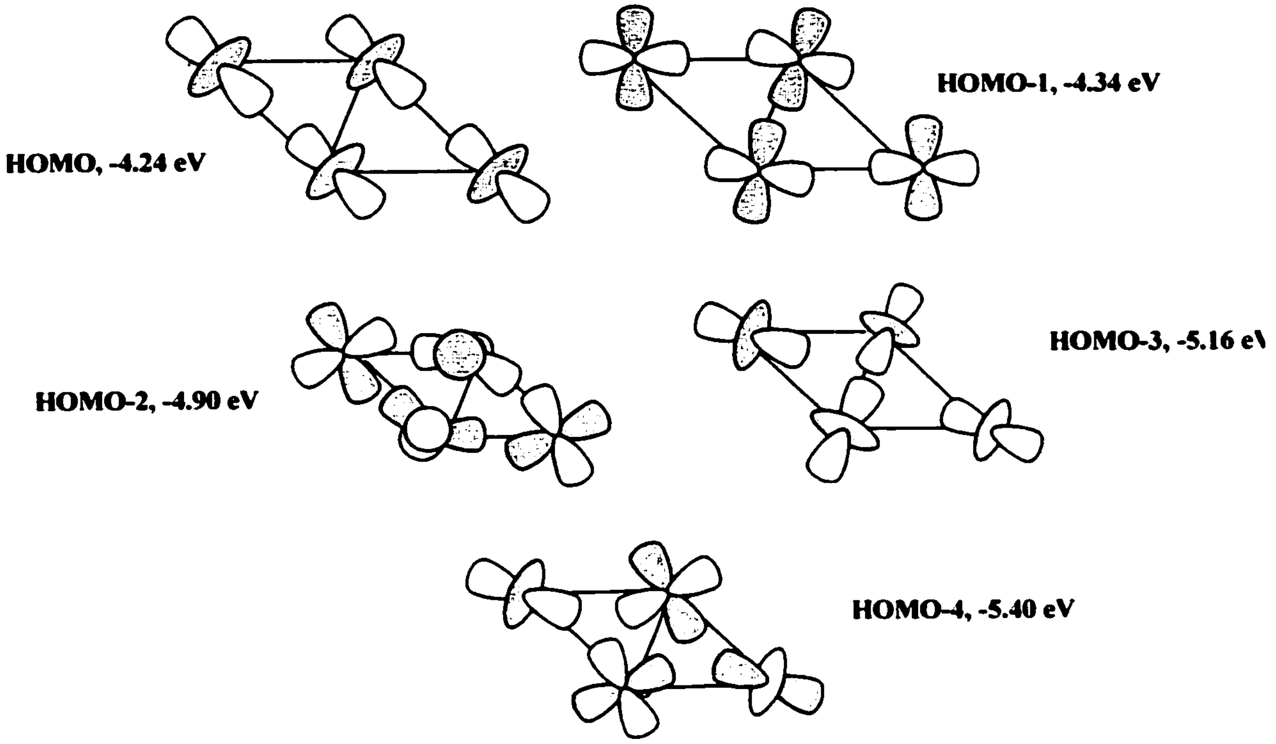


Chart 2.2. Pictorial view of most relevant MO's for complex **2.2**

HOMO-3 (-5.16 eV) is formed by the overlap of four similar hybrids each orienting one of the four lobes towards the center of the tetrametallic rhombus and featuring a large lobe delocalized in the center of the tetrametallic unit. The last (HOMO-4, -5.40 eV) is rather similar in shape to HOMO-2 except that the nodal plane is placed along the shortest diagonal. Another MO located lower in energy (HOMO-8, -6.14 eV) is mainly chlorine centered but display a minor Nb-Nb σ-bond component along the shortest diagonal. All the Nb-Nb bond centered molecular orbitals can be considered as Nb-Nb σ-bonds even though the overal symmetry of each MO may be more complex.

The overall calculated Mulliken bond order is 0.85 thus confirming the existence of five Nb-Nb single bonds.

Extended Hückel MO calculations were carried out for complex **2.3**[29,30]on a model compound with the atomic coordinates as obtained from the crystal structure. For the sake of simplicity, the adamantyl groups were transformed into *t*-Bu groups by replacing the unnecessary carbon atoms with hydrogen atoms introduced at their idealized positions. Similarly, the two methyls of the 3,5-Me_2Ph groups were replaced by hydrogen atoms.

The calculation showed a substantial HOMO-LUMO gap (0.8 eV) which is certainly sufficient to account for the observed diamagnetism. The HOMO (-11.7eV) is metal-metal bond centered with strong σ character (Chart 2.3). It is formed by two identical hybrid orbitals of each niobium atom [arising from the mixing of d_{z^2} (0.52) and

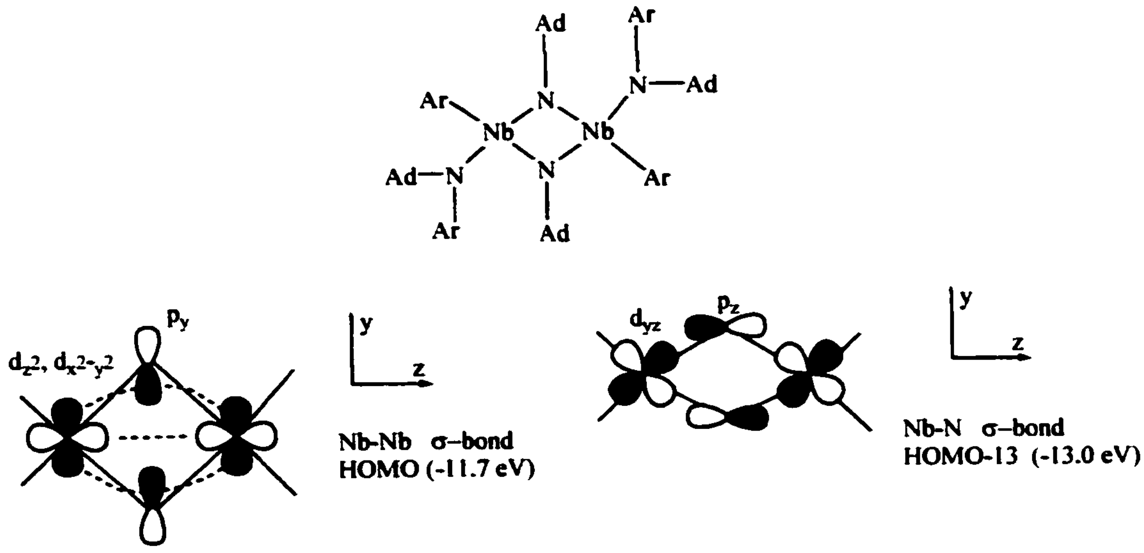


Chart 2.3 Pictorial view of most relevant MO's for complex

$d_{x^2-y^2}$ (0.33)] which undergo overlap of the two lobes lying on the intermetallic vector. However, the molecular orbital also requires a minor but significant participation of the bridging nitrogen p_y orbitals (perpendicular to the intermetallic vector which was chosen as the z axis) which overlap ***side-on*** with the perpendicular lobes of the *d* hybrid orbitals, thus forming two lobes on the two sides of the intermetallic vector connecting the two metal centers and encompassing the bridging nitrogen atoms. The bond between the bridging imido nitrogen atoms and the metal centers is provided by a molecular orbital located at -13.0 eV (HOMO-13) which is formed by the mixing of the d_{yz} orbitals of the two niobium atoms with the two bridging nitrogen p_z orbitals.

II. 5: X-ray Crystallography

Suitable crystals were mounted with cooled viscous oil on thin glass fibers. Data were collected on a Bruker AG SMART 1k CCD diffractometer using a proprietary hemisphere scan routine. Cell constants were calculated from reflection data obtained from 60 data frames collected at different parts of the Ewald sphere. Non-hydrogen atom positions were refined anisotropically, and hydrogen atoms were introduced at their idealized positions. In compound **2.1**, both carbon atoms of the two-ethylene bridges of the two TMEDA molecules were found disordered over two positions. The disorder was modeled by attributing occupancy of 0.75 to both C1 and C2 and of 0.25 to C1a and C2a, and of 0.5 to C7, C8, C7b and C8b. The significant improvement of the agreement factors during the last cycle of refinement supported the goodness of the model. The structure of complex **2.3** was solved by direct methods resulting in locating all the non-hydrogen atoms. Their positions were refined anisotropically. Hydrogen atom positions were calculated but not refined. Crystal data along with structure analysis results for **2.1-2.4** compounds are given in **Appendix A**.

The crystal structure of **2.1** (Figure 2.1) showed the molecule to include two niobium atoms with the short distance of Nb(1)-Nb(1a) = 2.4008(7) Å. The two niobium atom with five chlorine atoms and two TMEDA molecules, organized in an overall face-sharing bioctahedral geometry. Three chlorine atoms are bridged to the two metal centers [Nb(1)-Cl(4) = 2.5683(12), Nb(1)-Cl(3) = 2.5716(10), Nb(1)-Cl(2) = 2.5783(12) Å] while the other two are terminally bonded [Nb(1)-Nb(1a) = 2.4008(7), Nb(1)-Cl(1) = 2.5578(10) Å]. The geometry around each Nb atom is a distorted octahedral configuration [N(1)-Nb(1)-Cl(3) = 165.85(9) °, N(2)-Nb(1)-Cl(2) = 85.54(9) °, Cl(1)-Nb-Cl(2) = 179.39(4) °].

Complex **2.2** is a symmetry-generated tetramer with a planar Nb_4 core (Figure 2.2). There are two different octahedral coordination environments for the two sets of niobium atoms. The first is defined by the oxygen atom of one coordinated THF [Nb(2)-O(2) = 2.255(4)Å] one terminal chlorine [Nb(2)-Cl(5) = 2.5055(19)Å], two μ^2-chlorine [Nb(2)-Cl(1) = 2.4917(18)Å, Nb(2)-Cl(6a) = 2.4974(19)Å] located in trans to each other [Cl(1)-Nb(2)-Cl(6a) = 167.50(6)°] and two μ^3-chlorine atoms [Nb(2)-Cl(2) = 2.5001(18)Å, Nb(2)-Cl(2a) = 2.4862(18)Å] in cis to each other [Cl(2)-Nb(2)-Cl(2a) = 106.18(5)°]. The second set of Nb atoms also displays one terminally bonded THF [Nb(1)-O(1) = 2.212(4)Å] but has two μ^2-chlorine [Nb(1)-Cl(6) = 2.4360(18)Å , Nb(1)-Cl(1) = 2.4322(19)Å, Nb(1)-Cl(1)-Nb(2) = 72.60(5)°, Nb(1)-Cl(6)-Nb(2a) = 70.89(5)°] in cis to each other [Cl(1)-Nb(1)-Cl(6) = 93.19(6)°]. These two Nb atoms have only one μ^3-chlorine [Nb(1)-Cl(2) = 2.4566(18)Å] and two other μ^2-chlorine atoms [Nb(1)-Cl(3) = 2.5841(18)Å, Nb(1)-Cl(4) = 2.5416(18)Å] in cis to each other [Cl(3)-Nb(1)-Cl(4) = 83.52(6)°] which point towards the exterior of the cluster. These two chlorine atoms bridge a tetracoordinated Li atom [Li-Cl(3) = 2.317(13)Å; Nb(1)-Cl(3)-Li = 89.3(3)°] solvated by two molecules of THF.

The complex **2.3** is binuclear and is formed by two identical tetrahedral niobium atoms bridged by two N-Ad imido groups. One 3,5-Me_2Ph moiety is directly connected to each metal center and, together with one intact amido group, completes the tetrahedral coordination geometry of each niobium atom (Figure 2.3). The two imido nitrogen atoms [Nb-N2 = 1.988(2)Å] are distorted trigonal planar [Nb-N(2)-C(19) = 138.4(2)°, Nb-N(2)-Nb(a) = 84.4(1)°] and with the two Nb atoms form a planar Nb_2N_2 core. The Nb-N_{amide} [Nb-N1 = 2.013(2)Å] and Nb-C [Nb-C29 = 2.224(3)Å] distances are normal and compare well with those of other Nb and Ta derivatives.[31]

The crystal structure of **2.4** showed the molecule as consisting of one niobium, three chlorine atoms, one TMEDA molecule and one NC_6H_5 imido group (Figure 2.4). The equatorial plane of the coordination octahedron centered on niobium [N(2)-Nb-Cl(2) = 165.17(4) °, N(3)-Nb-Cl(2) = 103.97(5) °, N(2)-Nb-Cl(1) = 84.15(4) °] is defined by one of the two nitrogen atoms of TMEDA, two chlorine [Cl(2)-Nb-Cl(1) = 90.83(2) °, Cl(2)-Nb-Cl(3) = 93.42(2) °, Cl(1)-Nb-Cl(3) = 167.060(18) °] and the nitrogen atom of the imido function.. The Nb=N distance [Nb-N(3) = 1.7632(14)]Å] is considerably shorter than the other two Nb-N bonds present in the structure (from coordination of TMEDA to the niobium atom [Nb-N(2) = 2.3412(15) Å, Nb-N(1) = 2.5002(15) Å]) and is comparable to the Nb=N distance reported for the dinuclear $[NbCl_2(SMe_2)(NC_6H_5)]_2(\mu\text{-}Cl)_2$.[27]

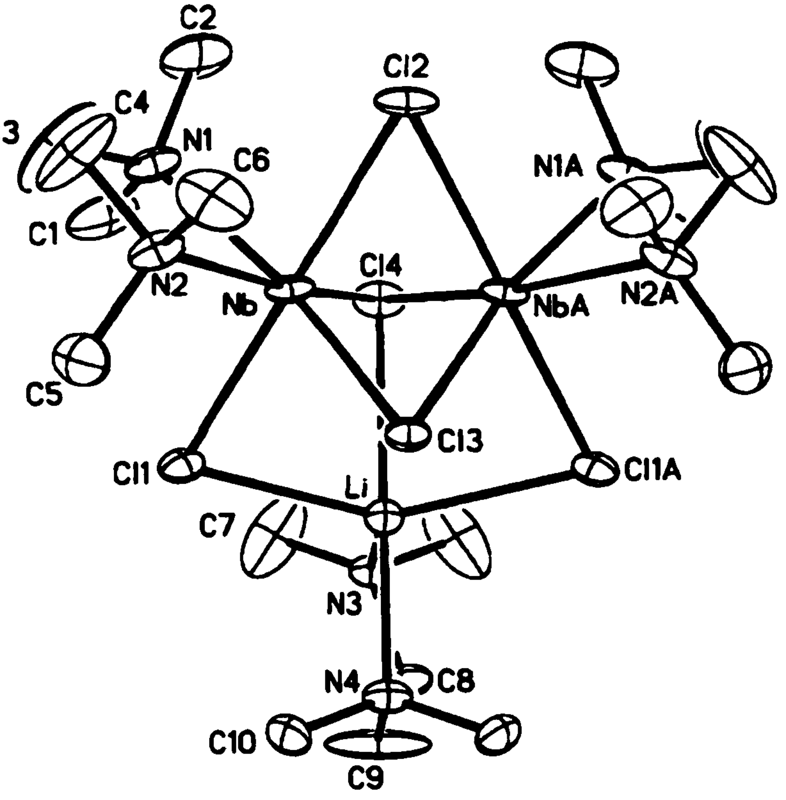


Fig. 2.1 X-ray structure of **2.1**. Selected bond distances (Å) and angles (°): Nb-N(2) = 2.362(3), Nb-N(1) = 2.387(3), Nb-Nb(a) = 2.4008(7), Nb-Cl(1) = 2.5578(10), Nb-Cl(4) = 2.5683(12), Nb-Cl(3) = 2.5716(10), Nb-Cl(2) = 2.5783(12), Nb-Li = 3.218(9), N(2)-Nb-N(1) = 80.26(11), N(2)-Nb-Nb(a) = 129.49(8), N(2)-Nb-Cl(1) = 95.00(9), N(1)-Nb-Cl(1) = 93.66(9), N(1)-Nb-Cl(3) = 165.85(9), Cl(1)-Nb-Cl(2) = 179.39(4), N(2)-Nb-Cl(4) = 165.74(8), N(1)-Nb-Cl(4) = 85.57(9), Cl(1)-Nb-Cl(4) = 84.21(4), N(2)-Nb-Cl(3) = 85.94(7), N(1)-Nb-Cl(3) = 165.85(9), Cl(1)-Nb-Cl(3) = 84.39(3), Cl(4)-Nb-Cl(3) = 108.11(3), N(2)-Nb-Cl(2) = 85.54(9), N(1)-Nb-Cl(2) = 86.13(9).

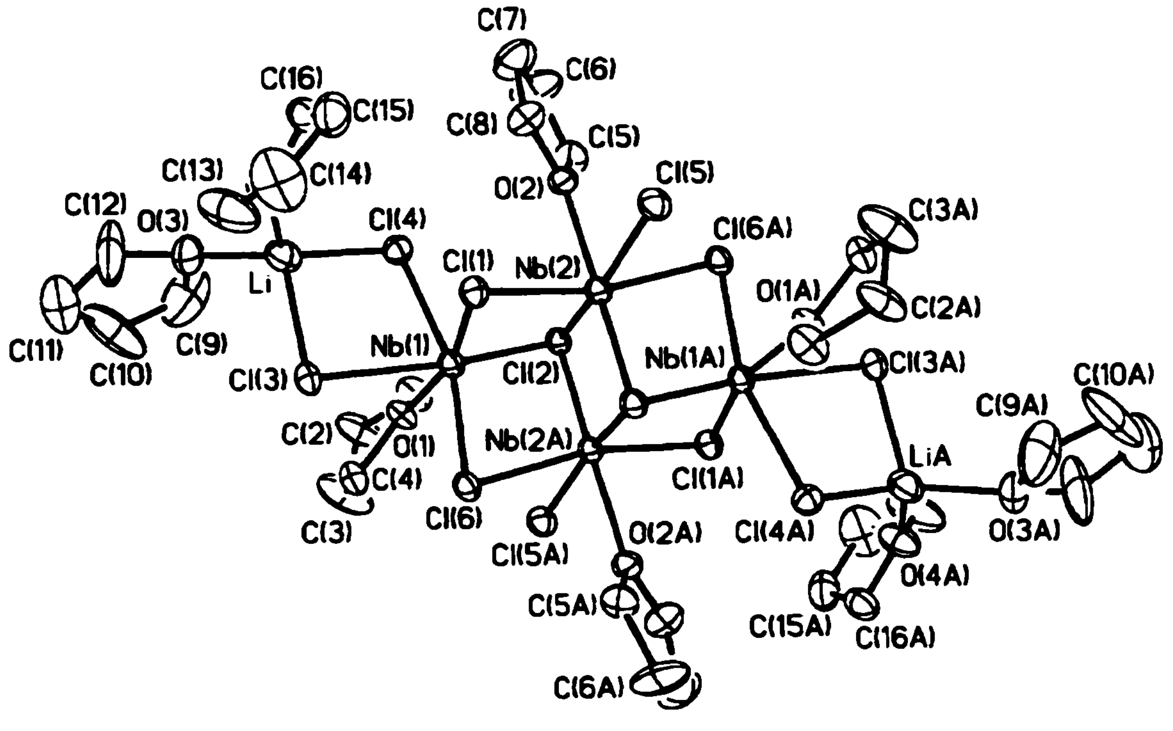


Fig. 2.2 X-ray structure of **2.2**. Selected bond distances (Å) and angles (°): Nb(1)-Cl(6) = 2.4360(18), Nb(1)-Cl(1) = 2.4322(19), Nb(1)-Cl(2) = 2.4566(18), Nb(1)-Cl(4) = 2.5416(18), Nb(1)-Nb(2) = 2.8615(9), Nb(1a)-Nb(2) = 2.9152(10), Nb(2)-Nb(2a) = 2.9947(12), Nb(1)-Li = 3.451(13), Nb(2)-Cl(5) = 2.5055(19), Cl(3)-Li = 2.317(13), O(1)-Nb(1)-Cl(6) = 90.96(12), O(1)-Nb(1)-Cl(1) = 164.52(13), Cl(6)-Nb(1)-Cl(1) = 93.19(6), O(1)-Nb(1)-Cl(2) = 84.23(13), Cl(6)-Nb(1)-Cl(2) = 109.76(6), Cl(1)-Nb(1)-Cl(2) = 108.26(6), O(1)-Nb(1)-Cl(4) = 82.32(12), Cl(6)-Nb(1)-Cl(4) = 164.11(7), Cl(1)-Nb(1)-Cl(4) = 89.79(6), Cl(2)-Nb(1)-Cl(4) = 83.98(6), Cl(6)-Nb(1)-Cl(3) = 81.33(6), Cl(1)-Nb(1)-Cl(3) = 83.43(6), Cl(2)-Nb(1)-Cl(3) = 162.83(6), Cl(4)-Nb(1)-Cl(3) = 83.52(6), Cl(1)-Nb(1A)-Nb(1) = 52.76(5), Nb(1)-Cl(1)-Nb(2) = 72.60(5), Nb(1)-Cl(2)-Nb(2) = 72.04(5).

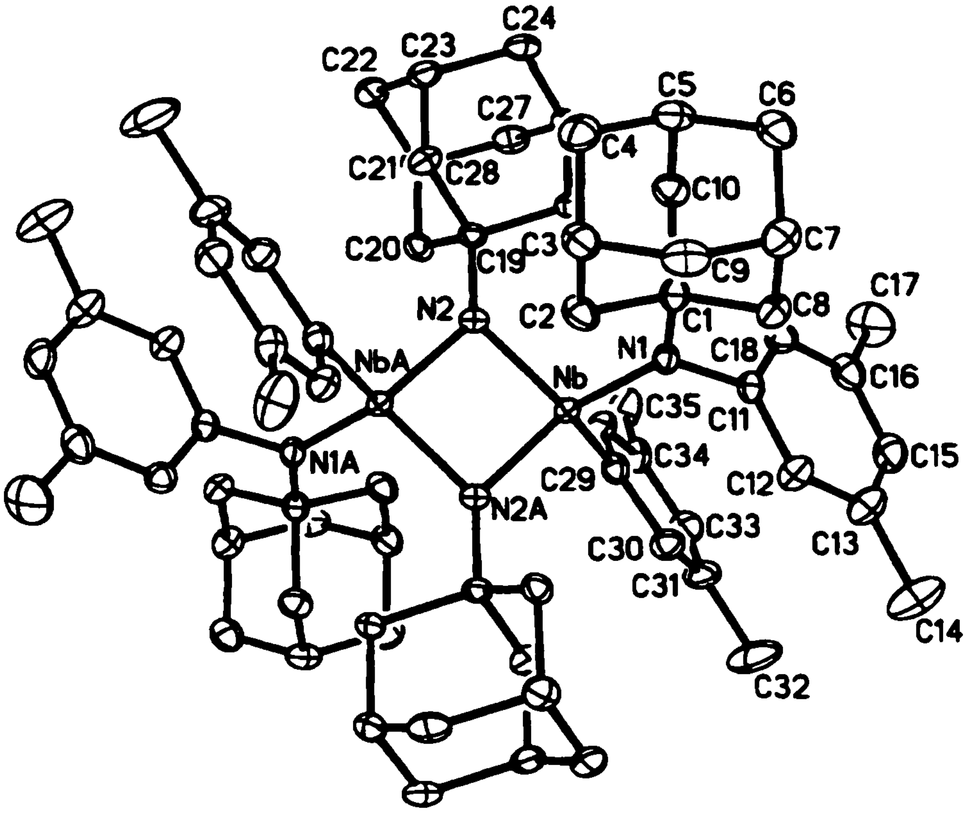


Fig. 2.3 X-ray structure of **2.3**. Selected bond distances (Å) and angles (°): Nb-N(2) = 1.988(2), Nb-N(1) = 2.013(2), Nb-C(29) = 2.224(3), Nb-C(11) = 2.639(3), Nb-Nba = 2.6794(5), N(2)-Nb-N(2)a = 95.79(9), N(2)-Nb-N(1) = 112.05(9), N(2)a-Nb-N(1) = 112.36(9), N(2)-Nb-C(29) = 105.34(10), N(2)A-Nb-C(29) = 108.97(10), N(1)-Nb-C(29) = 119.55(10), N(2)-Nb-C(11) = 129.19(9), N(2)a-Nb-C(11) = 126.93(9), N(1)-Nb-C(11) = 32.58(9), C(29)-Nb-C(11) = 87.09(9), N(2)-Nb-Nba = 48.20(7), N(2)a-Nb-Nba = 47.59(6), N(1)-Nb-Nba = 124.30(7), C(29)-Nb-Nba = 116.10(7), C(11)-Nb-Nba = 156.81(6), C(11)-N(1)-C(1) = 120.7(2), C(11)-N(1)-Nb = 98.45(15), C(1)-N(1)-Nb = 140.30(18), C(19)-N(2)-Nb = 138.40(18), Nb-N(2)-Nba = 84.21(9).

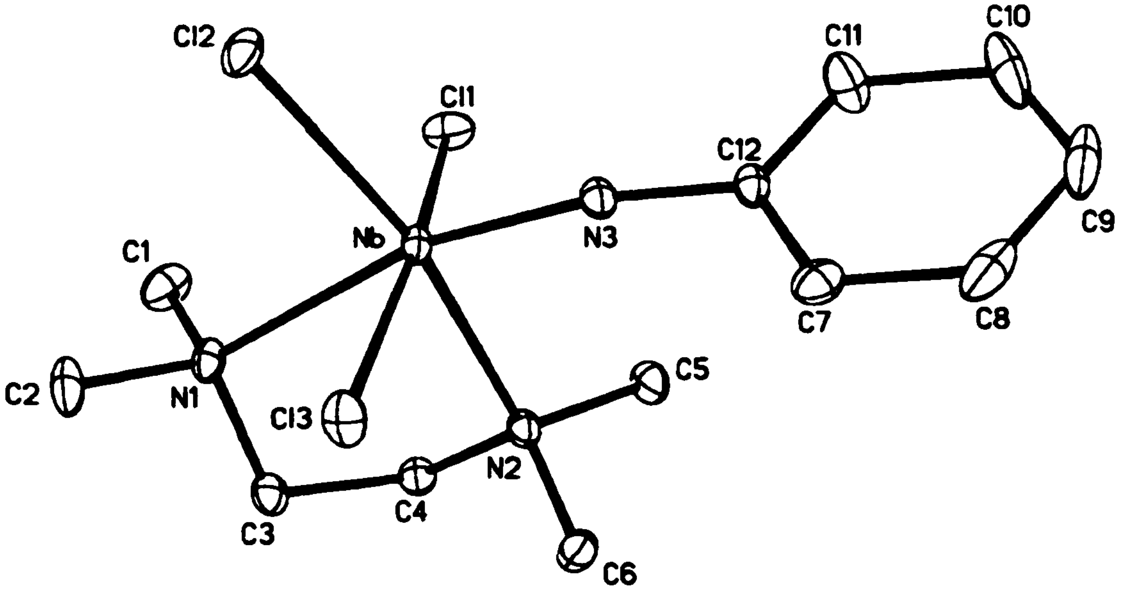


Fig. 2.4 X-ray structure of **2.4**. Selected bond distances (Å) and angles (°): Nb-N(3) = 1.7632(14), Nb-N(2) = 2.3412(15), Nb-Cl(2) = 2.3868(6), Nb-Cl(1) = 2.3914(7), Nb-Cl(3) = 2.4034(7), Nb-N(1) = 2.5002(15), N(3)-Nb-N(2) = 90.52(6), N(3)-Nb-Cl(2) = 103.97(5), N(2)-Nb-Cl(2) = 165.17(4), N(3)-Nb-Cl(1) = 97.10(5), N(2)-Nb-Cl(1) = 84.15(4), Cl(2)-Nb-Cl(1) = 90.83(2), N(3)-Nb-Cl(3) = 93.73(5), N(2)-Nb-Cl(3) = 88.70(4), Cl(2)-Nb-Cl(3) = 93.42(2), Cl(1)-Nb-Cl(3) = 167.060(18), N(3)-Nb-N(1) = 165.79(6), N(2)-Nb-N(1) = 75.82(5), Cl(2)-Nb-N(1) = 89.91(4), Cl(1)-Nb-N(1), 85.54(4) Cl(3)-Nb-N(1) = 82.25(4), C(2)-N(1)-Nb = 114.16(11), C(1)-N(1)-Nb = 114.88(12), C(3)-N(1)-Nb = 104.17(10).

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29. All molecular orbital calculations were performed on a Pentium computer by using the software package *Quantum CaCHE 2.0* The programs default parameters were used in the Extended Huckel calculations. The fractional atomic coordinates of the crystal structures were converted to the corresponding cartesian coordinates by using a special device of the NRCVAX program. The adamantyl groups were converted to t-Bu groups for simplicity. Hydrogen atoms were introduced at their idealized positions. The intermetallic vector was selected as a *z* axis.

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CHAPTER III

Preparation and Characterization of Niobium Complexes Stabilized by Tripodal Tripyrrolide Ligand

III. 1: Introduction

Complexes containing Nb and Ta in the oxidation states +2 and +3 are both highly reactive and surprisingly rare. Besides the cyclopentadienyl derivatives for which a rather extensive series of compounds is available, [1] so far only a few low-valent derivatives have been isolated and fully characterized for these metals. Low-valent non-Cp complexes of Nb and Ta remain basically limited to two recently reported amides,[2] the bulky silanolate derivatives,[3] a series of halides and related clusters,[4] one amidinate-borohydride,[5] two lantern-type compounds[6] and one thiolate.[7] Conversely, a wealth of promising reactivity and a remarkable variety of attractive transformations, almost invariably involving molecular activation processes, has been obtained by using mainly *in situ* generated low-valent complexes.[8] Reactivity of low-valent Nb and Ta complexes also include rare examples of C-N single bond cleavage.[3,8f-h,9]

Metal-metal bonding is another important and recurrent feature of the chemistry of low valent Nb and Ta.[10] Di- and trivalent Nb and Ta complexes display a variety of M-M distances which range from very short[6] to rather long.[4] In analogy to the case of first row transition metals, the geometry of the ligand system seems to play a critical role in determining the extent of electronic coupling, the magnetic properties and the intermetallic distance thus affecting the M-M bond multiplicity.[11]

A possible reason for the rarity of low-valent niobium and tantalum compounds may reside in another interesting characteristic of these systems, that is a tendency to disproportionate and/or to give substrate reduction via complex reaction pathways involving in some case the participation of more metals. For example the above-mentioned denitrogenation of the pyrrolide anion[10] required the occurrence of a parallel transformation involving both C-H and C-N bond activation in order to balance the number of electrons involved in the redox process.

In this chapter we describe the result of the reaction of low-valent niobium salts with a novel tripodal tripyrrolyl trianion. The study was prompted by the observation of the ability of pyrrolide anions to be involved at the same time in both the reactivity and stabilization of the metal center via formation of π-bonded complexes. Conversely, polypyrrole anions have recently proven to be more resistant to strongly reducing metals, to have an enhanced tendency towards π-donation,[12] to support clusterification reactions,[13] and even dinitrogen fixation/activation.[14] The particular tripodal geometry of the trianionic ligand employed for this study seemed especially promising to us for enhancing the chemical reactivity of niobium toward molecular activation processes via pyramidalization of the metal center.

III. 2: Experimental Section

All operations were carried out under nitrogen atmosphere using standard Schlenk techniques, or in a nitrogen-filled drybox. $NbCl_3(DME)$[15] $Nb_2Cl_6(TMEDA)_2$[4f] were prepared according to published procedure. Pyrrole-2-carboxaldeyde (Aldrich) was used as received. DME, TMEDA (Aldrich) were distilled under N_2 prior to use over $LiAlH_4$ and molten potassium respectively. Infrared spectra were recorded on a Mattson 9000 FTIR instrument from Nujol mulls prepared in a drybox. Samples for magnetic susceptibility measurements were prepared inside the drybox and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature. The magnetic moment was calculated by standard methods[16], and corrections for underlying diamagnetism were applied to the data[17]. Elemental analyses were carried out with a Perkin Elmer 2400 CHN analyser. NMR spectra were recorded with a Bruker AMX 500 MHz spectrometer.

Preparation of Tripyrrolemethane {$H\text{-}C(C_4H_4N)_3$}:

A solution of pyrrole-2-carboxaldeyde (4.0 g, 42 mmol) and pyrrole (19.34 g, 228 mmol) in $CHCl_3$ (30 mL) were stirred at room temperature under nitrogen for 10 min. The solution was cooled to 0°C, treated with a few drops of CH_3SO_3H and allowed to stir over-night. The solvent was removed in vacuum and the crude product was purified by column chromatography by using silica gel and $CHCl_3$ eluant, yielding analytically pure tripyrrolylmethane $H\text{-}C(C_4H_4N)_3$ (4.1g, 18.9 mmol, 45%). I.R. (Nujol mull, cm^{-1}) ν: 3448 (s), 3370 (s, br), 3127 (w), 3110 (w), 3005 (w), 3095(w), 1560 (s), 1398 (m), 1358 (s), 1311 (m), 1271 (w), 1267 (s), 1122 (m), 1091 (s), 1027 (vs), 973 (m), 887 (w), 817 (m), 777 (w), 736 (w), 765 (vs), 727 (vs). ^{1}HNMR ($CDCl_3$, 500MHz, 23°C) δ: 7.9 (s, N-H pyrrole, 3H), 6.6 (d, C-H pyrrole, 3H), 6.15 (m, C-H pyrrole, 3H), 6.05 (d, C-H pyrrole, 3H), 5.45 (s, C-H methine, 1H). ^{13}C-NMR ($CDCl_3$, 125.72 MHz, 23°C) δ: 249.81 (C-H methine), 171.18 (quaternary C pyrrole), 156.31 (C-H pyrrole), 144.05 (C-H pyrrole), 143.14 (C-H pyrrole). El. Anal. Calcd (found) for $C_{13}H_{13}N_3$: C 73.91(73.88), H 6.20(6.17), N 19.89(19.83). M.S.(E.I.) m/e 211.

Preparation of {[H-C(C_4H_3N)$_3$]Nb(THF)}$_2$•2THF (3.1):

A solution of tripyrrolemethane (1.0 g, 4.5 mmol) in THF (150 mL) was treated with KH (0.5 g, 13.5 mmol). A vigorous gas evolution was observed upon mixing and stirring was continued at room temperature for 1hr. The addition of $NbCl_3$(DME) (1.3 g, 4.5 mmol) to the resulting suspension turned the color dark green. After stirring for 10 minutes, the green solution was filtered to remove a small amount of light-colored material and the resulting solution was concentrated to small volume (10 mL) and transferred into a layering tube. Red crystals of **3.1** separated upon slow diffusion with ether (50 mL) at room temperature over a period of 7 days (0.8 g, 0.8 mmol, 40%). I.R. (Nujol mull, cm^{-1}) ν: 1396(w), 1274(w), 1241(w), 1209(s), 1180(s), 1160(s), 1132(s), 1101(vs), 1052(br), 1025(vs), 973(w), 960(s), 948(w), 892(br), 800(vs), 767(s), 721(vs), 692(w), 676(w). ^{1}H-NMR (d^8-THF, 500 MHz, 23°C) δ: 6.56 (d, C-H pyrrolyl, 3H), 5.91 (m, C-H pyrrolyl, 3H), 5.73 (d, C-H pyrrolyl, 3H), 5.37 (s, methine, 1H), 3.61 (broad s, coord. THF, 4H), 3.58 (broad s, free THF, 4H), 1.79 (broad s, coord. THF, 4H), 1.75 (broad s, free THF, 4H). ^{13}C-NMR (d^8-THF, 500 MHz, 23°C) δ: 212.81 (C-H methine), 134.17 (quaternary C pyrrolyl), 117.33 (C-H pyrrolyl), 107.80 (C-H pyrrolyl), 106.89 (C-H pyrrolyl), 68.22 (CH_2 free THF), 67.45 (CH_2 coord. THF), 26.38 (CH_2 coord. THF), 25.48 (CH_2 free THF). El. Anal. Calcd (found) for $C_{42}H_{52}N_6Nb_2O_4$: C 56.63(55.78), H 5.88(5.2), N 94.4(98.98).

Preparation of {([H-C(C_4H_3N)$_3$]$_2$NbK)$_2$}{Nb_4Cl_{11}[K(THF)$_2$]$_2$}•2THF (3.2):

A solution of tripyrrolylmethane (1.0 g, 4.5 mmol) in THF (150 mL) was treated with KH (0.5 g, 13.5 mmol). A vigorous gas evolution was observed upon mixing. The mixture was stirred at room temperature for 1hr and treated with solid Nb_2Cl_6(TMEDA)$_2$ (1.4 g, 2.2 mmol). The resulting suspension was refluxed overnight. The mixture was cooled, filtered to eliminate a small amount of insoluble material and the resulting solution allowed to stand overnight at room temperature upon which a crystalline solid mass separated. The solid was composed by red and orange crystals of well distinct shape present as the major and minor component respectively. The red crystals were identified as **3.1** by comparison of the I.R. and NMR spectra with those of analytically pure samples prepared as described above. The crystallographic cell parameters were also identical. The orange crystals of **3.2** were physically separated from **3.1** with the help of a stereomicroscope and characterized. El. Anal. Calcd (found) for $C_{100}H_{152}Cl_{11}K_4N_{20}Nb_6O_6$: C 42.38 (42.27), H 5.41 (5.39), N 9.88 (9.84). $\mu_{eff.}$= 1.77 μ_B per formula unit.

Preparation of {[H-C(C_4H_3N)$_3$]$_2$Nb}{Li(THF)$_4$}$_2$ (3.3):

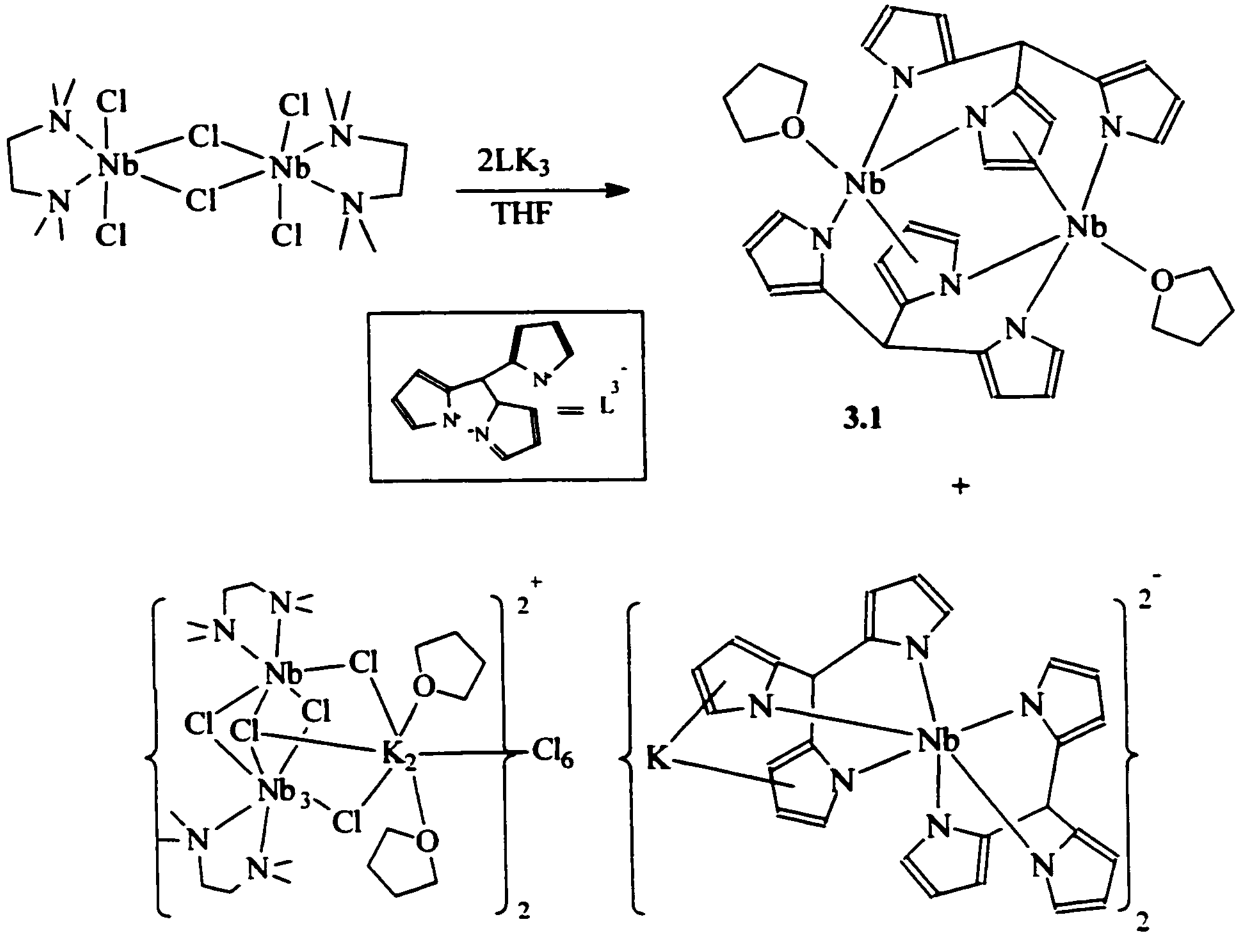
A solution of MeLi (9.7 mL, 1.39 M, 13.5 mmol) was added dropwise to a solution of tripyrrolylmethane (1.0 g, 4.5 mmol) in THF (150 mL) at 0°C. After stirring for 30 min. solid Nb_2Cl_6(TMEDA)$_2$ (1.4 g, 2.2 mmol) was added to the resulting solution forming a dark purple slurry. Upon refluxing the mixture overnight, the purple starting material disappeared to afford a reddish brown solution and a small amount of Nb_2Cl_5 (TMEDA)$_2$[20] which was identified by comparison of the I.R. spectrum with that of an analytically pure sample. The solution was concentrated to about 50 mL and layered with diethyl ether (30 mL). Red crystals of **3.3** separated upon standing a few days at room temperature (0.8 mg, 0.73 mmol, 17%). I.R. (Nujol mull, cm^{-1}) ν: 1396(m), 1376(s), 1344(w), 1290(w), 1274(m), 1258(w), 1234(m), 1207(s), 1178(s), 1170(s), 1139(vs), 1099(s), 1037(br), 1020(s), 970(s), 958(s), 916(w), 885(br), 804 (s), 736(w), 742(m), 709(s), 676(s). El. Anal. Calcd (found) for $C_{58}H_{84}N_6O_8Li_2Nb$: C 63.32(62.78), H 7.70(7.57), 7.64(7.56). $\mu_{eff} = 1.89\ \mu_B$.

III. 3: Results and Discussion

The reaction of $Nb_2Cl_6(TMEDA)_2$ with two equivalents of the tri-pyrrolyl-methane-tri-yl anion afforded a mixture from which two products have been isolated and characterized (Scheme 3.1). The first complex is the diamagnetic and dinuclear $\{[H\text{-}C(C_4H_3N)_3]Nb(THF)\}_2 \cdot 2THF$ (**3.1**). The dinuclear structure of this complex is held together by the two $[H\text{-}C(C_4H_3N)_3]^{3-}$ anions each adopting a curious bridging mode between the two niobium atoms. Each ligand caps the dimetallic unit using two of the three pyrrolyl rings to form a σ-bond with each of the two niobium atoms while the third ring is both *π*-bonded to one of the two niobium atoms and *σ*–bonded to the second.

Complex **3.1** displays a Nb-Nb distance [2.6583(15)Å] which suggests the existence of a possible Nb-Nb bonding interaction. The d^2 electronic configuration of the two trivalent Nb centers and the diamagnetism of the complex might indicate the presence of a *formal* Nb-Nb double bond in spite of the fact that the Nb-Nb distance is rather long for that.

Complex **3.1** could also be more conveniently prepared under similar conditions in analytically pure form and free of byproducts by using $NbCl_3$(DME) starting material.



3.1

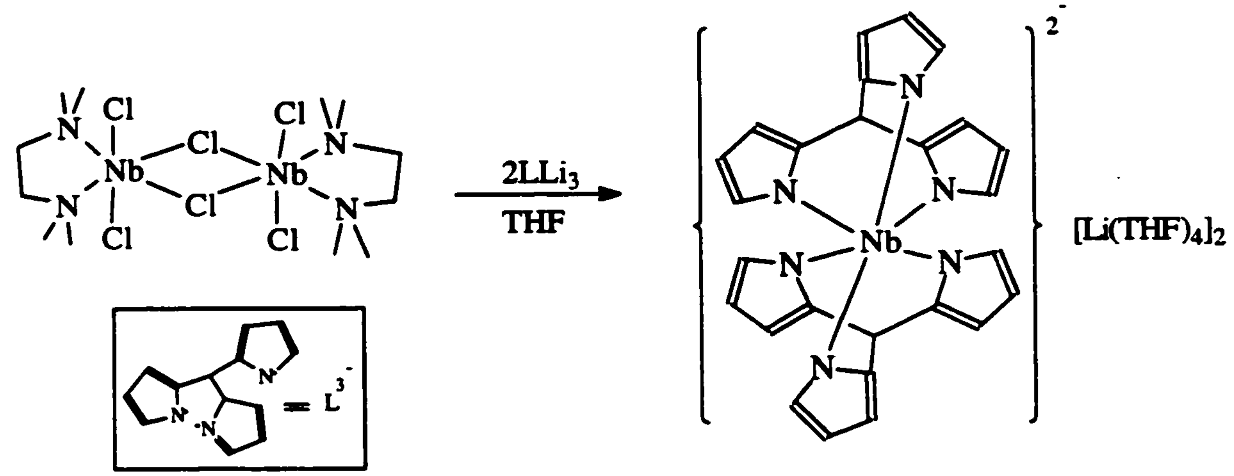
3.2

Scheme 3.1

A second complex was isolated as a byproduct of the reaction mixture but different from the case of **3.1**, its preparation could not be obtained through a selective synthetic procedure. Thus, its characterization remains necessarily limited. Nonetheless, the product presents some unique features. The complex is ionic with the anionic moiety formed by two identical tetravalent $[(H\text{-}C(C_4H_3N)_3]_2NbK$ units bridged together by potassium cations and composing an infinite *zig-zag* polymeric structure. The corresponding dication is a discrete $(TMEDA)_4Nb_4Cl_{11}K_2(THF)_4$ species, *formally* arising from the aggregation of two identical $(TMEDA)_2Nb_2Cl_5K(THF)$ units linked together by one additional chlorine atom, and structurally reminiscent of the divalent $Nb_2Cl_5Li(TMEDA)_3$[4t] and mixed valence $(TMEDA)_2Nb_2Cl_5$ derivative.[20] The ligand system, (eleven chlorides and four tripyrrolide trianions) accounts for 23 negative charges that are balanced by four potassium and six niobium atoms. This *formally* corresponds to five trivalent Nb atoms and one tetravalent. Thus, the formation of **3.2** requires elimination of one electron and implies that another species must be present in the reaction mixture as a result of the reduction process. A reasonable rationalization of the structure of **3.2** is to assume that each niobium atom of the anionic polymer is present in the tetravalent state. This possibility is also substantiated by the structure of complex **3.3** (*vide infra*) which doubtlessly contains tetravalent niobium. Given that the structure of **3.2** consists of *two* anionic moieties, the tetrametallic cation must necessarily bear a +2 charge. As a result, the cation has three of the four niobium atoms still present in the original +3 oxidation state while the fourth is the formal divalent state.

An interesting comparison can be made between the $\{(TMEDA)_4Nb_4Cl_{11}K_2\}^{2+}$ dication with the neutral $Nb_4Cl_{10}(PR_3)_8$ cluster[4u] also tetranuclear. In spite of having the niobium atoms in a slightly higher oxidation state, the dicationic cluster possess two significantly short Nb-Nb distances indicative of the presence of two Nb-Nb double bonds. By contrast, the tetranuclear $Nb_4Cl_{10}(PR_3)_8$ cluster shows four comparable Nb-Nb distances unlikely in agreement with the existence of any direct Nb-Nb interaction.

Reactions carried out under identical conditions but using the tri-lithium salt of the tripyrrole ligand led to a simple mononuclear tetravalent niobium complex with the metal encapsulated by two ligands and two solvated lithium cations in the lattice (Scheme 3.2).



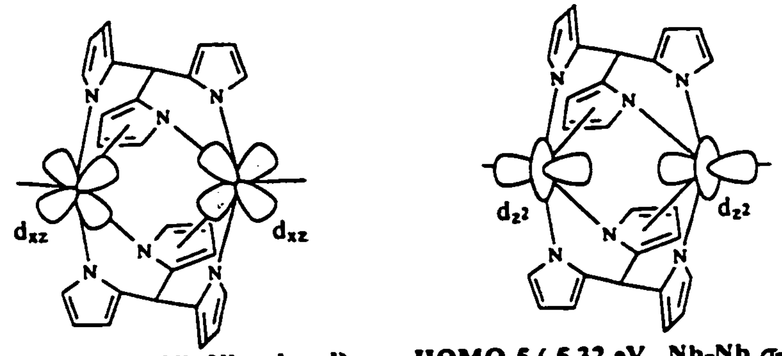
3.3

Scheme 3.2

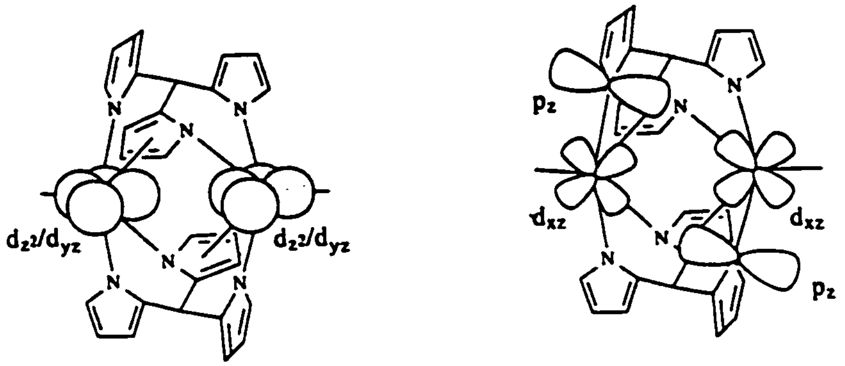
In this case, the oxidation of one tetravalent niobium to Nb(III) was accompanied by the formation of the insoluble, mixed-valence Nb(II)/Nb(III) $Nb_2Cl_5(TMEDA)_2$[20] resulting from the one-electron reduction of $Nb_2Cl_6(TMEDA)_2$. Complex **3.3** is paramagnetic with the magnetic moment as expected for the d^1 electronic configuration (spin-only) of a mononuclear Nb(IV) complex.

III. 4: Molecular Orbital Calculations

DFT-MO calculations were carried out on the geometrical parameters of **3.1** as obtained from the crystal structures by using a Silicon Graphics workstation and the Spartan 4.0 software package.[18] The significant HOMO-LUMO gap (1.66 eV) nicely accounts for the observed diamagnetism (Chart 3.1).



HOMO (-4.24 eV, Nb-Nb π-bond) HOMO-5 (-5.32 eV, Nb-Nb σ-bond)



HOMO-8 (-5.68 eV, "hybrid" σ-bond) HOMO-9 (-5.92 eV, "hybrid" π-bond)

Chart 3.1

Both orbitals display some extent of Nb-Nb π-bond character. In the LUMO (-2.58 eV), however, the Nb-Nb bond is rather marginal and the major feature is the π-bonding of Nb to the pyrrolyl ligand. Conversely, the HOMO (-4.24 eV) appears to be an almost "pure" Nb-Nb π-bond arising from the overlap of the niobium d_{xz} orbitals. Another orbital which displays a rather substantial character of Nb-Nb π-bond is HOMO-9 (-5.92 eV) where the π-bond is still realized by the overlap of the niobium d_{xz} orbitals but with a major participation of the p_z orbitals of the nitrogen atom of one of the σ-

bonded pyrrolyl ligand attached to each niobium. The Nb-Nb σ-bonding interaction is realized via three main MO's. All the three MO's rely on the overlap of the d_z2 orbitals. In the first (HOMO-3, -4.97 eV), the σ-bond contribution is only a minor component of the Nb-ligand interactions. The contribution of the overlap of the two d_z2 orbitals turns out to be the dominant feature of the second (HOMO-5, -5.32 eV). In the third (HOMO-8, -5.92 eV), the Nb-Nb σ-bond is very similar in shape to HOMO-5 except that the Nb-Nb σ-interaction is realized via the overlap of hybrid combinations of d_z2 and d_{yz} atomic orbitals. Both HOMO-5 and HOMO-8 display a minor yet significant involvement of the ligand. Thus, the DFT calculation supports the existence of a Nb-Nb double bond.

III. 5: X-ray crystallography

Suitable crystals were selected, mounted on thin, glass fibers using paraffin oil and cooled to the data collection temperature. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω-scans at 0, 90, and 180° in ϕ. Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied.[19]

No symmetry higher than triclinic was observed for **3.3**. Systematic absences in the diffraction data and unit-cell parameters were consistent with *C2/c* and *Cc* for **3.2** and, uniquely, $P2_1/c$ for **3.1**. Refinement in the centrosymmetric space group options yielded computationally stable and chemically reasonable results of refinement. The structures were solved by direct methods, completed with difference Fourier syntheses and refined with full-matrix least-squares procedures based on F^2. The molecular anion of **3.3** and the compound molecule of **3.1** were located at inversion centers. The anion in **3.2** is an infinite polymer propagated by two-fold symmetry while the molecular tetraniobium dication resides at a two-fold axis. A cocrystallized THF solvent molecule was located in each asymmetric unit for **3.1** and **3.2**. All non-hydrogen atoms were refined with anisotropic displacement parameters except the carbon atoms in **3.2** which were refined isotropically to conserve a favorable data/parameter ratio. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHEXTL 5.10 program library (Sheldrick, G. M., Bruker AXS, Madison, WI, 1997). Crystal data along with structure analysis results for **3.1-3.3** compounds are given in **Appendix B**.

Complex **3.1** is a symmetry generated dimer with two niobium atoms bridged by two tripyrrolymethane anions (Figure 3.1). Each niobium is also coordinated to one molecule of THF substantially deviating from the intermetallic vector [Nb-O(1) = 2.258(5)Å, Nb(a)-Nb-O(1) = 140.43(15)Å]. One interstitial molecule of THF completes the asymmetric unit. Each tripyrrolylmethane-tri-yl trianion [C(4)-C(13)-C(8) = 108.3(7)°, C(12)-C(13)-C(8) = 108.6(7)°, C(4)-C(13)-C(12) = 114.6(7)°] adopts a unique bridging mode. Two of the three pyrrolyl rings are σ-bonded each to one of the two Nb atoms [N(1)-Nb(a) = 2.176(7)Å, N(2)-Nb = 2.208(7)Å] while the third is π-bonded to one of the two Nb [Nb-N(3) = 2.262(6)Å], Nb-C(9) = 2.347(7)Å, Nb-C(10) = 2.487(8)Å, Nb-C(11) = 2.498(8)Å, Nb-C12) = 2.363(8)Å]. The π-bonded pyrrolyl ring also forms a σ-bond with the second Nb atom [Nb-N(1a) = 2.176(7)Å]. As a result, the coordination geometry around each Nb is sort of distorted square-pyramidal with the oxygen atom and three nitrogen atoms of σ-bonded pyrrolyl rings defining the basal plane [O(1)-Nb-N(2) = 74.4(2)°, O(1)-Nb-N(1a) = 76.2(2)°, O(1)-Nb-N(3a) = 86.6(2)°, N(2)-Nb-N(3a) = 87.4(2)°, N(2)-Nb-N(1a) = 149.5(2)°, N(1a)-Nb-N(3a) = 82.6(2)°] and the centroid of the π-bonded pyrrolyl ring on the apical position. The Nb-Nb distance [Nb-Nb(a) = 2.6583(15)Å] is fairly short and falls in the range expected for M-M bonding.

Complex **3.2** is ionic. The anionic part is composed by a linear polymer formed by discrete $[H-C(C_4H_3N)_3]_2Nb$ units bridged by a potassium atom which forms a network of π-bonds with four pyrrolyl rings from two ligands of two units (Figure 3.2). The asymmetric unit of the anionic polymer consists of a distorted octahedral niobium atom [N(1)-Nb(1)-N(2) = 81.7(4)°, N(1)-Nb(1)-N(3) = 86.6(4)°, N(1)-Nb(1)-N(4) = 166.9(4)°, N(3)-Nb(1)-N(6) = 162.8(4)°, N(2)-Nb(1)-N(5) = 162.0(4)°, N(2)-Nb(1)-N(3) = 84.8(4)°] surrounded by two $[H-C(C_4H_3N)_3]^{3-}$ ligands each adopting a regular tripodal like geometry [C(4)-C(13)-C(8) = 109.5(11)°, C(4)-C(13)-C(12) = 110.2(11)°, C(8)-C(13)-C(12) = 111.4(11)°]. The six N atoms of the σ-bonded pyrrolyl rings from the two ligands [Nb(1)-N(1) = 2.156(11)Å, Nb(1)-N(2) = 2.159(10)Å, Nb(1)-N(3) = 2.095(10)Å, Nb(1)-N(4) = 2.130(11)Å, Nb(1)-N(5) = 2.144(10)Å, Nb(1)-N(6) = 2.166(11)Å] define the coordination octahedron. Two pyrrolyl rings of one ligand are also π-bonded to one potassium atom [K(1)-N(1) = 3.207(11)Å, K(1)-(C1) = 3.324(14)Å, K(1)-C(2) = 3.293(14)Å, K(1)-C(3) = 3.141(14)Å, K(1)-C(4) = 3.096(13)Å] which in turns is π-coordinated to two other pyrrolyl rings of the next unit [K(1)-N(6a) = 3.197(11)Å, K(1)-C(25a) = 3.027(14)Å, K(1)-C(24a) = 3.150(14)Å, K(1)-C(22a) = 3.410(14)Å, K(1)-C(23a) = 3.412(15)Å, K(1)-C(16a) = 3.285(16)Å, K(1)-C(17a) = 3.244(13)Å, K(1)-N(4a)

= Å, K(1)-C(14a) = Å, K(1)-C(15a) = Å], thus assembling a polymeric polyanionic structure. The coordination environment of the alkali cation is rather unique and is defined by four π-bonded pyrrolyl rings. The cationic tetramer (Figure 3.3) is composed by two identical $[(TMEDA)Nb]_2Cl_5$ units, similar to the recently reported mixed valence $[(TMEDA)Nb]_2Cl_5$[20] and forming a comparable Nb-Nb distance [Nb(2)-Nb(3) = 2.506(2) Å]. The two identical units are hold together by a network of bridging interaction established by a formal $[(THF)K]_2Cl$ unit located between the two diniobium moieties. Each $(TMEDA)_2Nb_2Cl_5$ unit displays a face-sharing bioctahedral structure with each niobium atom in a fairly regular octahedral environment [Cl(1)-Nb(2)-Cl(3) = 178.43(15)°, N(7)-Nb(2)-Cl(4) = 166.5(10)°, N(8)-Nb(2)-Cl(5) = 167.6(8)°]. The bridging between each couple of niobium atoms is realized by three chlorine atoms [Nb(2)-Cl(3) = 2.524(4)Å, Nb(2)-Cl(4) = 2.474(4)Å, Nb(2)-Cl(5) = 2.507(6)Å]. The other two chlorine atoms bridge Nb to K [Nb(2)-Cl(1) = 2.498(4)Å, Cl(1)-K(2) = 3.042(6)Å]. One additional chlorine atom bridges the two heptacoordinated potassium atoms [K(2)-Cl(6)-K(2a) = 78.1(6)°]. The bridging interactions between the two potassium cations are provided by three chlorine atoms. The hepta-coordination of each potassium atom is defined by two terminally bonded molecule of THF and five chlorine atoms. Each couple of anionic $[H\text{-}C(C_4H_3N)_3]_2Nb$ units is counterbalanced by one tetranuclear cationic $[(TMEDA)Nb]_4(\mu\text{-}Cl)_{11}[K(THF)_2]_2$ aggregate. Two molecules of interstitial THF complete the structure.

The structure of **3.3** is composed by one octahedral $\{[H\text{-}C(C_4H_3N)_3]_2Nb\}^{2-}$ dianion and two tetrahedral $[Li(THF)_4]^+$ cations [Li-O(1) = 1.911(17)Å, O(1)-Li-O(2) =

109.2(8)°] (Figure 4). The niobium atom is located in the center of a slightly distorted octahedron [N(1)-Nb-N(2) = 84.1(2)°, N(1)-Nb-N(3) = 84.51(18)°, N(2)-Nb-N(3) = 83.97(18)°, N(3)-Nb-N(3a) = 180.0(3)°] defined by the N-donor atom [Nb-N(1) = 2.123(5)Å, Nb-N(2) = 2.144(5)Å, Nb-N(3) = 2.135(4)Å] of the two tripyrrolide methane-tri-yl anions. The two ligands adopted a tripodal-like bonding mode with niobium [C(4)-C(13)-C(12) = 110.6(4)°, C(4)-C(13)-C(8) = 110.2(4)°, C(8)-C(13)-C(12) = 109.8(5)°]. All the other bond distances and angles compare rather well with those of the polymeric anionic moiety of **3.2**.

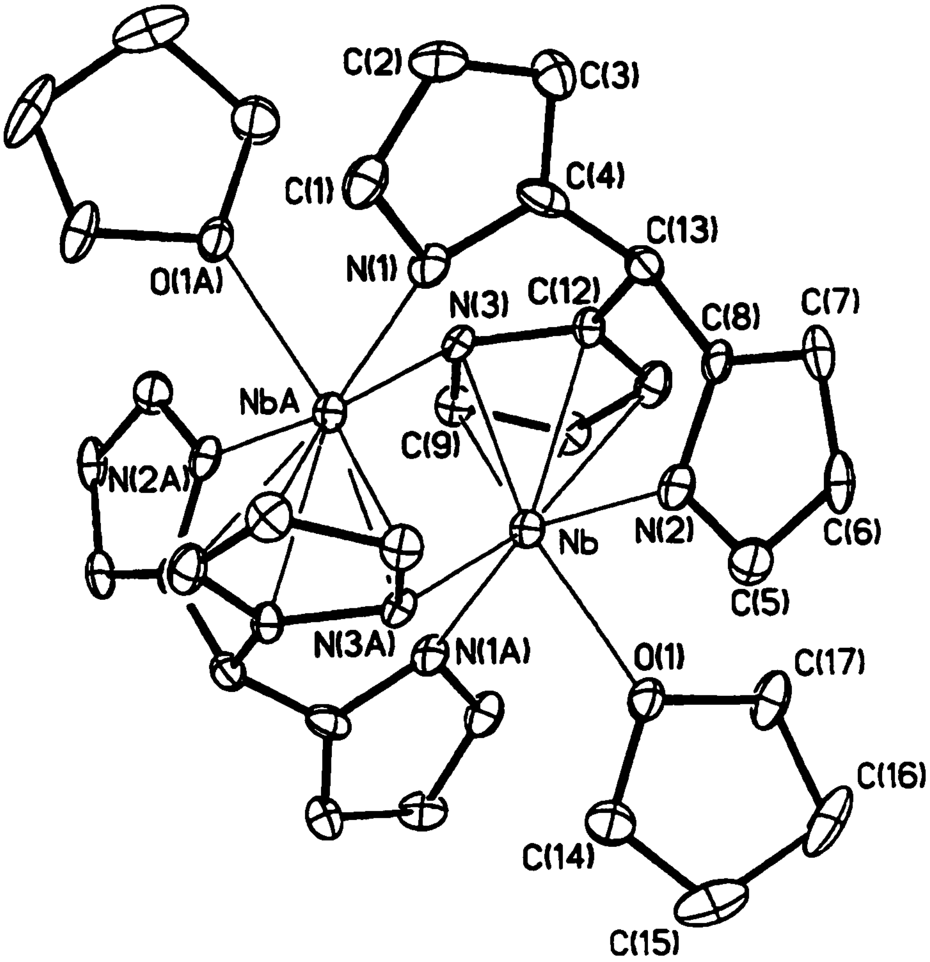


Fig 3.1: ORTEP drawing of the 3.1. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å), angles (°): Nb-N(2) = 2.208(7), Nb-O(1) = 2.258(5), Nb-N(3) = 2.262(6), Nb-C(9) = 2.347(7), Nb-C(12) = 2.363(8), Nb-C(10) = 2.487(8), Nb-C(11) = 2.498(8), Nb-Nba = 2.6583(15), N(1a)-Nb-N(2) = 149.5(2), N(1a)-Nb-N(3a) = 82.6(2), N(2)-Nb-N(3a) = 87.4(2), N(1a)-Nb-O(1) = 76.2(2), N(2)-Nb-O(1) = 74.4(2), N(3a)-Nb-O(1) = 86.6(2), N(1a)-Nb-N(3) = 110.7(2), N(2)-Nb-N(3) = 99.8(2), N(3a)-Nb-N(3) = 107.66(18), O(1)-Nb-N(3) = 164.5(2), N(1a)-Nb-C(9) = 81.5(3), N(2)-Nb-C(9) = 127.4(3), N(3a)-Nb-C(9) = 123.2(3), O(1)-Nb-C(9) = 139.9(3), N(3)-Nb-C(9) = 34.8(2). N(1a)-Nb-C(12) = 136.7(3), N(2)-Nb-C(12) = 71.4(3).

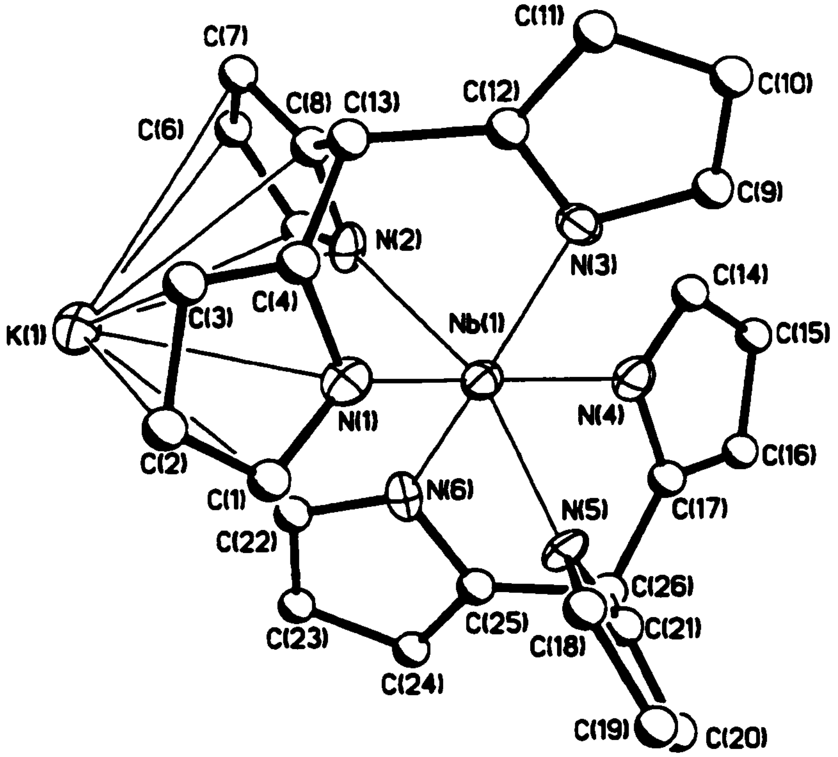


Fig 3.2: ORTEP drawing of the anion of 3.2. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å), angles (°): Nb(1)-N(3) = 2.095(10), Nb(1)-N(4) = 2.130(11), Nb(1)-N(5) = 2.144(10), Nb(1)-N(6) = 2.166(11), Nb(1)-N(1) = 2.156(11), Nb(1)-N(2) = 2.159(10), K(1)-C(4) = 3.096(13), K(1)-N(2) = 3.099(11), K(1)-C(8) = 3.106(14), K(1)-C(3) = 3.141(14), K(1)-N(1) = 3.207(11), K(1)-C(2) = 3.293(14), K(1)-C(1) = 3.324(14), N(3)-Nb(1)-N(4) = 85.2(4), N(3)-Nb(1)-N(5) = 107.8(4), N(4)-Nb(1)-N(5) = 86.6(4), N(3)-Nb(1)-N(6) = 162.8(4), N(4)-Nb(1)-N(6) = 82.8(4), N(5)-Nb(1)-N(6) = 83.7(4), N(3)-Nb(1)-N(1) = 86.6(4), N(4)-Nb(1)-N(1) = 166.9(4), N(5)-Nb(1)-N(1) = 86.2(4), N(6)-Nb(1)-N(1) = 107.2(4), N(3)-Nb(1)-N(2) = 84.8(4), N(4)-Nb(1)-N(2) = 107.7(4), N(5)-Nb(1)-N(2) = 162.0(4), N(6)-Nb(1)-N(2) = 87.2(4), N(1)-Nb(1)-N(2) = 81.7(4)

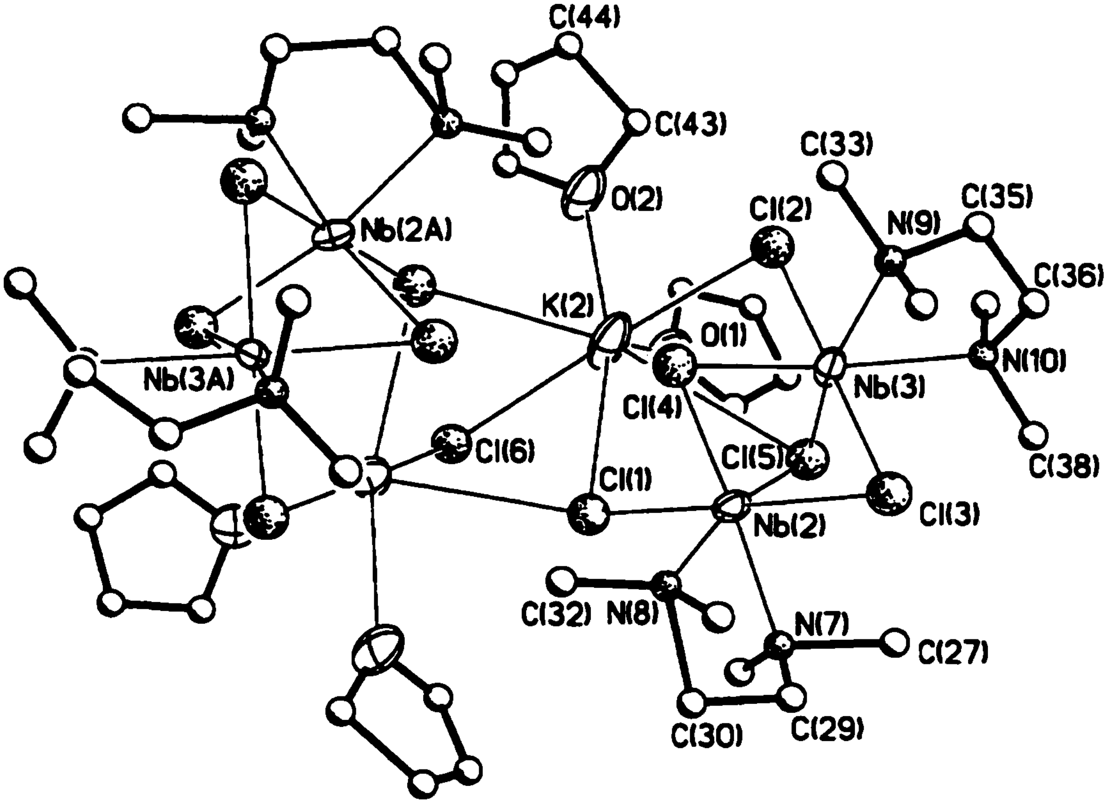


Fig 3.3: ORTEP drawing of the cation of **3.2**. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å), angles (°): Nb(2)-N(8) = 2.295(17), Nb(2)-N(7) = 2.291(17), Nb(2)-Cl(4) = 2.474(4), Nb(2)-Cl(1) = 2.498(4), Nb(2)-Nb(3) = 2.506(2), Nb(2)-Cl(5) = 2.507(6), Nb(2)-Cl(3) = 2.524(4), Nb(2)-K(2) = 4.107(4), Nb(3)-N(10) = 2.331(13), Nb(3)-N(9) = 2.38(2), Nb(3)-Cl(2) = 2.451(5), Nb(3)-Cl(5) = 2.467(7), Nb(3)-Cl(4) = 2.484(5), Nb(3)-Cl(3) = 2.496(4), Nb(3)-K(2) = 4.102(5), Cl(6)-K(2) = 3.53(2), N(8)-Nb(2)-N(7) = 80.9(12), N(8)-Nb(2)-Cl(4) = 85.9(8), N(7)-Nb(2)-Cl(4) = 166.5(10), N(8)-Nb(2)-Cl(1) = 92.0(4), N(7)-Nb(2)-Cl(1) = 93.0(4), Cl(4)-Nb(2)-Cl(1) = 90.09(18), N(8)-Nb(2)-Nb(3) = 130.9(7), N(7)-Nb(2)-Nb(3) = 128.5(8), Cl(4)-Nb(2)-Nb(3) = 59.83(12), Cl(1)-Nb(2)-Nb(3) = 119.60(12), N(8)-Nb(2)-Cl(5) = 167.6(8), N(7)-Nb(2)-Cl(5) = 86.7(10), Cl(4)-Nb(2)-Cl(5) = 106.5(3).

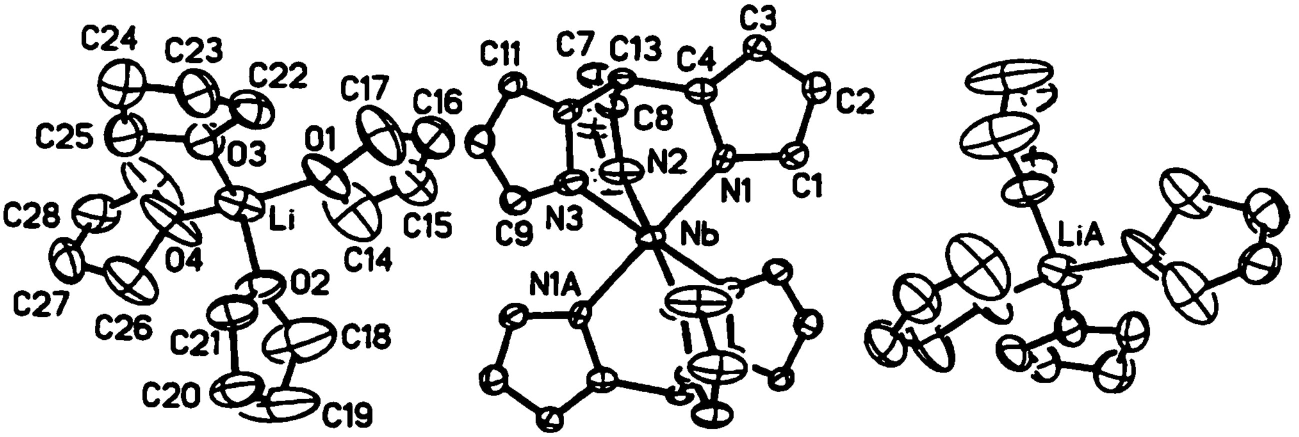


Fig 3.4: ORTEP drawing of the 3.3. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å), angles (°): Nb-N(1a) = 2.123(5), Nb-N(1) = 2.123(5), Nb-N(3a) = 2.135(4), Nb-N(3) = 2.135(4), Nb-N(2) = 2.144(5), Nb-N(2a) = 2.144(5), N(1a)-Nb-N(3) = 95.49(18), N(1)-Nb-N(3) = 84.51(18), N(3a)-Nb-N(3) = 180.0(3), N(1a)-Nb-N(2) = 95.9(2), N(1)-Nb-N(2) = 84.1(2), N(3a)-Nb-N(2) = 96.03(18), N(3)-Nb-N(2) = 83.97(18), N(1a)-Nb-N(2a) = 84.1(2), N(1)-Nb-N(2a) = 95.9(2), N(3a)-Nb-N(2a) = 83.97(18), N(3)-Nb-N(2a) = 96.03(18), N(2)-Nb-N(2a) = 180.0(3), O(2)-Li-O(3) = 105.4(6), C(17)-O(1)-Li = 129.3(8)

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19. DFT-MO calculations were carried out on the geometrical parameters of **3.1** as obtained from the crystal structures by using a Silicon Graphics workstation and the Spartan 4.0 software package (Blessing, R., *Acta Cryst.*, **1995**, A51, 33-38). The program's default parameters were used for the calculations. The fractional atomic coordinates of the crystal structures were converted to the corresponding

cartesian coordinates by using the XP program of the SHELXTL program library.

20. Chapter IV

CHAPTER IV

Molecular Rearrangements of a Low-valent Nb Amide: Ligand C-H Bond Oxidative Addition and Reductive Elimination

IV. 1: Introduction

Among early transition metals in low oxidation states, Nb and Ta occupy a prominent position because of the very distinctive chemical behavior displayed by their derivatives. An exciting reactivity which spans from metal-metal multiple bonding[1], to activation of small molecules,[2] dehydrogenation reactions,[3] C-N bond cleavage[4] and C-H bond activation[5] has been reported for the few cases where low-valent Nb and Ta complexes were either isolated[6] or *in situ* generated.[7] The homoleptic tris-silanolate derivatives $(\text{Silox})_3\text{M}$ [M = Nb, Ta][2a,6f] reported by Wolczanski and the phenoxide systems described by Rothwell[6a-e] provide the only examples of trivalent non-cyclopentadienyl systems successfully isolated and characterized, and for which it was possible to extensively demonstrate the ability of the oxidation state +3 to perform molecular activation processes. In the view of the calibre of the transformations accomplished by these species, it is interesting to investigate the reactivity of the oxidation state +2 for which an even more enhanced reactivity can be anticipated in analogy with the behavior of the vanadium congeners.[8] However, the chemistry of divalent niobium and tantalum is currently limited to the preparation and characterization of only a few Nb(II) salts.[1e,1i,6a-b,7b,9] Only recently a unique example of multiply bonded Nb(II) pyrimidinate was described,[1g] while previous attempts to prepare similar amidinate complexes led to ligand fragmentation.[10] Despite that these results indeed indicate a high and promising reactivity, the chemical behavior of Nb(II) species remains so far mainly unexplored.

The Nb(II) complex, $Nb_2Cl_5Li(TMEDA)_3$, described in Chapter II, was used to investigate the chemistry of Nb(II). Simple chloride replacement by amide ligands formed highly reactive Nb(II) amides which either cleaved the amide C-N single bond or performed oxidative addition into a C-H of the ligand. We describe the results of the intriguing reaction of $Nb_2Cl_5Li(TMEDA)_3$ with Ph_2NK which led to the formation of three compounds.

IV. 2: Experimental Section

All operations were performed under an inert atmosphere by using standard Schlenck techniques. $Nb_2Cl_5Li(TMEDA)_3$ was prepared according to the procedure described in the Chapter II. Ph_2NK was prepared *in situ* by treating the corresponding amine (Aldrich) with KH in THF. Solvents were dried with the appropriate drying agents and distilled prior to use. Infrared spectra were recorded on a Mattson 9000 FTIR instrument from Nujol mulls prepared in a drybox. Samples for magnetic susceptibility measurements were prepared inside a drybox and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature. The magnetic moment were calculated by standard methods,[11] and corrections for underlying diamagnetism were applied to the data.[12] Elemental analyses were carried out with a Perkin Elmer 2400 CHN analyzer. NMR spectra were recorded with a Bruker AMX 500 MHz spectrometer.

Preparation of [(TMEDA)NbCl]$_2$(μ-Cl)$_3$ (4.1):

Method A: A solution of Nb$_2$Cl$_5$Li(TMEDA)$_3$ (1.0 g 1.4 mmol) in THF (70 mL) was treated with Ph$_2$NK (1.55 g, 5.6 mmol). The homogeneous solution was allowed to stand at room temperature overnight without stirring upon which dark purple crystals of **4.1** separated (0.18g, 0.32 mmol, 23%). El. Anal. Calcd (found) for $C_{12}H_{32}N_4Nb_2Cl_5$: C 24.20(24.61), H 5.42(5.71), N 9.41(9.23). I.R. (Nujol, KBr plates, cm^{-1}) ν: 1407(w), 1287(m), 1261(m), 1240(m), 1194(w), 1120(m), 1100(w), 1064(m), 1040(m), 1014(s), 994(m), 951(s), 918(m), 793(s), 766(m), 722(w). $\mu_{eff} = 1.81\mu_B$.

Method B: A solution of Nb$_2$Cl$_5$Li(TMEDA)$_3$ (1.0 g, 1.4 mmol) in THF (70 mL) was treated with Nb$_2$Cl$_6$(TMEDA)$_2$ (0.88 g, 1.4 mmol) under vigorous stirring. The color changed immediately and a dark purple microcrystalline solid started to separate. Stirring was continued for two hours and microcrystalline **4.1** was isolated (0.76 g, 1.25 mmol, 90%) and identified by comparison of the spectroscopic, analytical and magnetic properties with those of an analytically pure sample prepared according to the method A.

Preparation of {[(Ph$_2$N)$_2$Nb]$_2$[μ-NPh(μ-η^1:η^2-C$_6$H$_4$)](μ-H)}{Li(TMEDA)$_2$}.toluene (4.2):

The mother liquor of the above reaction as described in Method A was evaporated to dryness. The residual solid was redissolved in toluene (250 mL) and the resulting solution was filtered to remove a small amount of insoluble material. The resulting solution was allowed to stand at –30°C overnight upon which dark orange crystals of **4.2** separated (0.36 g, 0.28 mmol, 33%). El. Anal Calcd (found) for $C_{79}H_{90}N_9Nb_2Li$: C 69.85(69.36), H

6.68(6.61), N 9.28(9.01). I.R. [Nujol, cm^{-1}] ν: 1589(s), 1307(m), 1287(m), 1261(s), 1172(m), 1079(m), 1027(s), 921(m), 887(m), 856(m), 798(s), 748(s), 727(s), 694(s). ^{1}H-NMR [500 MHz, d_8-THF, 23°C] δ: 8.38 (doublet, 1H, bridging amide terminal aromatic ring), 7.71 (doublet, 1H, bridging amide metallated ring), 7.30 (doublet, 2H, bridging amide terminal aromatic ring), 7.17 (multiplet, 5H, toluene), 6.84 (multiplet, 2H, bridging amide metallated ring), 6.80 (doublet, 1H, bridging amide metallated ring), 6.78 (pseudoquadruplet, 2H, bridging amide terminal aromatic ring), 6.64 and 6.43 (pseudotriplet, 40H, terminal amides rings), 2.31 (singlet, 8H, CH_2 TMEDA), 2.15 (singlet, 24H, CH_3 TMEDA), 2.08 (singlet, 3H, toluene), -8.24 (broad singlet, 1H, hydride). ^{13}C-NMR [127.7 MHz, d_8-THF, 23°C] δ: 157.5, 154.6, 154.4, 152.5, 151.2 (quaternary carbon), 142.4, 121.7, 120.9 (bridging amide terminal aromatic ring), 122.7, 127.9, 126.0, 124.6 (bridging amide metallated ring), 123.9-119.7 (series of lines, aromatic ring terminal amides), 137.5, 128.8, 128.0, 125.2 (toluene), 58.93 (CH_2 TMEDA), 46.18 (CH_3 TMEDA), 20.04 (CH_3 toluene).

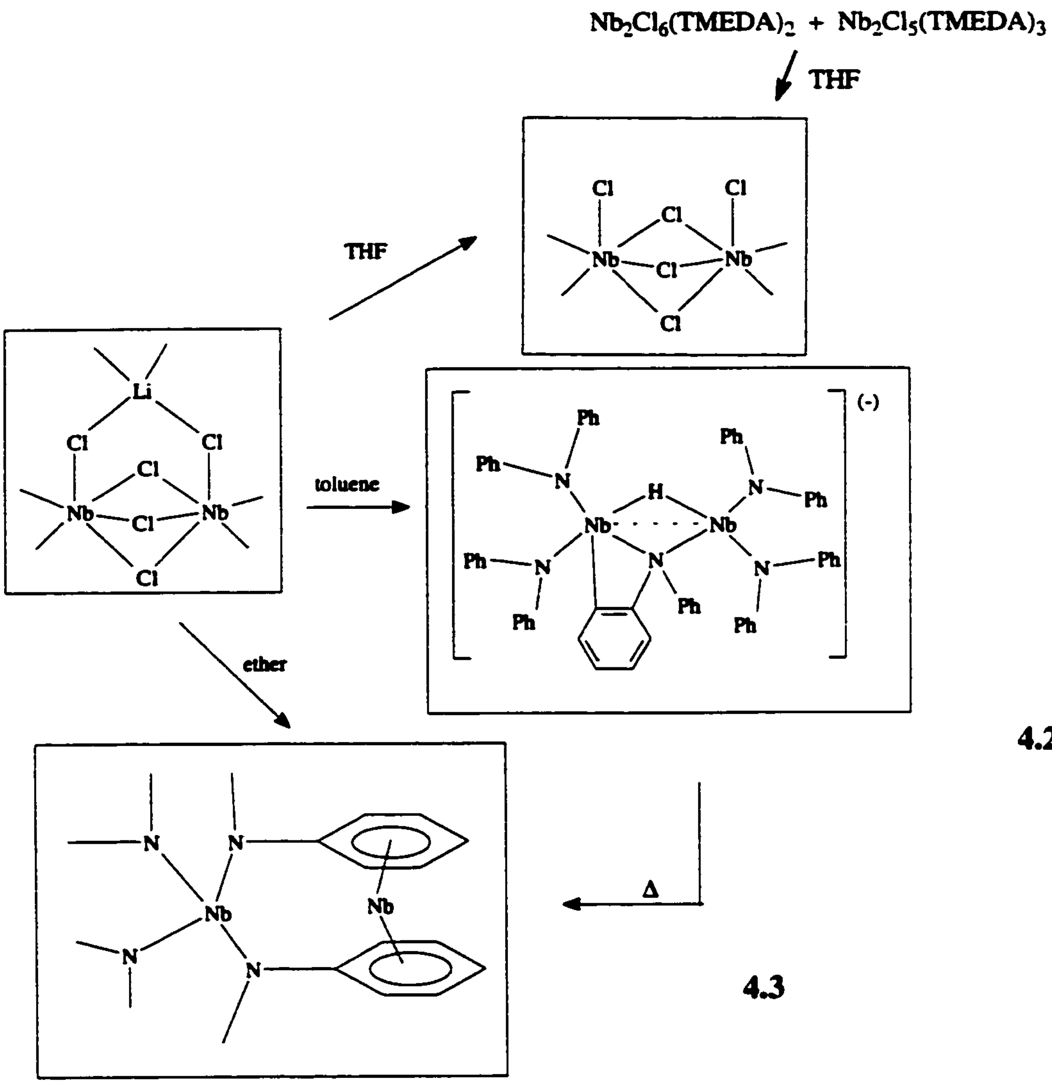
Preparation of $(Ph_2N)_2Nb\{[\mu\text{-}NPh(\eta^6\text{-}C_6H_5)]_2Nb\}$.ether (4.3):

Method A: The toluene solution obtained from the preparation of complex **4.2** was evaporated to dryness. The residual solid was redissolved in ether (70 mL) and the resulting solution was filtered to remove a small amount of insoluble material. The solution was allowed to stand for four days at room temperature upon which dark brown crystals of **4.3** separated (0.14 g, 0.16 mmol, 12 %). El. Anal. Calcd (found) for $C_{52}H_{50}N_4Nb_2O$: C 66.96(66.86), H 5.40(5.13), N 6.01(5.75). I.R. [Nujol, cm^{-1}] ν: 1587(s), 1572(w), 1421(m), 1326(w), 1291(s), 1267(s), 1227(m), 1194(m), 1167(s), 1120(m), 1079(m), 1027(m), 991(m), 959(m), 870(s), 840(m), 751(s), 696(s). ^{1}H-NMR [500 MHz, d_8-THF, 23°C] δ: 6.94 (multiplet, 20H, aromatic rings terminal amide), 6.74 (multiplet, 10H, terminal aromatic rings bridging amides), 5.25 (pseudotriplet, 4H, π-bonded aromatic ring *meta* C-H), 4.85 (pseudodoublet, π-bonded aromatic ring *ortho* C-H, 4H), 4.09 (pseudotriplet, π-bonded aromatic ring *para* C-H, 2H), 3.39 (quadruplet, CH_2 ether, 4H), 1.12 (triplet, CH_3 ether, 6H). ^{13}C-NMR [127.7 MHz, d_8-THF, 23°C] δ: 154.2 (ring quaternary C), 152.4 (ring quaternary C), 129.4, 125.4, 119.5 (CH ring terminal amide) 129.1, 124.4, 119.6 (CH ring bridging amide), 98.9 (quaternary C π-ring), 88.5 (*ortho* CH π-ring), 82.5 (*meta* CH π-ring), 73.4 (*para* CH π-ring).

Method B: A sample of analytically pure **4.2** (1.0 g, 0.75 mmol) was added to toluene (70 mL) and heated for 15 min at 100°C. The solvent was then removed by evaporation *in vacuo*, and the residual solid redissolved in ether. The solution was filtered to remove a small amount of insoluble material and allowed to stand at room temperature for four days, upon which dark-brown crystals of **4.3** separated (0.42 g, 0.45 mmol, 60%). The compound was identified by comparison of the analytical and spectroscopic properties with those of an analytically pure sample.

IV. 3: Results and Discussion

The reaction of $Nb_2Cl_5Li(TMEDA)_3$ with four equivalents of Ph_2NK in THF gave a rapid reaction accompanied by color change. Three different compounds were isolated in crystalline form from the same reaction mixture after suitable work up (Scheme 4.1).



4.1

4.2

4.3

Scheme 4.1

The first compound $Cl_2Nb_2(\mu\text{-}Cl)_3(TMEDA)_2$ (4.1) was obtained in analytically pure form as dark purple, paramagnetic and moderately air-sensitive crystals (yield 23%) upon allowing the reaction mixture to stand overnight at room temperature. The I.R. spectrum and combustion analysis data clearly ruled out the presence of the amide ligand. Qualitative analytical tests excluded the presence of lithium, while the presence of TMEDA was clearly identified in the NMR spectrum of samples previously exposed to air. Combustion analysis X-ray fluorescence data and X-ray crystal structure determination confirmed the formulation of **4.1** as the mixed valence complex $Cl_2Nb_2(\mu\text{-}Cl)_3(TMEDA)_2$ (Figure 4.1). The magnetic moment was also in agreement with the presence of one unpaired electron per dimeric unit [μ_{eff} = 1.81 BM].

Complex **4.1** is insoluble in most common organic solvents including pyridine. Therefore, after filtration of the original reaction mixture and replacement of the solvent with toluene, it was possible to isolate a second species **4.2** in acceptable yield (33%) and analytically pure form. The IR and NMR spectra of this diamagnetic compound clearly indicated the presence of both the amide ligand and TMEDA. The complex tested positive for the presence of lithium while the presence of non-coordinated toluene, probably interstitial, was clearly indicated by the NMR spectra. The amount of interstitial toluene was not always reproducible, thus indicating tendency of the solid samples to spontaneously lose solvent. This, together with a particularly enhanced air-sensitivity and thermal instability, was probably responsible for the difficulties encountered in obtaining reproducible analytical data and good quality crystals. The formulation of compound **4.2** as $\{[(Ph_2N)_2Nb]_2[\mu\text{-}NPh(\mu\text{-}\eta^1{:}\eta^2\text{-}C_6H_4)](\mu\text{-}H)\}\{Li(TMEDA)_2\}$.toluene was elucidated by an X-ray crystal structure (Figure 4.2). According to the positions of the heavy atoms, the structure of **4.2** arises from the complete substitution of the five chlorine atoms of the starting material $Nb_2Cl_5Li(TMEDA)_3$ by five Ph_2N moieties. In addition, one of the two phenyl rings of the bridging amide is metallated in the *ortho* position and forms a σ-bond with one of the two niobium atoms thus leading to a Nb(III)/Nb(III) species. This formulation necessarily requires the complex to be paramagnetic whereas complex **4.2** is diamagnetic in both the solid state and solution. Therefore, the formulation of **4.2** as a dinuclear d^2 Nb(III) hydride $\{[(Ph_2N)_2Nb]_2[\mu\text{-}NPh(\mu\text{-}\eta^1{:}\eta^2\text{-}C_6H_4)](\mu\text{-}H)\}\{Li\ (TMEDA)_2\}^{(-)}$ remains the sole possibility. A difference Fourier map yielded one residual peak on the side of the Nb-Nb vector opposite to that of the bridging nitrogen atom at a distance of 1.83Å from each of the niobium atoms and at 2.71Å from the cyclometallated carbon atom. However, given the poor crystal quality and the presence of heavy atoms in the structure, we prefer not to draw definite conclusions from the diffraction data about the presence of the hydride. Conversely, the hydride was clearly shown by NMR. The ^1H-NMR spectrum showed the presence of a broad singlet [δ = –8.24 ppm] which did not correlate with any carbon atom in HQMC experiments. The resonance integrated correctly for the Nb-H moiety of the proposed formulation. The resonance assigned to the bridging hydride rapidly decreased in intensity upon exposure of a THF solution of **4.2** to D_2 gas. At the same time, both the characteristic triplet of DH and the singlet of H_2 appeared at 4.55 and 4.70 ppm respectively while the resonance of the corresponding deuteride was present at –8.24 ppm of the ^2H-NMR spectrum. The chemical shift of the hydride is unusually upfield in comparison to the known Nb and Ta hydride derivatives[2,3,13a-h] in oxidation states +4 and +5 but is in agreement with the resonances of $Cp_2NbH(L)$ [L = phosphine, phosphite] derivatives.[13i] No resonance was observed in the region 2500-1690 cm^{-1} of the IR spectrum that could be conclusively be assigned to terminal Nb-H. A broad and intense band which instead may tentatively be assigned to the bridging hydride, is present at 1070 cm^{-1} in the IR spectrum. The poor thermal stability of **4.2** prevented isotopic labeling experiments to conclusively identify the Nb-H resonance in the IR spectrum. The aromatic region of the ^1H-NMR spectrum, *albeit* rather complicated, was informative and through COSY experiments it was possible to obtain a reasonable interpretation of the spectral features. The spectrum clearly shows the signals of three different types of aromatic rings correctly integrating in the ratio 4:5:40. The signals of the cyclometallated ring are well resolved as two doublets at 7.71 and 6.80 ppm and one multiplet (doublet of doublets) at 6.84 ppm. The terminal ring of the bridging amide presents two distinctive doublets (8.38 and 7.30 ppm) and one pseudoquadruplet (6.78 ppm). The terminal amide ring resonances consist of two large pseudotriplets (6.64 and 6.43 ppm) and one broad feature partially overlapping with one of the two triplets. The quaternary carbon atoms and the carbon attached to the Nb atom also display unusual chemical shifts (157.5 ppm). Spontaneous loss of solvent, conformational disorder of the interstitial molecule of toluene and elevated thermal motions of the TMEDA molecules coordinated to lithium in the cationic unit were responsible for the relatively high values of the agreement factors in the diffraction data. However, the anionic part of the molecule was well behaved with normal thermal parameters for all the atoms, thus allowing a reliable determination of the connectivity.

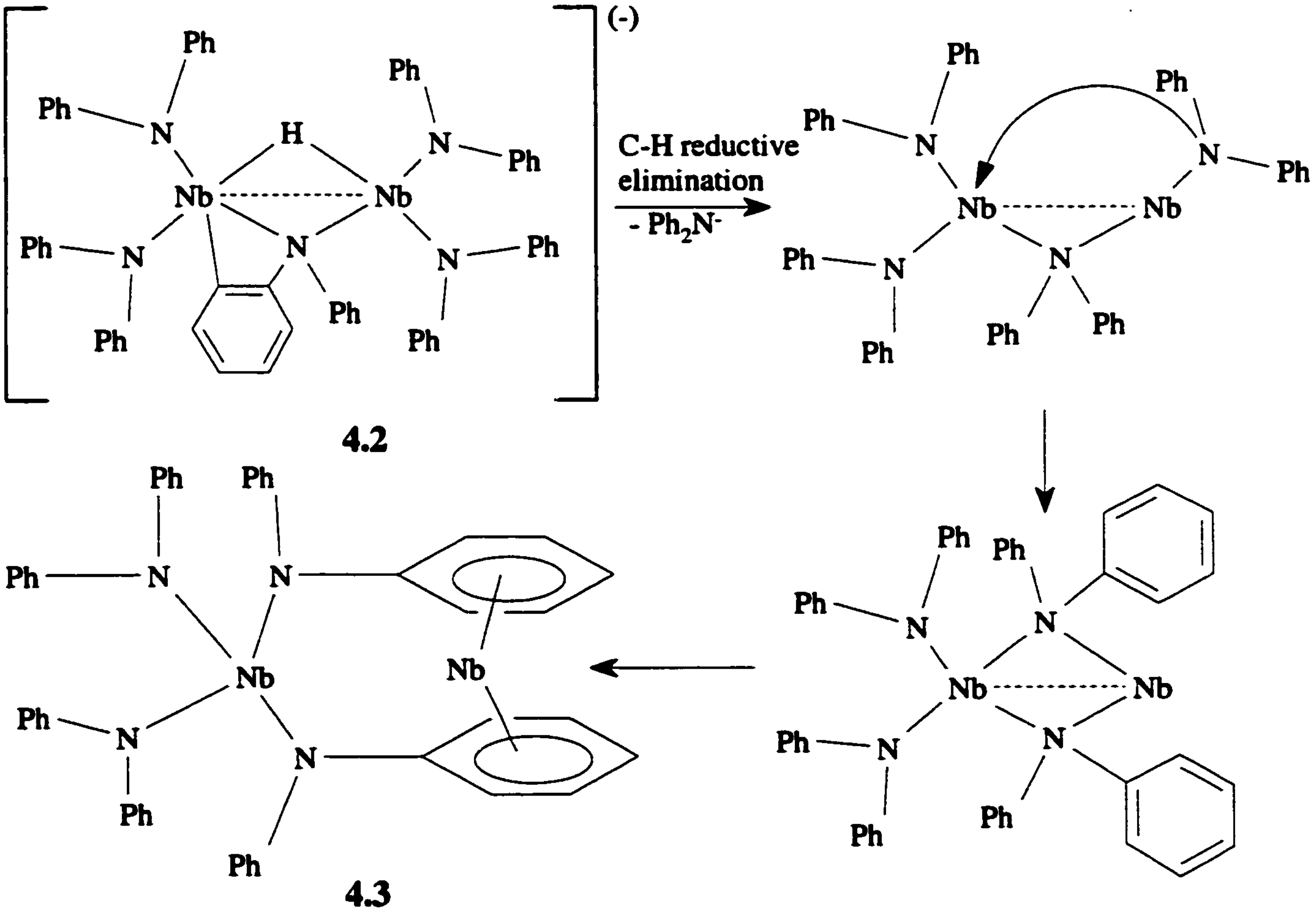
The third compound (4.3) present in the reaction mixture was isolated in rather poor yield (12%) from the mother liquor after replacement of the solvent by ether, followed by filtration. This third compound, also diamagnetic, tested negative for chlorine and lithium. The I.R. clearly indicated the presence of the amide ligand, while combustion analysis data were in good agreement with the formulation $(Ph_2N)_2Nb\{[\mu\text{-}NPh(\eta^6\text{-}C_6H_5)]_2Nb\}$.ether (4.3) which was confirmed by an X-ray crystal structure (Figure 4.3). No significant features were observed in the ^{1}H-NMR spectrum other than the presence of the aromatic amide resonances.

The rings engaged in the formation of the metallocenic structure presented three distinctive bands, two pseudotriplets at 5.25 and 4.09 ppm, and one pseudodoublet at 4.85 ppm. The ^{13}C-NMR spectrum was also consistent with these observations. The other aromatic signals of the molecule were observed in the usual range.

The complexity of the reaction of $Nb_2Cl_5Li(TMEDA)_3$ with Ph_2NK poses some puzzling mechanistic questions. The formation of the mixed-valence niobium compound **4.1** as a significant component of the reaction mixture occurs in spite of using a rigorous stoichiometric ratio of amide/Nb of 2:1 and has no explanation at this stage. Probably, its formation occurs *via* disproportionation of some intermediate able to generate a "$NbCl_3(TMEDA)$" unit. This species is rapidly scavenged by the Nb(II) starting material to form the highly insoluble mixed valence species **4.1,** as indicated by the fact that the direct reaction of $Nb_2Cl_5Li(TMEDA)_3$ with $Nb_2Cl_6(TMEDA)_2$ led to the nearly quantitative formation of **4.1** through a rapid reaction (Scheme 4.1). It is interesting to observe that similar reactions of $MCl_2(TMEDA)_2$ [M = V, Ti][14] with Ph_2NK also form halogenated clusters $[M_3Cl_5(TMEDA)_3]^{(+)}$, triangular and cationic in these particular cases. The counteranion of these species are $[(Ph_2N)_2M\{[\mu\text{-}NPh(\eta^6\text{-}C_6H_5)]_2M\}]^{(-)}$ anions [M = V,[15] Ti] possessing structures related to that of **4.3.**

The formation of **4.2** may be regarded as the result of chlorine replacement of the divalent $Nb_2Cl_5Li(TMEDA)_3$ by five $Ph_2N^{(-)}$ anions. The resulting $Nb_2(NPh_2)_5Li$ intermediate, also divalent, forms compound **4.2** *via* oxidative addition of the two Nb(II) centers to the C-H σ-bond of one aromatic ring. The one-electron oxidation of each of the two metal centers provides the two electrons necessary for the C-H bond cleavage and formation of the trivalent **4.2.** The reaction may be also regarded as a formal metathesis of the Nb-Nb triple bond, perhaps present in $Nb_2Cl_5Li(TMEDA)_3$ (calculated Nb-Nb bond order 2.76), with the ligand C-H bond to form a Nb-Nb doubly bonded Nb(III) complex (calculated Nb-Nb bond order 1.63). This behavior is in striking contrast with that of similar reactions performed with different amides where similar cooperative interaction of the two Nb atoms gave instead C-N bond cleavage.[16] Examples of transformations involving intermediate C-H bond activation are abundant in the literature,[17] while examples of oxidative addition of metal centers to C-H bonds to form characterizable alkyl/hydride derivatives remain relatively few.[18] Although we do not know the mechanism for the formation of complex **4.2**, from the formal point of view this species is the result of the oxidative addition performed by the attack of two group 5 metals on the same C-H bond forming a stable alkyl hydride compound.[19] A relatively complex reorganization of complex **4.2** (dissociation of amide Li and shift of one of the two Nb atoms) is probably the origin of **4.3** (Scheme 4.2).

However, with this reaction the amide ligand is restored thus indicating that both the hydride and the metallated ring were reductively eliminated by the metal center. Accordingly, we did not observe during this process hydrogen evolution which could possibly indicate alternative pathways. The overall transformation implies an internal redox process and does not require electrons to be added to or removed from **4.2.** In agreement with the proposal that **4.3** is a product of the evolution of **4.2**, thermolysis of an analytically pure sample of **4.2** in toluene afforded a higher yield (60%) of complex **4.3.** The conversion of **4.2** to **4.3** may also be monitored by NMR during a reaction which is slow at room temperature (about 5 days) but much faster at high temperature. NMR tube experiments clearly indicate that the formation of **4.3** is also accompanied by the appearance of a new thermally stable hydride, probably high-valent (δ = +9.8 ppm not correlated with any carbon resonance). Unfortunately, attempts to isolate this fourth species were so far unsuccessful.



Scheme 4.2

IV. 4: Molecular Orbital Calculations

Ab initio HF calculations with an STO-3G basis were carried out on complex **4.1** using a Silicon Graphics workstation and the Spartan 4.0 software package.[20] Given the molecular complexity, simple EHMO calculations were performed on complexes **4.2** and **4.3**. In these two cases, calculations were carried out with a Pentium-PRO 266 computer using the *Quantum CaCHE 2.0* software package.[21] The program's default parameters were used for both calculations. The fractional atomic coordinates of the crystal were of structures converted to the corresponding cartesian coordinates by using the XP program the SHELXTL program library.

The comparison between the geometry of **4.1** with that of the starting $Nb_2Cl_5Li(TMEDA)_3$ complex is somewhat interesting. The most visible difference lies in the absence of the lithium cation and the value of the Nb-Nb distances [respectively 2.545(1)Å and 2.401(5)Å, for **4.1** and the starting material]. The deviation from the regular octahedral coordination geometry of the metal center is rather similar in the two complexes and only slightly more pronounced in complex **4.1** [Cl3-Nb1-Cl4 angle is 174.94(5) compared to the value of 179.43(3) for $Nb_2Cl_5Li(TMEDA)_3$ complex], in spite of the absence of coordinated lithium. The absence in complex **4.1** of the attractive force applied by the lithium cation between the two vertices of the two octahedra of the starting material, might well be a critical factor in determining the elongation of the intermetallic vector of **4.1**. However, it is also possible that given that complex **4.1** is a mixed valence species, the absence of one electron with respect to the starting Nb(II) complex depopulates the HOMO (a MO with some Nb-Nb δ-bond character) thus decreasing the formal Nb-Nb bond order and ultimately lengthening the Nb-Nb distance.

Ab initio Hartree-Fock calculations were carried out with the geometrical parameters of **4.1** as determined by the crystal structure. The frontier orbitals (HOMO, HOMO-1 and HOMO-2) are basically the same as calculated for the $Nb_2Cl_5Li(TMEDA)_3$ complex (Chart 4.1) with a comparable HOMO-LUMO gap. As for the starting material, these orbitals are mainly Nb-Nb centered MOs with a metal atom contribution mainly of *d*-orbital character and a significant contribution from the bridging chlorine *p* orbitals. For both complexes, the orbitals originate from the same hybrid combinations of *d* orbitals. In the case of complex **4.1**, the contribution of the bridging halide *p* orbitals to the formation of the M-M bond is even higher than it is in the starting material. The most visible difference between the two complexes arises from bridging halide *p* orbitals to the formation of the M-M bonds is even higher than it is in the starting material. The most visible difference between the two complexes arises from the fact that the orbital which has the higher δ character in complex **4.1** is more stable than the "π" orbital and becomes the HOMO. As a probable result of an increased involvement of the bridging ligand orbitals in complex **4.1** and of the potential depopulation of the HOMO, the formal Nb-Nb bond order decreases from 2.76 in the starting material to 1.45. It is tempting at this stage to conclude that the partial depopulation of the HOMO, rather than the absence of the lithium cation, is the factor that determines the lengthening of the Nb-Nb distance. The Nb-Nb distance in the trivalent **4.2** [Nb(1)-Nb(2) = 2.569(12)Å] and the diamagnetism may indicate the presence of a significant Nb-Nb bonding

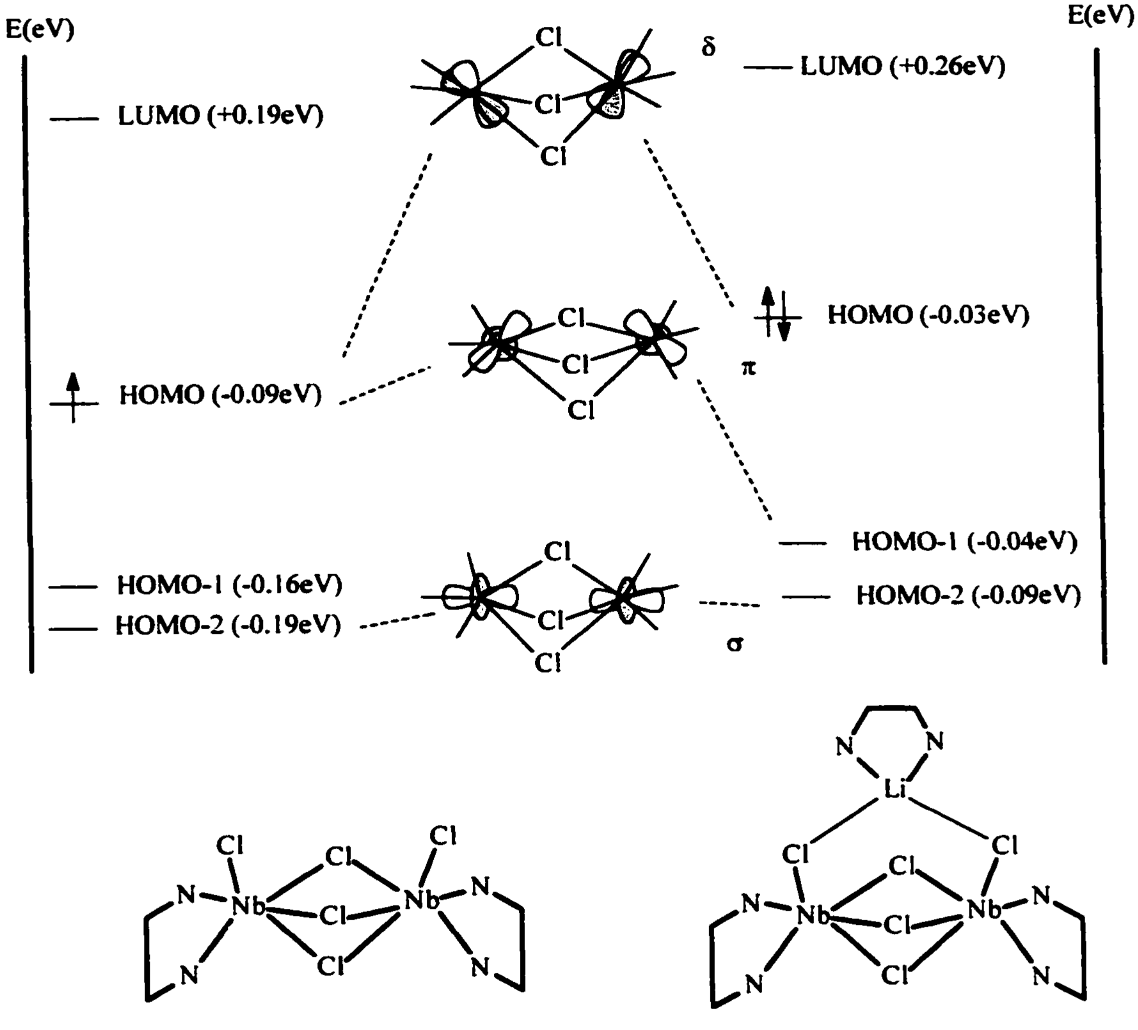


Chart 4.1

interaction. The results of the EHMO calculation carried out on the anionic moiety of **4.2** showed a HOMO-LUMO gap (0.46 eV) sufficient to account for the observed diamagnetism. There are six MOs of interest (Chart 4.2). The Nb-Nb σ–interaction is realized via two MOs: the HOMO-1 (-11.85eV) and HOMO-2 (–12.22 eV), (Chart 4.2). Both orbitals are mainly Nb-Nb centered and originate from hybrid combinations of Nb *d* orbitals which overlap their lobes placed on the intermetallic vector to form weak Nb-Nb bonds of mainly σ-character. The HOMO-3 orbital arises from two identical hybrid combinations of *d* orbitals of the two metal atoms which overlap two lobes on one side of the intermetallic vector. This orbital, which is somewhat reminiscent of a π-orbital, is very similar in shape to the HOMO of complex **4.1**. These three orbitals together account for a calculate Nb-Nb bond order of 1.63. The next MO of interest is HOMO-8 (-12.82eV). This orbital is a simple Nb-C σ-bond and is formed by the overlap of a $d_{x^2-y^2}$, d_{xz}, d_{yz} hybrid combination of the metal atom with the p_z orbital of the carbon atom. The Nb-H-Nb interaction is realized with two orbitals. The first, HOMO-36 (-15.56 eV), is formed *via* the overlap of the Nb d_{z^2} orbitals with the hydrogen *s* orbital. The second. HOMO-41 (-16.67 eV), is very similar to the previous one except that is constructed by two different orbitals of the two different Nb atoms (d_{z^2} and $d_{x^2-y^2}$ respectively).

Compound **4.3** may be regarded either as a Nb(IV)/Nb(0) mixed valence species or as a Nb(II) derivative. The coordination geometry of the amide nitrogen atoms, invariably trigonal planar, indicates that each amide ligand acts as a 4 electron donor.

In the hypothesis of a mixed-valence formulation, each niobium atom will possess a 17 electron configuration. Therefore, the presence of a simple Nb-Nb bond will provide a formal 18 electron configuration that would explain the observed diamagnetism. Conversely, in the case of the formulation as a Nb(II) derivative the formal electron count will be of 19 and 15 electrons for the two Nb atoms respectively. The fairly large HOMO-LUMO gap (1.05 eV) accounts well for the observed diamagnetism. Three frontier orbitals (HOMO, HOMO-1 and HOMO-4) have a significant Nb-Nb bond character (Chart 4.3).

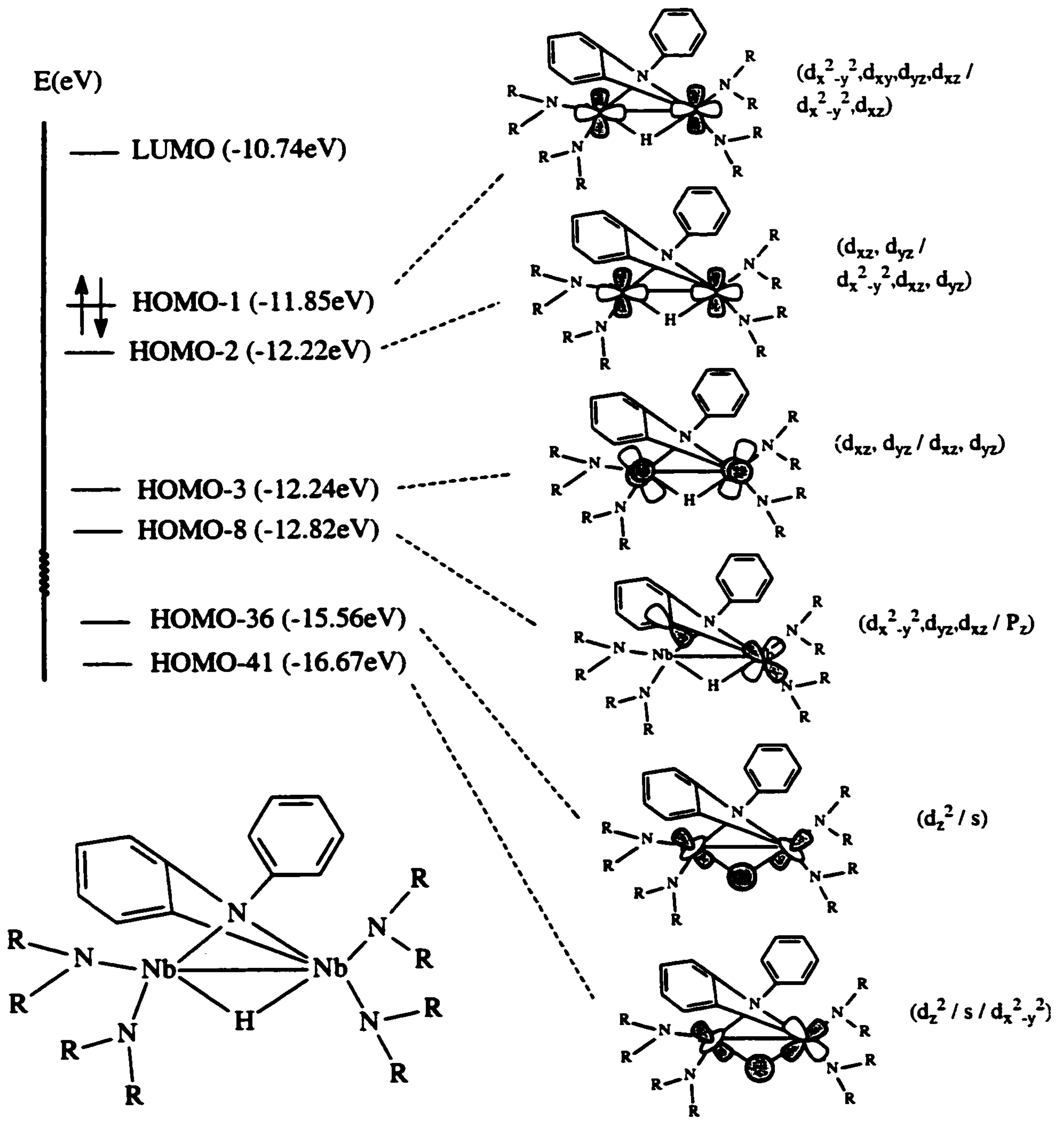


Chart 4.2

The HOMO (-11.64 eV) originates from the overlap of one lobe of the d_{z2}, d_{xy}, d_{yz} hybrid used by the "metallocenic" niobium for bonding the two aromatic rings, with one lobe of the d_{xy} orbital of the second niobium atom. The resulting MO consists of a large lobe symmetrically distributed along the Nb-Nb vector. The next MO (HOMO-1, –12.22 eV) is a regular π-orbital and is originated by the overlap of two identical $d_{x^2-y^2}$, d_{yz} hybrid combinations. The orbital has two lobes symmetrically placed on the two sides of the Nb-Nb vector with a nodal plane bisecting the two parallel aromatic rings π-bonded to the second niobium atom. The next MO with a significant Nb-Nb bond character is the HOMO-4 (-12.60 eV). The orbital is also mainly *d*-centered with a weak but significant Nb-Nb σ-bond character. It is formed by the overlap of two lobes of two identical d_{xy}, d_{xz} hybrid combinations of each Nb atom forming a lobe symmetrically placed along the intermetallic vector. The calculated Nb-Nb bond order (0.83) is surprisingly high and might suggest the presence of a significant Nb-Nb bonding interaction. The partial Mulliken atomic charges

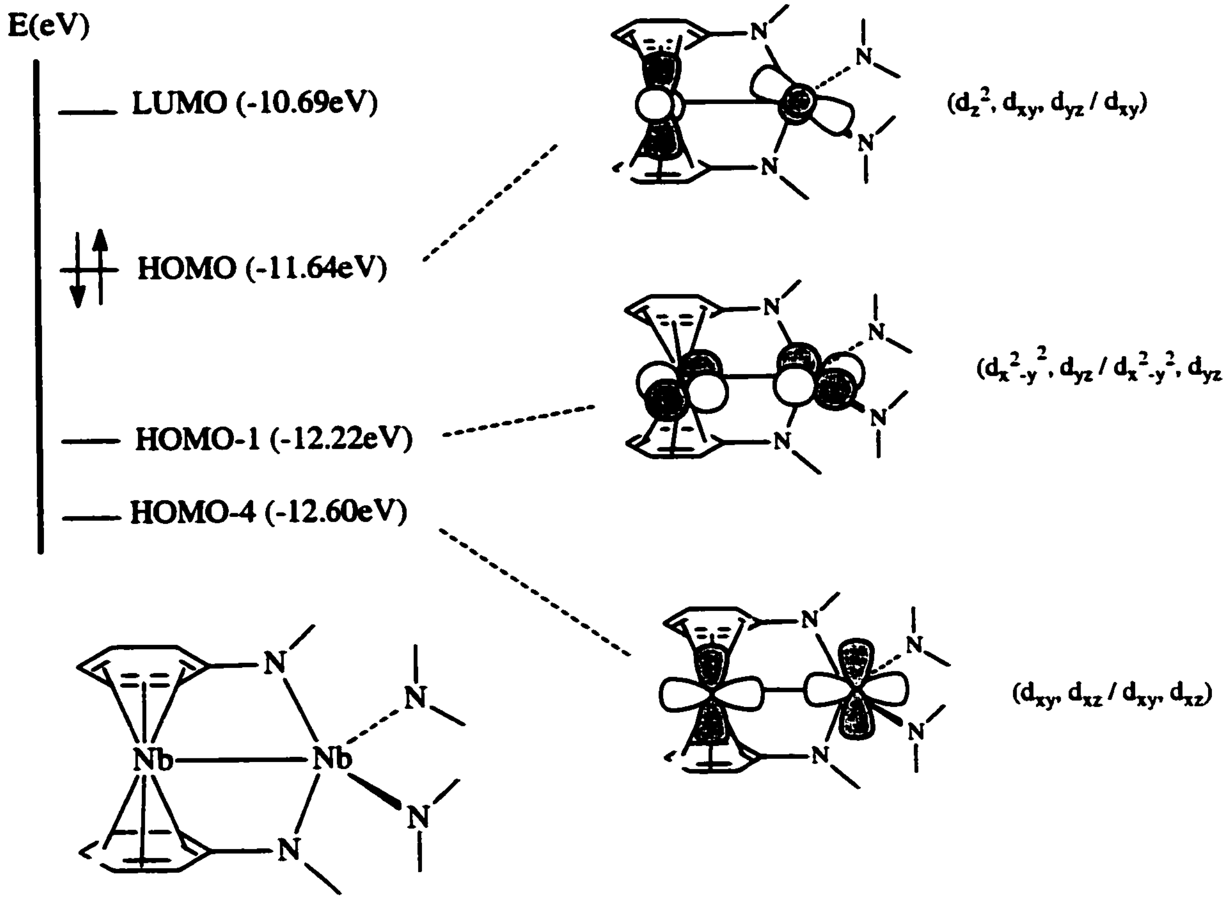


Chart 4.3

calculated for the two niobium atoms are consistent with the mixed valence Nb(IV)/Nb(0) formulation.

IV. 5: X-ray crystallography

Suitable crystals were mounted with cooled viscous oil on thin glass fibers. Data were collected on a Bruker AG SMART 1k CCD diffractometer using a proprietary hemisphere scan routine. Cell constants were calculated from reflection data obtained from 60 data frames collected at different parts of the Ewald sphere. The data for **4.1** were corrected for absorption effects using redundant data at different effective azimuthal angles. No absorption corrections were applied to the data sets for **4.2** and **4.3**. The reflection data for **4.1** were consistent for $Pna2_1$ and *Pnam* (*Pnma*), however, only the eccentric option yielded chemically reasonable and computationally stable results of refinement. The reflection data for **4.1** and **4.3** were uniquely consistent with the reported space groups. The structures were solved by direct methods, completed with subsequent Fourier synthesis and refined with full-matrix least-squares procedures based on F^2. A molecule of solvent of crystallization was located in the asymmetric unit for **4.2** and **4.3**. All non-hydrogen atoms, excluding the atoms of the cocrystallized solvent molecule of **4.2**, were refined with anisotropic displacement coefficients. Phenyl groups were refined as idealized, flat, rigid hexagons. Hydrogen atoms were assigned with idealized geometry, and constrained with an isotropic, riding model. Additional information for compounds **4.1-4.3** are given in **Appendix C**. All scattering factors are contained in the SHELXTL 5.03 program library (Sheldrick, 1994, WI).

The crystal structure of **4.1** showed the molecule to be composed of two niobium atoms, five chlorine atoms and two molecules of TMEDA, organized in an overall face-sharing bi-octahedral geometry (Figure 4.1). Three chlorine atoms are bridging the two metal centers [Nb(1)-Cl(1) = 2.530(2)Å, Nb(1)-Cl(2) = 2.536(3)Å, Nb(1)-Cl(3) = 2.540(2)Å] while the other two are terminally bonded [Nb(1)-Cl(4) = 2.467(2)Å, Nb(2)-Cl(5) = 2.474(2)Å].

The distorted octahedral coordination geometry around each Nb atom [Cl(1)-Nb(1)-Cl(2) = 110.26(7)°, Cl(1)-Nb(1)-Cl(3) = 92.60(6), Cl(2)-Nb(1)-Cl(3) = 85.15(5), Cl(1)-Nb(1)-Cl(4) = 88.72(6), Cl(2)-Nb(1)-Cl(4) = 89.81(5)°, Cl(3)-Nb(1)-Cl(4) = 174.94(5)°, N(1)-Nb(1)-N(2) = 80.6(2)°, N(1)-Nb(1)-Cl(4) = 97.62(13)°, N(1)-Nb(1)-Cl(3) = 87.38(13)°, N(1)-Nb(1)-Cl(2) = 164.36(12)°, N(1)-Nb(1)-Cl(1) = 83.77(13)°] is completed by the two nitrogen atom of the chelating TMEDA [Nb(1)-N(1) = 2.337(5)Å, Nb(1)-N(2) = 2.347(5)Å]. The Nb-Nb distance [Nb(1)-Nb(2) = 2.545(1)Å] is in the M-M bonding range but is significantly longer than that observed in $Nb_2Cl_5Li(TMEDA)_3$[9] in spite of the close structural similarity.

The molecule of **4.2** is formed by two separate ionic moieties (Figure 4.2). The cationic unit is composed of one lithium atom surrounded by two TMEDA molecules [Li(1)-N(101) = 2.12(3)Å, Li(1)-N(102) = 2.16(4)Å, N(101)-Li(1)-N(102) = 100(2)Å]. The anionic moiety features a dinuclear unit composed by two almost identical $(Ph_2N)_2Nb$ moieties connected by one bridging amide group [Nb(1)-N(1) = 2.177(9)Å, Nb(2)-N(1) = 2.377(9)Å]. The two terminal amides are rather normal with usual bond distances [Nb(1)-N(2) = 2.107(9)Å, Nb(1)-N(3) = 2.108(10)Å] and the characteristic trigonal planar coordination geometry around the nitrogen atoms [Nb(2)-N(4)-C(66) = 136.1(7)°, Nb(2)-N(4)-C(76) = 103.1(6)°, C(66)-N(4)-C(76) = 120.3(8)°]. Conversely, the bridging amide [Nb(1)-N(1) = 2.177(9)Å, Nb(2)-N(1) = 2.377(9), Nb(1)-N(1)-Nb(2) = 68.5(3)°] has some unique features. One of the two phenyl rings attached to the bridging nitrogen is normal and points away from the two Nb atoms [N(1)-C(16) = 1.448(11)Å, Nb(1)-N(1)-C(16) = 138.2(7)°, Nb(2)-N(1)-C(16) = 128.2(6)°]. The second one is bent towards both Nb atoms [Nb(1)-N(1)-C(6) = 87.1(7)°, Nb(2)-N(1)-C(6) = 93.3(6)°] showing two different types of interaction with the two metals. This is emphasized by the presence of a short bonding contact between one metal center and one of the two ring *ortho* carbon atoms [Nb(2)-C(1) = 2.197(12)Å]. This short contact is consistent with the presence of a Nb-C σ-bond thus indicating metallation of the aromatic ring. Furthermore, the metal is nearly coplanar with the ring [torsion angle Nb(2)-N(1)-C(6)-C(1) = 7.1°]. The same ring carbon atom and the adjacent quaternary are also engaged in the formation of rather short contacts with the second Nb atom [Nb(1)-C(1) = 2.573(12)Å, Nb(1)-C(6) = 2.549(16)Å] which is elevated above the plane of the aromatic ring [2.026Å] and nearly perpendicular to the C-C bond [Nb(1)-C(1)-C(6) = 72.9(7)°, Nb(1)-C(6)-C(1) = 105.0(9)°, torsion angles Nb(1)-N(1)-C(6)-C(5) = 117.1°, Nb(1)-N(1)-C(6)-C(1) = 61.1°]. This indicates the presence of a significant π-interaction of a portion of the aromatic ring with the metal center not engaged in the *ortho* metallation.

Complex **4.3** is also dinuclear (Figure 4.3). It is formed by a $(Ph_2N)_4Nb$ unit with the niobium atom placed in the center of a rather distorted coordination tetrahedron [N(1)-Nb(1)-N(2) = 149.93(6)°, N(1)-Nb(1)-N(3) = 105.94(6)°, N(1)-Nb(1)-N(4) = 95.99(6)°, N(2)-Nb(1)-N(3) = 95.63(6)°, N(2)-Nb(1)-N(4) = 91.06(6)°, N(3)-Nb(1)-N(4) = 119.65(5)°]

defined by the four nitrogen atoms of four amide groups [Nb(1)-N(1) = 2.071(2)Å, Nb(1)-N(2) = 2.099(2)Å, Nb(1)-N(3) = 2.037(2)Å, Nb(1)-N(4) = 2.027(2)Å]. A second niobium atom is placed between the two nearly parallel aromatic rings of two different amides and is symmetrically connected to the two aromatic rings [Nb(2)-C(1) = 2.365(2)Å, Nb(2)-C(2) = 2.337(2)Å, Nb(2)-C(3) = 2.346(2)Å, Nb(2)-C(4) = 2.344(2)Å, Nb(2)-C(5) = 2.324(2)Å, Nb(2)-C(6) = 2.345(2)Å] thus forming a bis-arene niobium structure [[Nb(2)-CentrA = 1.864Å, Nb(2)-CentrB = 1.875Å]. The Nb-Nb distance [Nb(1)..Nb(2) = 3.0250(2)Å] is rather long and perhaps not in agreement with the formation of significant M-M bonding interaction. However, there is a rather pronounced distortion in the coordination geometry of the two metal centers. Both metal atoms are pushed inward the center of the molecule [N(1)-Nb(1)-N(2) = 149.93(6)°, CentrA-Nb(2)-CentrB = 163.5°] resulting in a significant attractive force between the two metal centers.

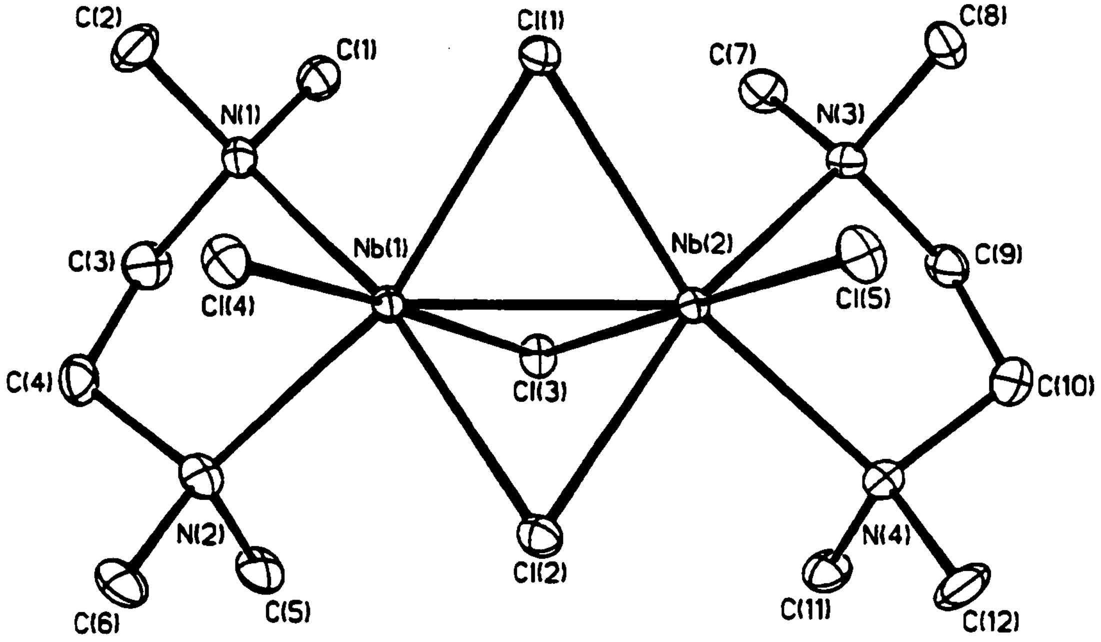


Fig. 4.1 X-ray structure of **4.1**. Selected bond distances (Å) and angles (°): Nb(1)-Nb(2) = 2.545(1), Nb(1)-Cl(1) = 2.530(2), Nb(1)-Cl(2) = 2.536(3), Nb(1)-Cl(3) = 2.540(2), Nb(1)-Cl(4) =2.467(2), Nb(1)-N(1) = 2.337(5), Nb(1)-N(2) = 2.347(5), Cl(1)-Nb(1)-Cl(2) = 110.26(7), Cl(1)-Nb(1)-Cl(3) = 92.60(6), Cl(1)-Nb(1)-Cl(4) = 88.72(6), Cl(1)-Nb(1)-Cl(3) = 92.60(6), Cl(1)-Nb(1)-Cl(4) = 88.72(6), Cl(1)-Nb(1)-N(1) = 83.77(13), Cl(1)-Nb(1)-N(2) = 163.76(12), Cl(2)-Nb(1)-Cl(3) = 85.15(5), Cl(2)-Nb(1)-Cl(4) = 89.81(5), Cl(1)-Nb(1)-Cl(4) = 88.72(6), Cl(1)-Nb(1)-N(1) = 83.77(13), Cl(1)-Nb(1)-N(2) = 163.76(12), Cl(2)-Nb(1)-Cl(3) = 85.15(5), Cl(2)-Nb(1)-N(1) = 164.36(12).

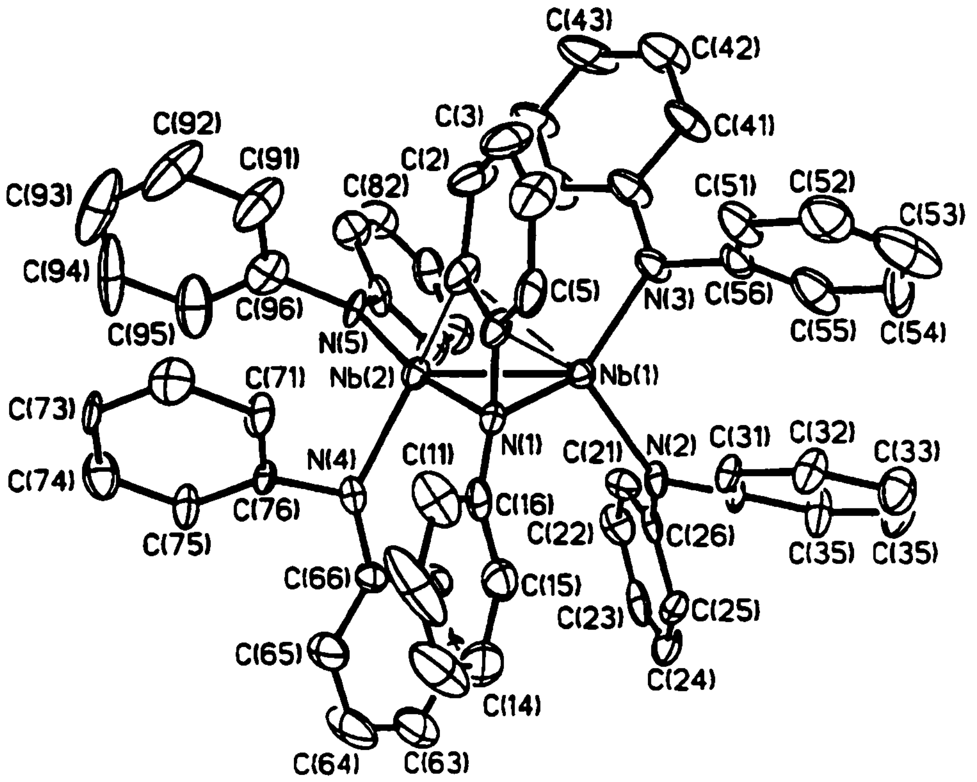


Fig. 4.2 X-ray structure of the anion of 4.2. Selected bond distances (Å) and angles (°): Nb(1)-Nb(2) = 2.569(12), Nb(1)-N(1) = 2.177(9), Nb(1)-N(2) = 2.107(9), Nb(1)-N(3) = 2.108(10), Nb(1)-C(1) = 2.573(12), Nb(1)-C(6) = 2.549(12), Nb(2)-N(1) = 2.377(9), Nb(2)-N(4) = 2.155(10), Nb(2)-N(5) =2.108(9), Nb(2)-C1 = 2.197(12), N(1)-Nb(1)-N(3) = 139.6(4), N(1)-Nb(1)-N(2)= 107.5(4), Nb(1)-N(1)-Nb(2) = 68.5(3), N(1)-Nb(2)-N(4) = 86.6(3), N(1)-Nb(1)-N(2) = 107.5(4), N(2)-Nb(1)-N(3) =106.4(4), N(4)-Nb(2)-C(1) = 136.9(4), N(5)-Nb(2)-C(1) = 107.2(4).

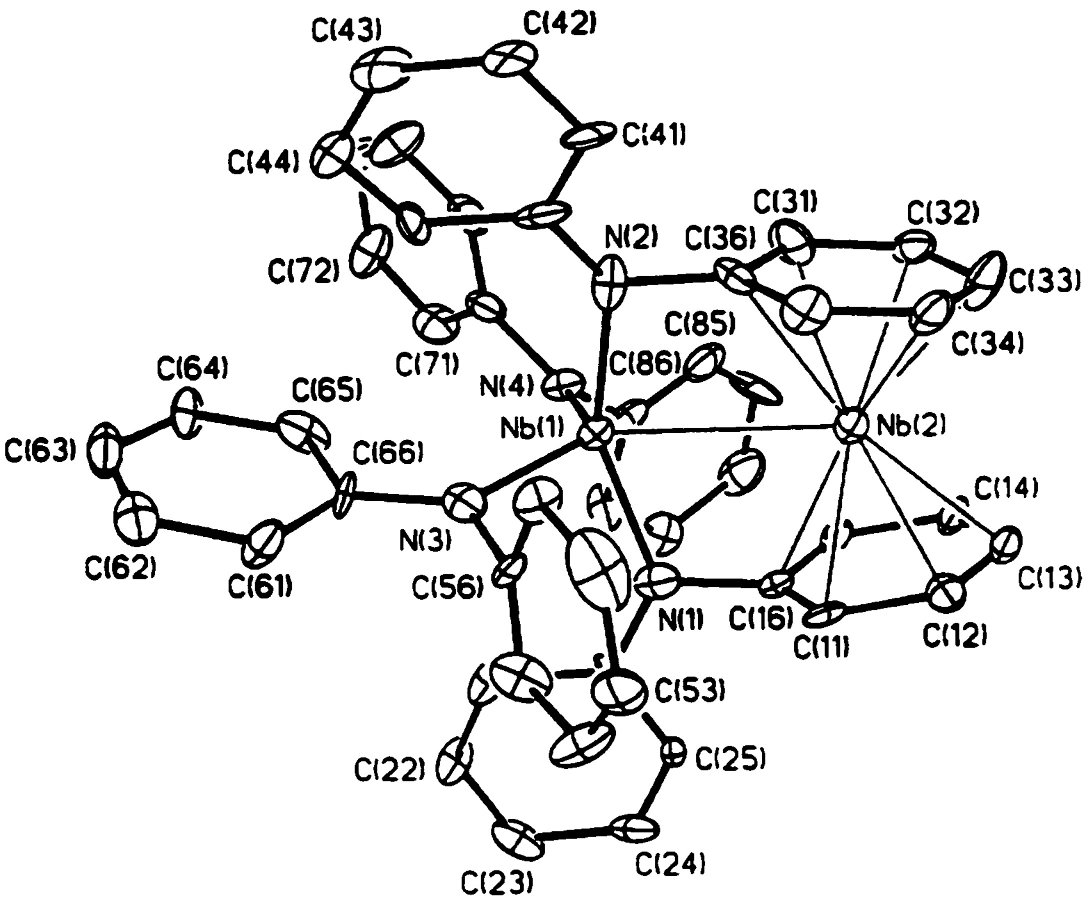


Fig. 4.3 X-ray sructure of 4.3. Selected bond distances (Å) and angles (°): Nb1...Nb2 = 3.0250(2), Nb1-N1 = 2.071(2), Nb1-N2 = 2.099(2), Nb1-N3 = 2.037(2), Nb1-N4 = 2.027(2), N1-Nb1-N2 = 149.93(6), N1-Nb1-N3 = 105.94(6), N1-Nb1-N4 = 95.99(6), N2-Nb1-N3 = 95.63(6), N2-Nb1-N4 = 91.06(6), N3-Nb1-N4 = 119.65(5), Nb1-N1-C6 = 101.40(11), Nb1-N1-C12 = 138.13(12).

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CHAPTER V

Formation of Nitride Complexes; C-N and N-N Bond Cleavages Promoted by a Nb II Cluster.

V. 1: Introduction

The key to understand the steady growth of interest in the reactivity of transition metals leading to cleavage of C-X bonds [X = O, S, N][1] lies in the fact that understanding this type of behavior may lead to new chemical transformations with practical implications for several industrial processes. Dehydro-desulfurization,[2] deoxygenation[3] and -denitrogenation[4] of crude oil, catalytic degradation of halocarbons,[5] catalysis and extrusion of nitrogen and ammonia from organic compounds[6] are the most prominent examples among a plethora of reactions which involve C-X bond cleavage. Although some of these processes are well understood, reactions leading to the cleavage of the C-N bonds are particularly challenging and information remains scarce.[7,8] The oxidative cleavage of C=N multiple bonds has been clearly identified in a few cases[7] and the mechanism was elucidated in detail.[7a] There are also a few examples of cleavage of a C-N single bond which have been documented in the literature.[8] However, if we remove from this category the opening of strained rings such as aziridines or cleavage of amidinates, only two examples of amine C-N single bond cleavage remain.[8a,b] The first is an observation made in 1985 by Chishom,[8b] who isolated a carbide/imide cluster, probably originated by degradation of an amide ligand. More recently, Wolczanski has described a unique case of oxidative addition of a Ta(III) complex into the C-N bond of aniline to form a mixture of $L_3Ta(H)(NHPh)$ and $L_3Ta(Ph)(NH_2)$ ($L = {}^tBu_3SiO$).[8a] In spite of this paucity in the literature, reactions leading to C-N bond cleavage have a tremendous synthetic potential.[9] For example, the Pd-catalyzed scrambling of alkyl groups between different amines is today a viable synthetic methodology for the preparation of a large number of amines.[10] Therefore, for synthetic purposes it is important to understand this type of reactivity and to shed some light onto the factors which promote C-N bond cleavage.

In this chapter, we describe the result of the reaction of the two anionic amides, dicyclohexyl (Cy_2N) and bis-pyridylamide (Py_2N), with the triply bonded Nb(II) complex $Nb_2Cl_5Li(TMEDA)_3$, which resulted in the formation of unique examples of nitrido bridged species through oxidative cleavage of possibly both dinitrogen and the C-N bond of the ligand.

V. 2: Experimental Section

All operations were performed under an inert atmosphere by using standard Schlenck techniques. $Nb_2Cl_5Li(TMEDA)_3$ was prepared according to the procedure described in Chapter II. $(Cy_2NLi)_4$[11] was prepared according to published procedures. 2,2'-dipyridylamide lithium was prepared by addition of proper amount of MeLi to 2,2'-dipyridylamine (purchased from Aldrich) in diethyl ether. Solvents were dried with the appropriate drying agents and distilled prior to use. Infrared spectra were recorded on a Mattson 9000 FTIR instrument from Nujol mulls prepared in a drybox. Samples for magnetic susceptibility measurements were prepared inside a drybox and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson

Matthey) at room temperature. The magnetic moment was calculated by standard methods,[12] and corrections for underlying diamagnetism were applied to the data.[13] Elemental analyses were carried out with a Perkin Elmer 2400 CHN analyzer. NMR spectra were recorded with a Bruker AMX 500 MHz spectrometer.

Preparation of $\{[(Cy_2N)_2Nb]_2(\mu\text{-}N)\}(\mu^3\text{-}N)Li(TMEDA)$ (5.1):

A solution of $Nb_2Cl_5Li(TMEDA)_3$ (1.0 g, 1.4 mmol) in THF (75 mL) was treated with freshly prepared $[Cy_2NLi]_4$ (1.0 g, 5.6 mmol). The mixture was stirred at room temperature overnight after which the solvent was removed *in vacuo*. The addition of ether (40 mL) allowed the elimination on of unreacted starting material which separated as a fine yellow microcrystalline solid. The ether mother liquor was concentrated to small volume and allowed to stand at room temperature upon which orange crystals of **5.1** separated (0.18 g, 0.17 mmol, 12%). El. Anal Calcd (found) for $C_{54}H_{104}N_8Nb_2Li$: C 61.29(61.15), H 9.91(9.85), N 10.59(10.41). I.R. [Nujol, cm^{-1}] ν: 1330(sh), 1255(s), 1143 (m), 1130(m), 1109(s), 1060(m), 1036(s), 990(m), 954(s), 889(s), 835(m), 799(m), 771(s), 760(m), 720 (s), 689(m). [$\mu_{eff} = 1.76\ \mu_B$].

Preparation of $[(py_2N)_2Nb]_2(\mu\text{-}C_5H_4N)(\mu\text{-}Npy)[Li(THF)_2]$ $(THF)_2[Li_2Cl_2(THF)_4]$ (5.2):

A freshly prepared solution of 2,2'-dipyridylamide lithium (1.33 g, 5.5 mmol) in THF (100 mL) was reacted with $Nb_2Cl_5Li(TMEDA)_3$ (1.0 g, 1.4 mmol). The mixture was stirred for a few minutes and allowed to stand at room temperature for four days. Intensely colored dark-brown crystals of **5.2** separated (0.64 g, 0.4 mmol, 30%). El. Anal

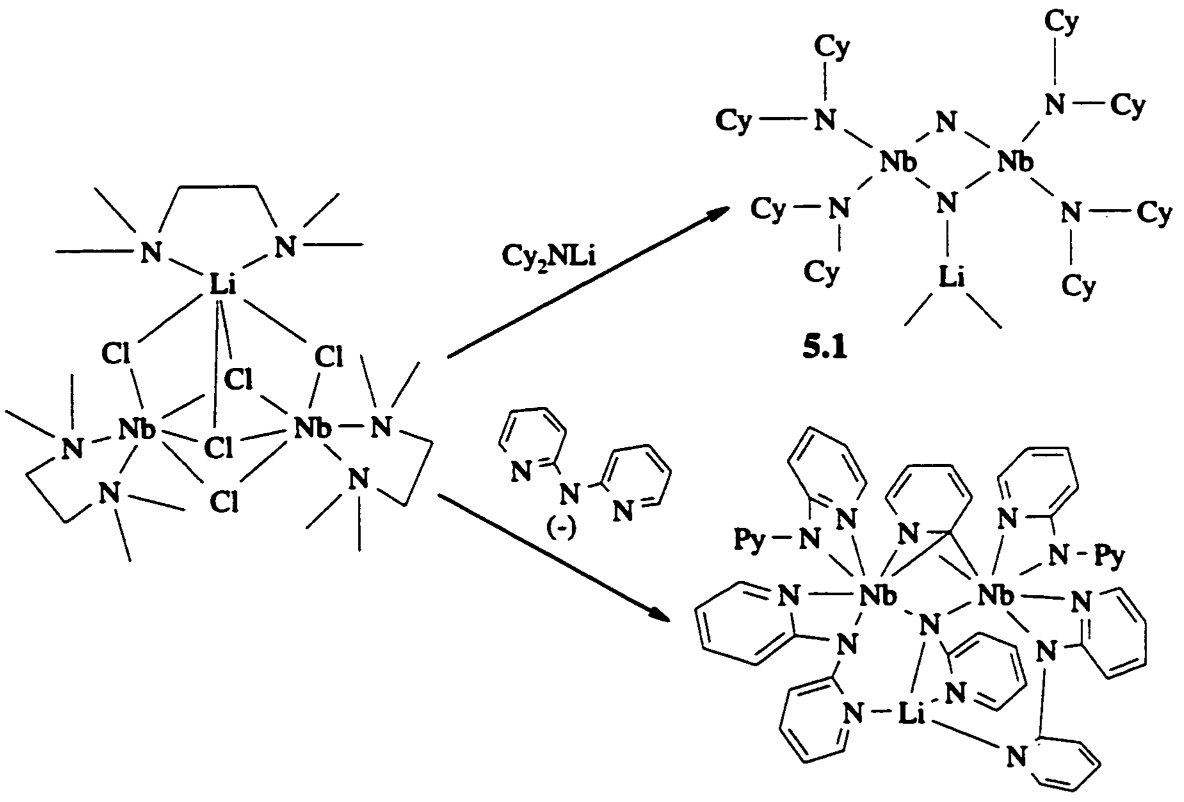
Calcd (found) for $C_{66}H_{71}N_{15}Nb_2Li_2O_4Cl$: C 57.71(57.74), H 5.21(5.14), N 15.30(15.89). I.R. [Nujol, cm^{-1}] ν: 1581(s), 1548(s), 1483(sh), 1425(vs), 1377(vs), 1302(s), 1284(s), 1245(s), 1149(s), 1105(m), 1052(s), 1008(s), 989(m), 939(w), 896(m), 877(w), 846(m), 800(m), 771(s), 735(s), 644(m). ^{1}H-NMR [500 MHz, C_6D_6, 23°C] δ: 8.37(m, 2H), 8.15(m, 4H), 8.12(d, 1H,), 7.62(d, 2H), 7.24(m, 2H), 7.21(d, 2H), 6.91 (two m., 4H), 6.73(three m., 3H), 6.64(m, 1H,) 6.59(d, 3H), 6.58(m, 2H), 6.35(d, 2H), 6.33(two m., 4H), 6.11(dd, 2H), 5.71(m, 2H), 5.68(two m., 3H), 5.42 (t, 1H), 3.55(m, 16H, THF), 1.41(m, 16H, THF). ^{13}C-NMR [127.7 MHz, C_6D_6, 23°C] δ: 201.3 (quaternary), 165.6, 163.5, 163.3, 161.1 (quaternary), 148.7 (quaternary), 147.4, 146.9, 144.9, 137.5, 137.2, 136.9, 136.4, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 119.8, 115.6, 115.2, 114.0, 113.9, 112.9, 111.3, 111.2, 111.1, 109.0.

V. 3: Results and Discussion

Reaction of the diamagnetic cluster $Nb_2Cl_5Li(TMEDA)_3$ with Cy_2NLi_4 [Cy = cyclohexyl] gave a nitride-bridged mixed-valence Nb(IV)/Nb(V) species $\{[(Cy_2N)_2Nb]_2(\mu\text{-}N)\}(\mu^3\text{-}N)Li(TMEDA)$ **(5.1)** (Scheme 5.1). This paramagnetic, moderately air-sensitive complex was isolated from ether solutions as a bright orange homogeneous crystalline material in rather poor but reproducible yield. Attempts to improve the yield by usual work up with solvents revealed the presence in the mother liquor of a substantial amount of unreacted $Nb_2Cl_5Li(TMEDA)_3$. Reactions carried out with larger amounts of $[Cy_2NLi]_4$, with the aim to complete the conversion, surprisingly gave only intractable mixtures. Qualitative analytical tests on the orange crystalline compound showed the absence of chlorine and the presence of lithium. Combustion analysis data were consistent with a formula $(Cy_2N)_4Nb_2N_2Li(TMEDA)$ (**5.1**), indicative of the formation of a mixed valence complex probably containing dinitrogen. The presence of TMEDA was revealed by the NMR spectrum of this paramagnetic species. The magnetic moment [$\mu_{eff} = 1.76\ \mu_B$] was consistent with the presence of one unpaired electron per unit formula. The origin of the bridging nitride (C-N cleavage or N_2 activation) could not be conclusively demonstrated in this case. However, we observed that identical reactions carried out under an Ar atmosphere are remarkably different and form products of a different nature, perhaps indicating that complex **5.1** originates from N_2 activation.

Reaction of $Nb_2Cl_5Li(TMEDA)_3$ with dipyridylamide lithium salt was carried out in THF and the crystalline product was obtained in moderate yield after suitable work up (Scheme 5.1). This compound was diamagnetic, inevitably retained lithium and was correctly analyzed for the formulation elucidated by the X-ray crystal structure as $[(py_2N)_2Nb]_2(\mu\text{-}C_5H_4N)(\mu\text{-}Npy)[Li(THF)_2](THF)_2[Li_2Cl_2(THF)_4]$ (**5.2**). Formation of **5.2** arises from the ligand C-N bond cleavage.

The formation of both **5.1** and **5.2** arises from the cooperative oxidative addition of the two metal centers into either dinitrogen or the C-N bonds of the two different ligands. In the case of reaction with Cy_2NLi, five electron from the six necessary to cleave dinitrogen are provided by the two niobium atoms. Therefore there must be other species in this reaction mixture, which were isolated because of the high solubility of the products. In the case of the reaction with dipyridylamide lithium the two electrons necessary for the oxidative addittions are provided by the one electron oxidation of the two Nb(II) centers. It is reasonable to assume that in this case, the reaction starts with the formation of (amide)$_5$Nb$_2$Li intermediates and proceeds with the oxidative cleavage of



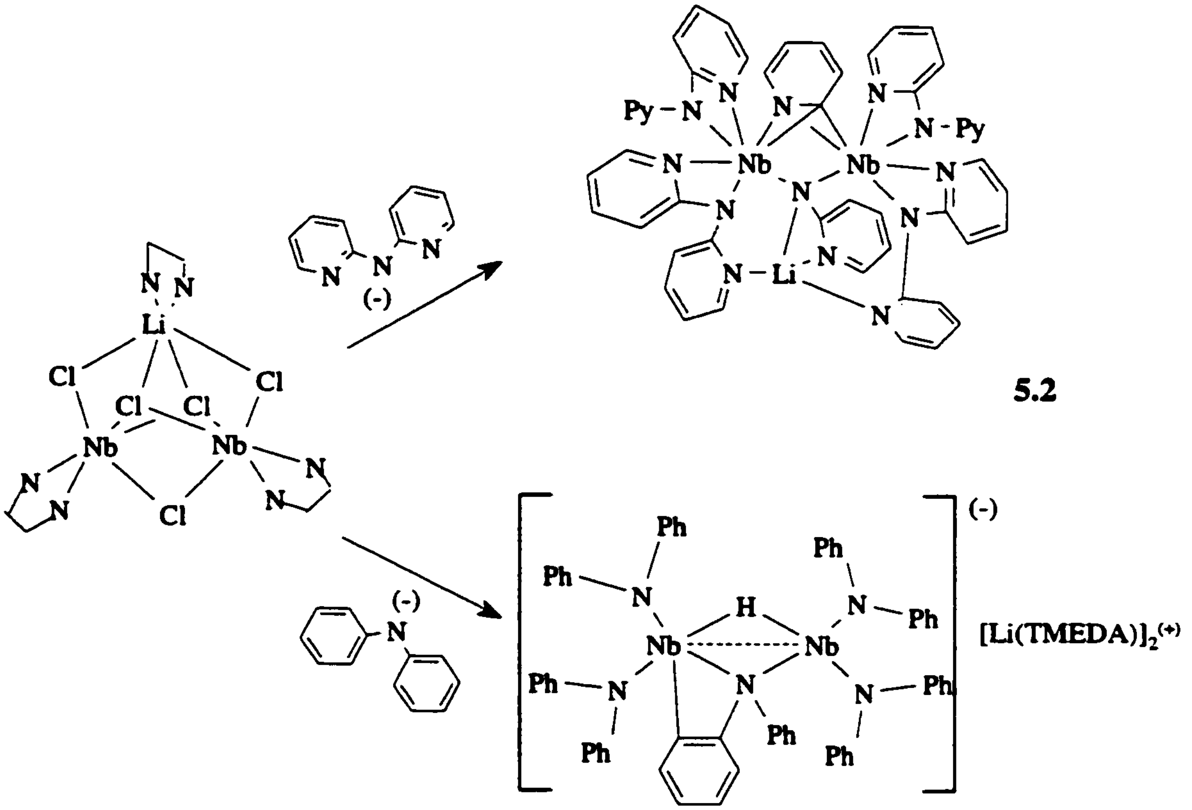
Scheme 5.1 5.2

the C-N bond and formation of the resulting [NC$_5$H$_4$] and [N(NC$_5$H$_4$)] fragments. Compound **5.2** is diamagnetic. This, in combination with the short intermetallic distance [Nb1-Nb2 = 2.7022(4) Å] which might be consistent with the presence of Nb-Nb double bonds. However, the distance is significantly longer and comparable to that of the face-sharing bioctahedral Nb(II)Cl$_3$ derivatives which are instead paramagnetic.[14] This suggests the presence of a significant participation of the bridging moieties in the Nb-Nb interactions. The potassium or lithium salts of bis-pyridylamine and diphenylamine [$(C_5H_4N)_2N^-$, Ph_2N^-] react with $Nb_2Cl_5Li(TMEDA)_3$ in THF to afford two different compounds (**5.2** and **4.2**) arising from the cooperative oxidative addition of the two metal centers on either the C-H or the C-N bond of the amide ligand (Scheme 5.2). Both compounds were diamagnetic, inevitably retained lithium and were correctly analyzed for the formulations elucidated by the X-ray crystal structures (Figure 5.2 and Figure 4.3). In both cases, the two electrons necessary for the oxidative additions are provided by the one electron oxidation of the two Nb(II) centers. This, in combination with the short intermetallic distances [Nb1-Nb2 = 2.7022(4)Å, 2.569(12)Å for **5.2** and **4.2** respectively] might be consistent with the presence of Nb-Nb double bonds. However, we observed that while in the case of **4.2** the intermetallic distance is perhaps in agreement with this proposal, in the case of **5.2** the distance is significantly longer. This suggests the presence of a significant participation of the bridging moieties in the Nb-Nb interactions.

V. 4: Molecular Orbital Calculations

All molecular orbital calculations were performed on a Pentium computer by using the software package *Quantum CaCHE 2.0* [15] The program's default parameters were used in the Extended Huckel calculations. The fractional atomic coordinates of the crystal structures were converted to the corresponding cartesian coordinates by using a special device of the NRCVAX program. The adamantyl groups were converted to t-Bu groups and the cyclohexyl to i-Pr for simplicity. Hydrogen atoms were introduced at their idealized positions. The intermetallic vector was selected as a *z* axis.

The intermetallic distance in complex **5.1** is rather long [Nb1-Nb2 = 2.8252(6) Å] and not in agreement with the presence of a significant M-M bonding interaction.



5.2

4.2

Scheme 5.2

Extended Huckel MO calculations were carried out on the geometrical parameters as obtained from the crystal structure and confirmed the absence of M-M centered bonding molecular orbitals. While the HOMO-LUMO gap appears to be rather modest (0.4 eV), the HOMO is well above all the other occupied molecular orbitals (gap HOMO/HOMO-1 = 2.2 eV). The singly occupied HOMO, located at -11.0 eV, is mainly a δ^* M-M antibonding orbital and originates from the out of phase combination of the two parallel d_{xy} atomic orbitals of the two niobium atoms. The bonding between the two niobium atoms and the the two bridging nitrides is provided by two MO located well below in energy and which are respectively the Nb-N σ (HOMO -19 at -13.7eV) and π (HOMO-22 at -14.1 eV bonds (Figure 5.1). The first originates from the overlap of the two d_{yz} orbitals of the two niobium atoms lying on the Nb_2N_2 plane with the in plane p_y orbitals of the two bridging nitrides. The second is formed by the combination of the d_{xy} metal orbitals with the nitride p_x orbitals perpendicular to the molecular plane.

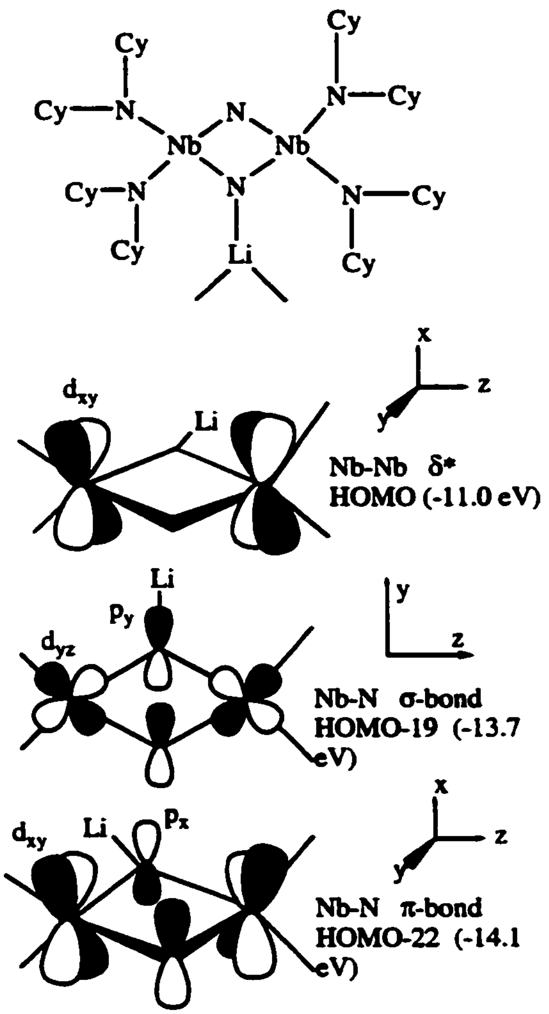


Figure 5.1: Pictorial view of most relevant MO's for complex **5.1**.

V. 5: X-ray Crystallography

Data were collected at -153°C for suitable air-sensitive crystals mounted on glass fibers inside a drybox and transferred under the liquid nitrogen stream of the cooling system of a Siemens CCD X-ray diffractometers. The ω-2θ scan technique was used. Cell constants and orientation matrices were obtained from the least-squares refinement of 25 centered reflections. The intensities of three standard reflections, measured after every 150 reflections, showed no statistically significant decay over the duration of the data collections. Data were corrected for Lorentz and polarization effects and for absorption (PSI scan). The structures were solved by direct methods resulting in locating all the non-hydrogen atoms. Their positions were refined anisotropically. Hydrogen atom positions were calculated but not refined. In the case of **5.1**, refinement was attempted by replacing the two nitride with oxygen atoms. The higher values of the residuals supported the formulation indicated by combustion analysis data. The data were processed using the NRCVAX software packages on a Silicon Graphics workstation. Refinements were carried out by using full-matrix least-squares techniques on F minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$ and F_o and F_c are the observed and calculated structure factors. Atomic scattering factors and anomalous dispersion terms were taken from the usual sources (Cromer & Waber).[16]

The X-ray analysis for complex **5.1** revealed a dinuclear structure composed of two identical $(Cy_2N)_2Nb$ units linked together by two bridging nitride atoms (Figure 5.2). One of the two bridging nitride atoms is also bonded to a Li(TMEDA) unit [N2-Li = 1.99(1) Å] forming a Nb_2N_2Li planar core. The coordination geometry around each niobium is distorted tetrahedral [N1-Nb1-N2 = 86.3(2)°, N1-Nb1-N3 = 116.1(2)°, N1-Nb1-N4 = 110.3(2)°, N3-Nb1-N4 = 110.0(2)°] and is defined by two nitrogen atoms of the terminal amide [Nb1-N3 = 2.040(4) Å, Nb1-N4 = 2.032(4) Å] and two bridging nitrides. The two bridging nitrides form comparable bond distances [Nb1-N1 = 1.893(4) Å, Nb1-N2 = 1.965(4) Å, Nb2-N1 = 1.937(4) Å, Nb2-N2 = 1.943(4) Å] and angles [Nb1-N1-Nb2 = 95.1(2)°, Nb1-N2-Nb2 = 92.6(2)°] with the two niobium metal centers in spite of the coordination of the alkali cation to only one of them, and compare well with those of a Mo-N cluster reported in the literature.[8b] The distorted trigonal coordination geometry of the alkali cation is completed by one molecule of TMEDA [N2-Li1-N8 = 131.0(6)°, N2-Li1-N7 = 141.9(6)°]. The geometry around the amide nitrogen atoms is trigonal planar as usual [Nb1-N3-C1 = 118.8(4)°, Nb1-N3-C7 = 124.7(4)°].

The structure of **5.2** is dinuclear and is formed by two similar $(py_2N)_2Nb$ moieties (Figure 5.3) bridged by one $[NC_5H_4]$ fragment and one pyridylimido moiety $[(C_5H_4N)N]$. One $Li(THF)_2$ unit is also placed on one side of the Nb-Nb vector and is connected to the N atoms of the two pyridyl rings of two intact amides and to the nitrogen atom of the bridging $[(C_5H_4N)N]$ group. The bridging NC_5H_4 fragment is placed on one side of the Nb-Nb vector and perpendicular between the two metal centers. The bonding with the two metal atoms is realized using both the deprotonated carbon atom and the adjacent nitrogen atom. The crystal structure is completed by two interstitial molecules of THF and one half molecule of $(THF)_4Li_2Cl_2$. Crystal data along with structure analysis results for **5.1** and **5.2** are given in **Appendix D**.

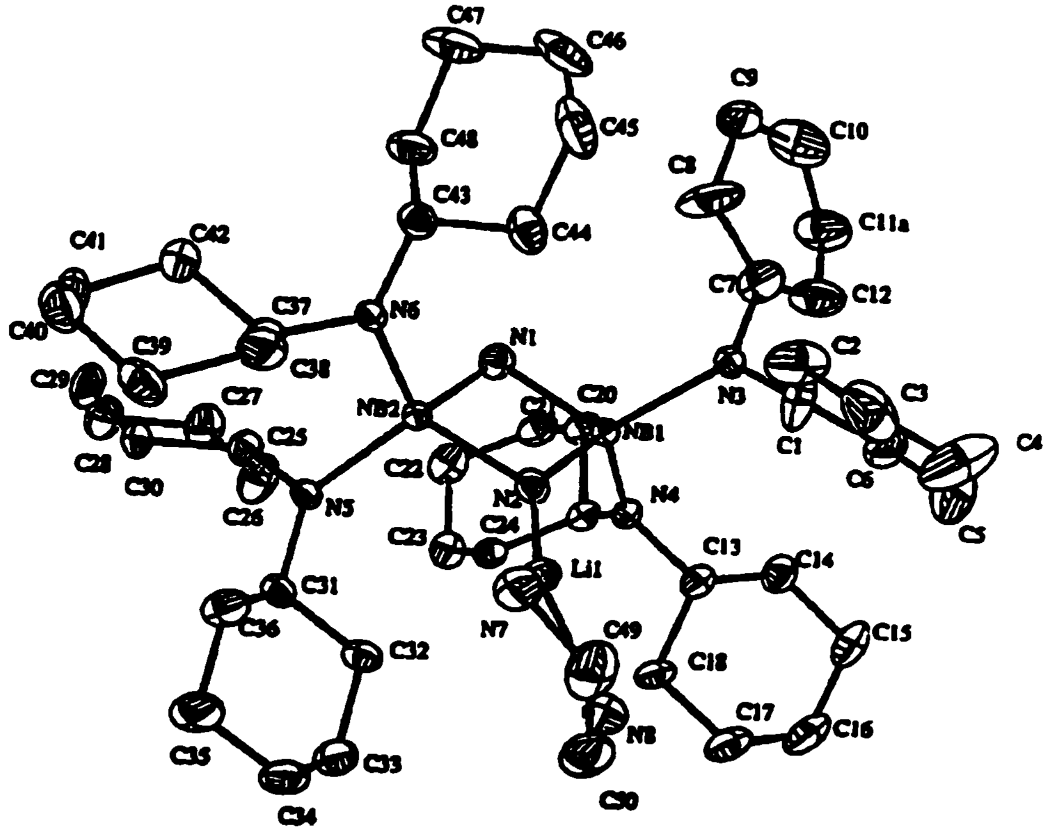


Fig 5.2: ORTEP drawing of **5.1**. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å), angles in deg (°): Nb1-Nb2 = 2.8252(6), Nb1-N1 =1.893(4), Nb1-N2 = 1.965(4), Nb1-N3 = 2.040(4), Nb1-N4 = 2.032(4), Nb2-N1 = 1.937(4), Nb2-N2 = 1.943(4), N1-Nb1-N2 = 86.3(2), N1-Nb1-N3 = 116.1(2), N1-Nb1-N4 = 110.3(2), N2-Nb1-N3 = 116.4(2), N2-Nb1-N4 = 115.9(2), N3-Nb1-N4 = 110.0(2), Nb1-N1-Nb2 =95.2(1), Nb1-N2-Nb2 = 92.6(2), Nb1-N2-Li1 = 144.5(4), Nb2-N2-Li1 = 112.9(4), N2-Li1-N7 = 141.9(6), N2-Li1-N8 = 131.0(6), N7-Li1-N8 = 85.9(4), Nb1-N3-C1 = 118.8(4), Nb1-N3-C7 = 124.7(4), C1-N3-C7 =116.4(5).

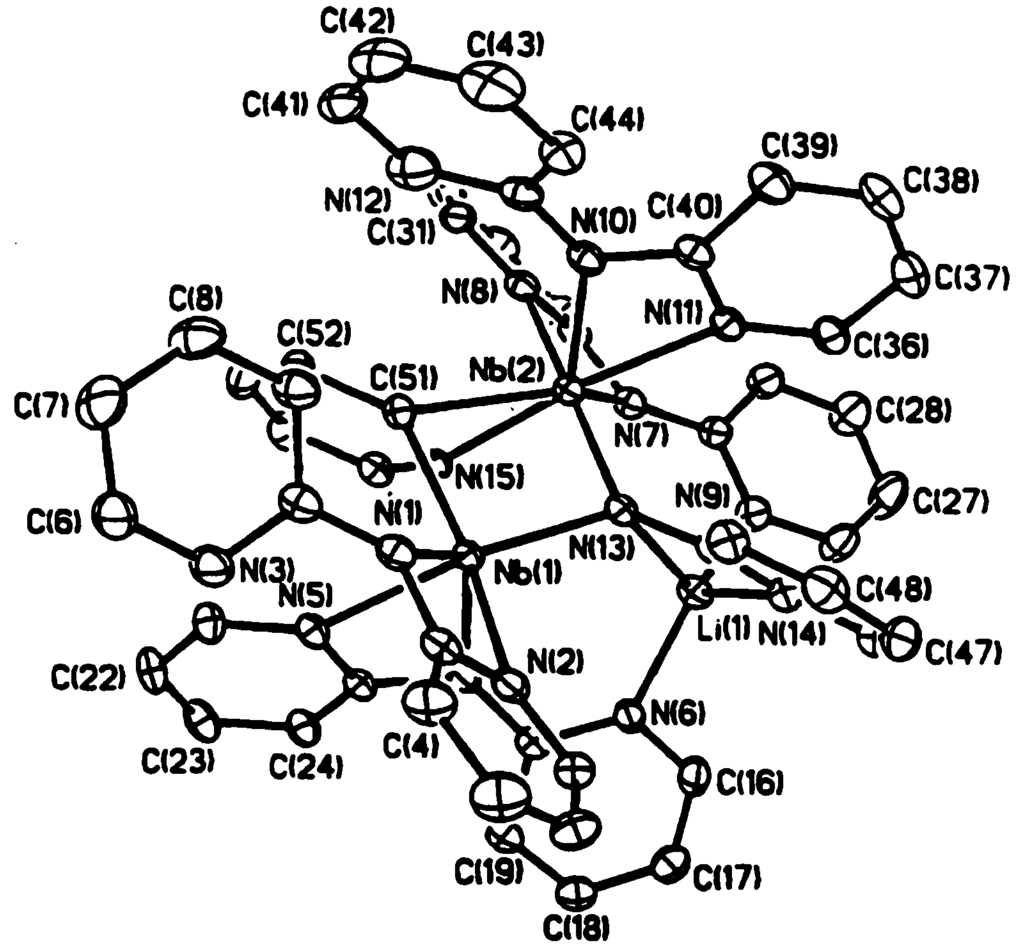


Fig 5.3: ORTEP drawing of **5.2**. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances are in angstroms (Å) and angles in deg (°): Nb1-Nb2 = 2.7022(4), Nb(1)-N(13) = 2.011(3), Nb(1)-N(15) = 2.125(3), Nb(1)-C(51) = 2.164(3), Nb(1)-N(1) = 2.184(3), Nb(1)-N(4) = 2.244(3), Nb(1)-N(2) = 2.277(3), Nb(1)-N(5) = 2.315(3), Nb(2)-N(15) = 2.125(3), Nb(2)-C(51) = 2.174(3), Li(1)-N(6) = 2.003(7), N(13)-Nb(1)-C(51) = 97.19(12), C(51)-Nb(1)-N(1) = 91.72(12), C(51)-Nb(1)-N(4) = 120.37(11), C(51)-Nb(1)-N(2) = 150.64(12), N(1)-Nb(1)-N(2) = 59.30(11), C(51)-Nb(1)-N(5) = 89.50(11), N(13)-Nb(2)-N(15) = 94.55(11), N(15)-Nb(2)-C(51) = 38.86(11), N(13)-Nb(2)-N(7) = 108.78(11), C(51)-Nb(2)-N(7) = 121.83(11).

V. 6: References

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CHAPTER VI

Reactions of a Niobium II Cluster, $Nb_2Cl_5Li(TMEDA)_3$, With Dimethylpyrrole; Pyrrole Dinitrogenation , TMEDA Fragmentation and Formation of Niobium IV Monomers

VI. 1: Introduction

Metal-promoted cleavage of C-N bond of amines is a very rare but desirable transformation. So far, this is limited to the cleavage of C-N bonds of strained amines[1] or amidines[2]. Only by using highly reactive trivalent group 5 metals (Nb and Ta) was it possible to rupture the C-N single bond of aniline[3] and to afford ring opening of the pyridine aromatic ring[4]. These remarkable reactions are important from the perspective of and the possibilities in industrial applications such as denitrogenation[5] of crude oil, catalytic degradation of heterocycles,[6] catalysis and extrusion of nitrogen and ammonia from organic compounds.[7]

In Chapter II we have described the serendipitous preparation and characterization of a Nb(II) cluster $Nb_2Cl_5Li(TMEDA)_3$ and described how this species, upon ligand replacement by anionic amides, performs C-N, N-N, and C-H bond cleavage.[8] In this chapter, we describe the first example of nitrogen atom abstraction from a pyrrolyl ring to form a dinuclear nitrido- and dienyl bridged complex during the reaction of $Nb_2Cl_5Li(TMEDA)_3$ with $2,5\text{-}Me_2C_4H_2N^{(-)}$. A second product from the same reaction shows fragmentation of the TMEDA molecule to originate an unprecedented amido/carbene/hydride complex. Both compounds were isolated in analytically pure form by fractional crystallization and their structures were elucidated by X-ray diffraction.

Conversely, when the $C_4H_4N^-$ or $C_8H_6N^-$ ligands were treated with $Nb_2Cl_5Li(TMEDA)_3$ a disproportionation reaction occurred in both cases only the oxidized Nb(IV) species were isolated. The structures of the isolated products produced in these reactions were elucidated by X-ray diffraction.

VI. 2: Experimental Section

All operations were performed under an inert (N_2 or Ar) atmosphere using standard Schlenk techniques, or in a nitrogen-filled drybox (Vacuum Atmosphere). Solid $Nb_2Cl_5Li(TMEDA)_3$ was prepared according to the procedure described in Chapter II. 2,5-dimethylpyrrole (Aldrich) was distilled under vacuum. 2,5-dimethylpyrrole lithium salt was prepared by treating the corresponding amine with MeLi in ether. Infrared spectra were recorded on a Mattson 9000 FTIR instrument from Nujol mulls prepared in a drybox. Samples for magnetic susceptibility measurements were prepared inside a drybox and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature. The magnetic moments were calculated by standard methods[9] and corrections for underlying diamagnetism were applied to the data.[10] Elemental analyses were carried out with a Perkin Elmer 2400 CHN analyzer. NMR spectra were recorded with a Bruker AMX 500 MHz spectrometer.

Preparation of $\{[(2,5\text{-}Me_2C_4H_2N)_2Nb][(\eta^5\text{-}2,5\text{-}Me_2C_4H_2N)(2,5\text{-}Me_2C_4H_2N)Nb](\mu\text{-}N)(\mu,\eta':\eta':\eta^4\text{-}1,4\text{-}Me_2C_4H_2)\}\{[(TMEDA)NbCl]_2(\mu\text{-}Cl)_3Li(TMEDA)\}$.2(toluene) (6.1):

Solid $Nb_2Cl_5Li(TMEDA)_3$ (2.0 g, 2.8 mmol) was added to a solution of 2,5-dimethylpyrrole lithium salt (1.1 g, 11.0 mmol) in THF (100 mL) at room temperature. The mixture was evaporated to dryness and the residual solid was redissolved in toluene (70 mL). After filtration, the addition of ether (30 mL) and standing at –30°C afforded dark crystals of **6.1** (0.2 g, 0.13 mmol, 14%). El. Anal. Calcd (found) for $C_{62}H_{105}N_{11}Nb_4LiCl_5$: C 47.72(47.66), H 6.78(6.43), N 9.87(9.27). I.R. [Nujol mull, cm^{-1}] ν: 1495(w), 1376(s), 1290(w), 1255(m), 1242(m), 1233(m), 1059(s), 1036(m), 1011(m), 949(m), 916(w), 792(s), 763(m), 743(m), 729(s), 697(w), 578(m). [$\mu_{eff} = 1.76\ \mu_B$]. ^1H-NMR [500 MHz, C_6D_6, 23°C, the tube was centrifugated to remove the purple insoluble $Nb_2Cl_5(TMEDA)_2$] δ: 7.13(m, 10H, toluene), 5.88(s, 2H, diene), 5.44(s, 4H, pyrrole), 5.41(s, 4H, pyrrole), 2.64(s, 6H, Me-pyrrole), 2.49(s, 6H, Me-pyrrole), 2.30(s, 8H, CH_2-tmeda), 2.15(s, 24H, Me-tmeda), 2.12(s, 6H, toluene), 2.08(broad-s, 12H, Me-pyrrole), 0.88(s, 6H, Me-diene). ^{13}C-NMR [127.7 MHz, C_6D_6, 23°C] δ: 139.2(quaternary-diene), 138.4, 135.3, 132.3(quaternary-pyrrole), 128.7, 128.9, 126.0 (toluene), 115.9(CH-diene), 107.6, 107.0(CH-pyrrole), 58.9(CH_2-tmeda), 46.2(Me-tmeda), 29.2(Me-diene), 21.4, 18.5, 18.4, 17.5(Me-pyrrole), 13.0(Me-toluene).

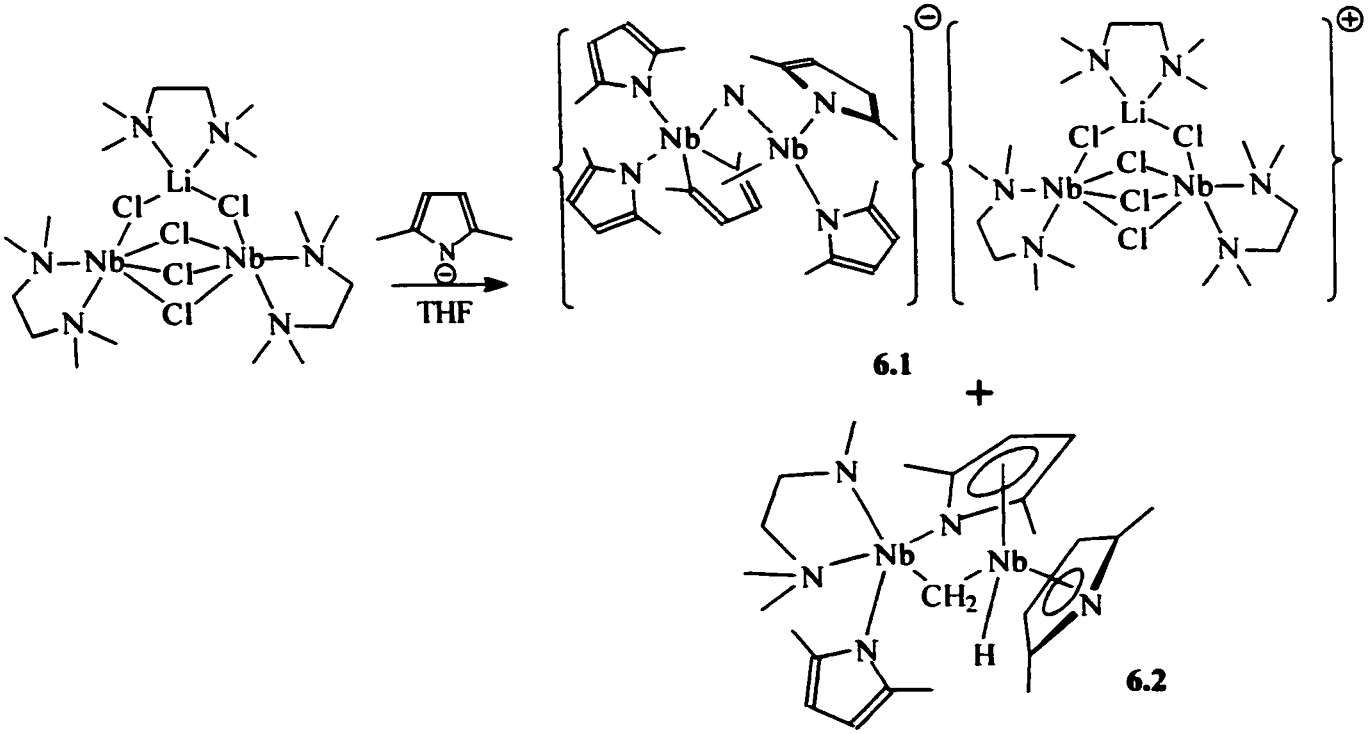
Preparation of $[(\eta^5\text{-}2,5\text{-}Me_2\ C_4H_2N)Nb][(2,5\text{-}Me_2C_4H_2N)(Me_2NCH_2CH_2NMe)Nb](\mu\text{-}H)(\mu\text{-}CH_2)(\mu,\eta^1:\eta^4\text{-}2,5\text{-}Me_2C_4\,H_2N)$ (6.2):

The mother liquor of the above preparation was evaporated to dryness. The solid residue was redissolved in ether (100 mL), quickly filtered and allowed to stand undisturbed at room temperature for a few hours. Dark green crystals of **6.2** separated (0.05 g, 0.08 mmol, 9%). El. Anal. Calcd (found) for $C_{24}H_{40}N_5Nb_2$: C 49.32 (48.94), H 6.90(6.71), N 11.98(11.83). I.R. [Nujol mull, cm^{-1}] ν: 1637(m), 1374(s), 1341(w), 1278(w), 1260(m), 1240(s), 1195(m), 1161(w), 1103(br-s), 1055(s), 1053(s), 1018(s), 1015(s), 949(m), 871(m), 836(w), 822(m), 801(br-m), 790(s), 730(s), 670(w), 641(w). ^{1}H-NMR [500 MHz, C_6D_6, 23°C] δ: 9.22(br-s, 2H, bridging CH_2), 5.59(s, 4H, CH-pyrrole), 4.91(br-s, 1H, hydride), 1.85(s, 12H, Me-pyrrole). [$\mu_{eff} = 1.77\ \mu_B$].

VI. 3: Results and Discussion

According to Scheme 6.1 reaction of $Nb_2Cl_5Li(TMEDA)_3$ with the dimethyl pyrrole lithium salt 2,5-$Me_2C_4H_2NLi$ gave a rapid reaction in THF to afford a mixture of two different compounds: the ionic {[(2,5-$Me_2C_4H_2N)_2Nb$][(η^5-2,5-Me_2 C_4H_2N)(2,5-$Me_2C_4H_2N$)Nb](μ-N)(μ,η':η':η^4-1,4-$Me_2C_4H_2$)}{[(TMEDA)NbCl]$_2$(μ-Cl)$_3$ Li(TMEDA)}·2(toluene) (**6.1**) and the neutral [(η^5-2,5-$Me_2C_4H_2N$)Nb][(2,5-$Me_2C_4H_2N$)($Me_2NCH_2CH_2NMe$)Nb](μ-H)(μ-CH_2)(μ,η^1:η^4-2,5-$Me_2C_4H_2N$) (**6.2**) through a complex redox reaction. Both compounds were isolated in analytically pure form by fractional crystallization and their structures were elucidated by X-ray diffraction (Figure 6.1 and 6.2).

The cationic unit of **6.1** is a mixed valence Nb(II)/Nb(III) {[(TMEDA)NbCl]$_2$(μ-Cl)$_3$Li(TMEDA)}$^{(+)}$ species. The structural data clearly indicate that complex **6.1** is a mixed valence species containing a Nb(II)/Nb(III) cation, necessarily paramagnetic, and a Nb(IV)/Nb(IV) anion probably, diamagnetic (Scheme 6.1). Accordingly, the complex shows a magnetic moment [μ_{eff} = 1.76 μ_B per formula] indicative of the presence of only one unpaired electron per formula unit. Furthermore, treatment of crystalline **6.1** with THF separated the paramagnetic mixed valence {[(TMEDA)NbCl]$_2$(μ-Cl)$_3$ as a insoluble, paramagnetic purple solid[8b] and produced a diamagnetic solution whose NMR spectra were consistent with the formulation {[(2,5-Me$_2$C$_4$H$_2$N)$_2$Nb][(η^5-2,5-Me$_2$C$_4$H$_2$N)(2,5-Me$_2$C$_4$H$_2$N)Nb](μ-N)(μ,η':η':η^4-1,4-Me$_2$C$_4$ H$_2$)}{Li(TMEDA)$_2$}. The diamagnetism of this anion may be explained with the presence of a Nb-Nb single bond which is in agreement with the fairly short Nb-Nb distance [Nb1-Nb2 = 2.7872(7)Å].



Scheme 6.1

Complex **6.2** is a paramagnetic mixed valence Nb(III)/Nb(IV) species and shows a value of the magnetic moment consistent with the presence of one unpaired electron per formula unit [μ_{eff} = 1.77 μ_B per formula]. In this case it was not possible to obtain satisfactory NMR data in agreement with the proposed formulation. However, chemical degradation experiments carried out with anhydrous HCl in a closed vessel connected to a Toepler pump yielded 64% of the expected amount of H_2 and CH_4. The presence of a medium intensity resonance at 1637cm^{-1} of the IR spectrum (Nb-H stretching) suggests that complex **6.2** should be regarded as a terminal rather than bridging hydride species. Unfortunately, isotope exchange experiments with D_2 failed due to the fact that the complex reacts in a destructive manner with hydrogen gas. In spite of the paramagnetism, reproducible ^{1}H-NMR spectra show the resonances of two pyrrolyl rings as sharp and well solved peaks. Two rather broad features possibly show the proper integration for the presence of the hydride (4.91 ppm) and the methylene group (9.22 ppm). Conversely, no resonances were conclusively identified for the de-methylated TMEDA. Perhaps the partial spectrum resolution may be ascribed to either the 18 electron configuration of the niobium atom π-bonded to two pyrrolyl ring, or to possible dissociation of the dimeric structure in solution.

The formation of **6.1** and **6.2** arises from two different processes within the same reaction. Complex **6.1** is clearly the result of the cooperative attack of the two Nb(II) centers on one pyrrolyl anion. The *four* electrons necessary to form the nitride and the dienyl dianion are obtained from the *five* electrons provided by the oxidation of the four Nb(II) centers during the formation of **6.1**. The formation of **6.2** arises instead from the cleavage of one CH_3-N bond of the TMEDA molecule and subsequent oxidative addition of Nb atoms into the C-H bond of the cleaved CH_3 group. This process also requires *four* electrons. However, complex **6.2** is a mixed valence Nb(III)/Nb(IV) species and thus only *three* electrons were obtained from the two metal centers. Therefore, the formation of the two complexes appears to be interconnected in the sense that the total of eight electrons necessary for the pyrrole denitrogenation and TMEDA fragmentation are provided by the formal oxidation of five niobium(II) to originate three Nb(IV) and two Nb(III) centers. A sixth niobium atom preserves the original divalent oxidation state and forms the mixed-valence Nb(II)/Nb(III) countercation of **6.1.**

VI. 4: X-ray Crystallography

Suitable crystals were selected, mounted on thin, glass fibers using paraffin oil and cooled to the data collection temperature. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω-scans at 0, 90, and 180° in ϕ. Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied .[11]

No symmetry higher than triclinic was observed for **6.1**, monoclinic for **6.2.** Systematic absences in the diffraction data and unit-cell parameters were consistent with P1 and $P\bar{1}$ for **6.1** and *Cc* and *C2/c* for **6.2**. The structures were solved by direct methods, completed with difference Fourier syntheses and refined with full-matrix least-squares procedures based on F^2. Solutions in certain space groups yielded computationally stable and chemically reasonable results of refinement. The compound molecules were located at inversion centres. All non-hydrogen atoms were located and refined with anisotropic displacement parameters except the cocrystallized solvent atoms which were refined isotropically to conserve a favorable data/parameter ratio. All hydrogen atoms were introduced at their idealized positions and refined with a riding mode. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 5.10 program library.[12]

The cation in complex **6.1** displays isostructural connectivity with the starting material $Nb_2Cl_5Li(TMEDA)_3$ but with significantly different bond distances and angles. The most striking difference arises in the Nb-Nb distance [Nb3-Nb4 = 2.5211(6)Å] which is considerably longer than in the neutral starting complex [Nb-Nb 2.400(2)Å][8] and compares very well with that of the neutral mixed valence species $\{[(TMEDA)NbCl]_2(\mu\text{-}Cl)_3$ [Nb-Nb = 2.545(1)Å].[8b] The anionic unit (Figure 6.1) is formed by two tetravalent niobium atoms linked together by one bridging nitride and one bridging dienediyl moiety, both arising from dimethylpyrrole denitrogenation. This moiety is σ-bonded to the first metal center using the two terminal carbon atoms thus forming a planar nioba-cyclopentadiene ring, and is also symmetrically π-bonded to the second metal center.

Complex **6.2** features a dinuclear structure with two inequivalent niobium atoms (Figure 6.2). The first niobium is π-bonded to two pyrrolyl rings forming a bent metallocene-like structure. One of the two pyrrolyl ring is also σ-bonded to the second niobium atom which, in turn, is σ-bonded to another pyrrolyl ring and to one de-methylated TMEDA. One bridging methylene group [Nb1-C1 = 2.098(4), Nb2-C1 = 2.272(4)] and one hydride [Nb1-H1 = 2.270(6)Å, Nb2-H1 = 1.708(6)Å] are asymmetrically placed between the two metal centers and complete the structure. The crystal structure was of sufficient quality to locate and refine the hydride and the methylene hydrogen atom positions. Crystal data along with and structure analysis results for **6.1-6.2** compounds are given in **Appendix E**.

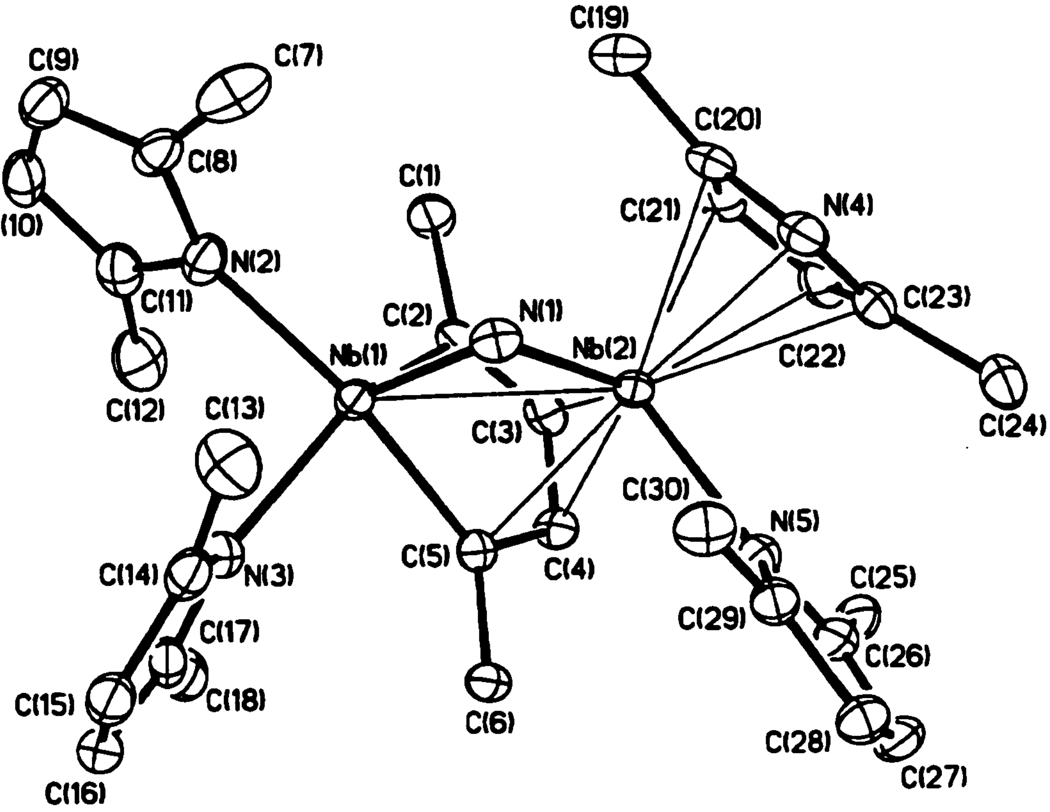


Fig 6.1: ORTEP drawing of the anion of **6.1**. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å), angles (°), and torsion angles (°): Nb(1)-Nb(2) = 2.7872(7), Nb(1)-N(1) = 1.857(3), Nb(2)-N(1) = 1.948(3), Nb(1)-C(2) = 2.162(4), Nb(1)-C(5)= 2.166(4), Nb(1)-C(2)-C(3)-C(4) = 5.5(2), Nb(1)-C(5)-C(4)-C(3) = 2.6(2), Nb(2)-C(2) = 2.423(4), Nb(2)-C(3) = 2.379(4), Nb(2)-C(4) = 2.378(4), Nb(2)-C(5) = 2.390(4), Nb(1)-N(2)-C(8)-C(9) = 193.2(2), Nb(1)-N(2) = 2.166(3), Nb(1)-N(3) = 2.154(3), Nb(2)-N(4) = 2.483(4), Nb(2)-C(20) = 2.468(4), Nb(2)-C(21) = 2.437(4), Nb(2)-C(23) = 2.519(4).

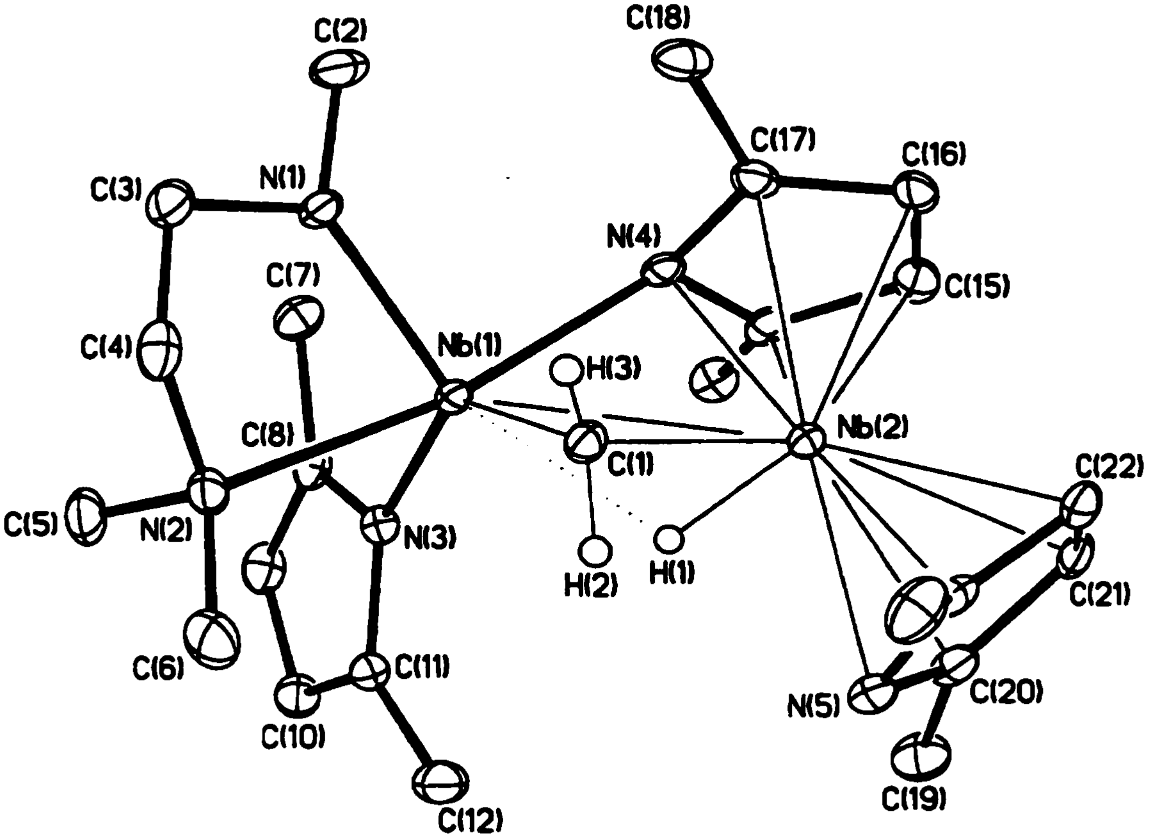


Fig. 6.2: ORTEP drawing of **6.2**. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (°): Nb(2)-N(4) = 2.201(3), Nb(2)-C(17) = 2.319(4), Nb(2)-C(16) = 2.417(4), Nb(2)-N(5) = 2.341(3), Nb(2)-C(20) = 2.355(4), Nb(2)-C(21) = 2.442(4), Nb(1)-N(2) = 2.404(4), Nb(1)-N(1) = 2.004(3), Nb(1)-N(3) = 2.172(3), Nb(1)-N(4) = 2.201(3), Nb(1)-C(1) = 2.098(4), Nb(2)-C(1) = 2.272(4), Nb(1)-C(1)-Nb(2) = 85.7(2), $C_4N_{centroid}$-Nb(2)-$C_4N_{centroid}$ = 136.6(2).

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CHAPTER VII

Reactions of Di- and Trivalent Niobium Halides with Pyrrolide Anions

VII. 1: Introduction

Anionic organic amides as supporting ligands are well known for their unique ability to stabilize highly reactive low-valent early transition metal complexes and to support unusual reactivity such as dinitrogen fixation activation.[1] However, attempts of taking advantage of the unique properties of these ligands for rationally developing the chemistry of di- and trivalent niobium provided instead an uncontrollable reactivity which resulted in a series of serendipitous yet attractive transformations including rare examples of C-N single bond cleavage.[2]

As described in the previous chapter, simple chlorine replacement reaction with pyrrolide anion of a $Nb_2Cl_5Li(TMEDA)_3$ cluster triggered a complex series of reactions leading to both nitrogen abstraction from the pyrrolide ring and oxidative addition to a C-H bond of a saturated tertiary amine.

The uniqueness and the caliber of these reactions prompted us to the most obvious next step of this study which was an investigation of the behavior of low-valent niobium species with different pyrrolides. In particular, we were interested in examining the behavior of divalent Nb with the less crowded derivative of the series, the pyrrolide anion itself, and the indenyl anion. This second anion was regarded as particularly interesting because of the condensation with an aromatic ring which may substantially modify the electronic configuration of the pyrrolide moiety thus affecting in the end the chemical reactivity of the metal center. In addition, we were also interested in probing the behavior of the recently prepared dipyrrolide anions given the ability of these ligands to assemble polymetallic structures capable of performing cooperative reduction on the same substrate.

In this chapter we wish to report the formation of Nb(IV) complexes with pyrrolyl, indolyl monoanions and diphenylmethanedipyrrolyl dianions resulting from disproportionation pathways that ensue upon reaction of Nb(II) with these ligands.

VII. 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). Solid $Nb_2Cl_5Li(TMEDA)_3$ and $Nb_2Cl_6(TMEDA)_2$ were prepared according to the procedure described in chapter II and in the literature.[3] Pyrrole (Aldrich) was distilled under vacuum. Indole (Aldrich) was deaerated under vacuum at 25°C. Diphenyldipyrrolyl methane was prepared according the reported procedure.[4] A suspension of KH in mineral oil was washed with anhydrous hexane and dried under vacuum. The lithium salts of pyrrole and indole were prepared by treating the corresponding amines with MeLi in ether. Infrared spectra were recorded on a Mattson 9000 FTIR instrument from Nujol mulls prepared in a drybox. Samples for magnetic susceptibility measurements were prepared inside a drybox and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature. The magnetic moments were calculated by standard methods[5] and corrections for underlying diamagnetism were applied to the data.[6] Elemental analyses were carried out with a Perkin Elmer 2400 CHN analyzer.

Preparatio of $(C_4H_4N)_6Nb[Li(thf)_4]_2.thf$ (7.1):

Solid $Nb_2Cl_5Li(TMEDA)_3$ (2.0 g, 2.8 mmol) was added to a solution of pyrrolylLi (0.86 g, 11.16 mmol) in THF (100 mL) at room temperature. The mixture was allowed to stir for one hour. The volume of the solution was reduced (70 mL). Standing at room temperature for three days afforded yellow crystals of **7.1** (2.25 g, 1.96 mmol, 35%). El. Anal. Calcd (found) for $C_{60}H_{96}N_6O_9Li_2Nb$: C 62.54(61.43), H 8.40(7.78), N 7.29(7.02). I.R. [Nujol mull, cm^{-1}] ν: 1683(s), 1567(s), 1436(vs), 1340(w), 1282(s), 1197(m), 1143(vs), 1091(s), 1060(s), 1066(s), 1024(s), 950(w), 912(s), 890(s0, 838(s), 800(w), 752(vs), 734(vs), 671(w), 649(s). [$\mu_{eff} = 1.68\ \mu_B$].

Preparation of $(C_8H_6N)_6Nb[Li(thf)_4]_2$ (7.2):

To a solution of indolylLi (1.37 g, 11.13 mmol) in THF (100 mL), $Nb_2Cl_5Li(TMEDA)_3$ (2.0 g, 2.8 mmol) was added. The mixture was allowed to stir for one hour. The volume of the solution was reduced (50 mL) and layered with ether (30 mL). Standing at room temperature for two days afforded dark red crystals of **7.2** (2.17 g, 1.57 mmol, 28%). El. Anal. Calcd (found) for $C_{80}H_{100}N_6O_9Li_2Nb$: C 69.60(68.97), H 7.30(6.88), N 6.09(5.78). I.R. [Nujol mull, cm^{-1}] ν: 1596(w), 1432(br), 1336(w), 1276(s), 1201(W), 1151(s), 1130(br), 1110(w), 1064(s), 1037(br), 1010(s), 954(s), 935(s), 879(s), 759(w), 738(vs), 669(w), 620(s). [$\mu_{eff} = 1.70\ \mu_B$].

Preparation of $[Ph_2C(C_4H_4N)_2]_3Nb[K(thf)_2]_2$ (7.3):

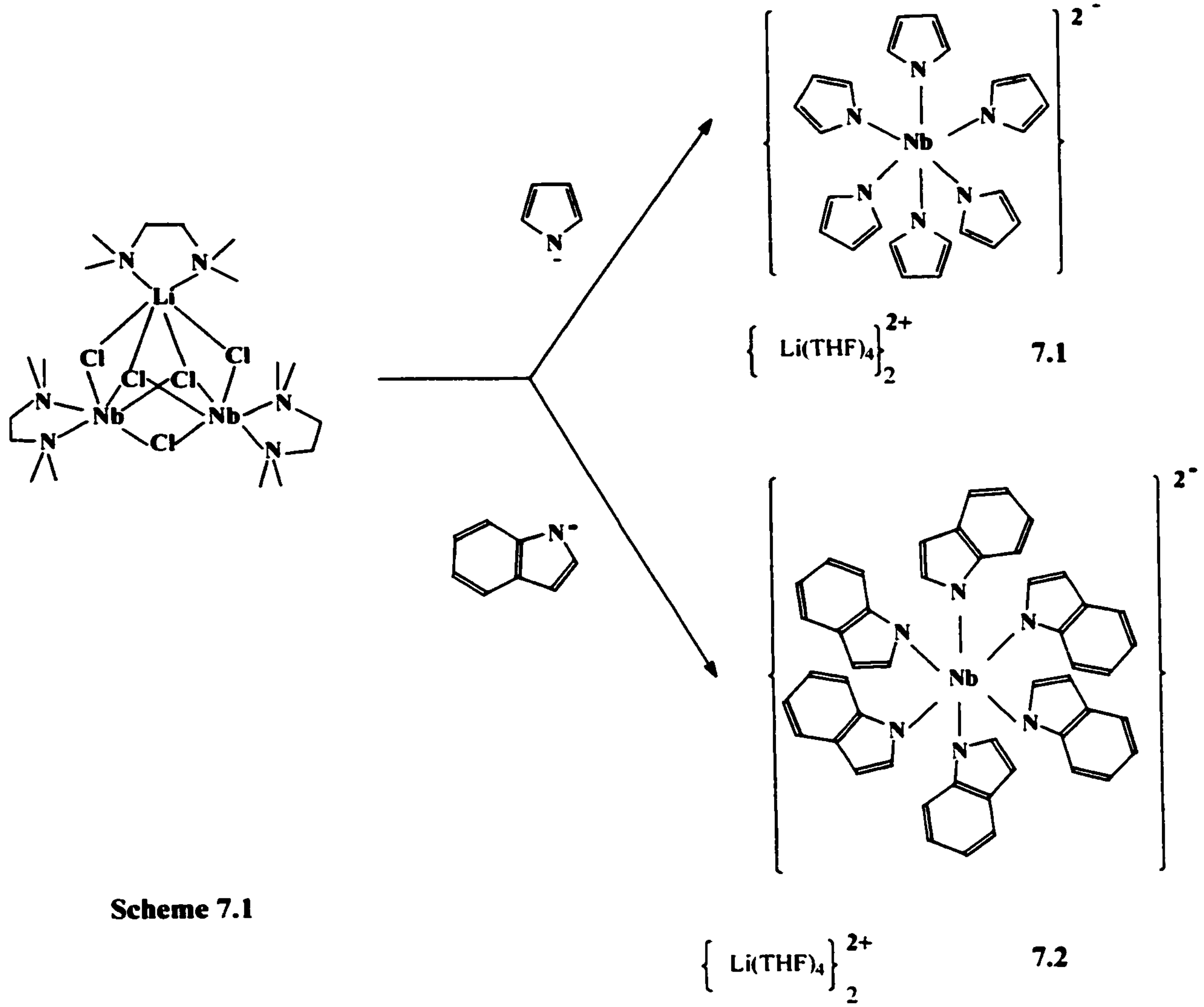
A solution of $Ph_2C(C_4H_4N)_2H_2$ (1.9 g, 6.4 mmol) in THF (150 mL) was treated with KH (0.51 g, 12.75 mmol). Solid $Nb_2Cl_6(TMEDA)_2$ (1.0 g, 1.6 mmol) was added to the resulting suspension. The slurry was refluxed overnight during which time the insoluble starting materials were dissolved. After filtration of a small amount of insoluble material, the solution was concentrated *in vacuo* to 70 mL and layered with hexane which afforded dark red crystals of **7.3** (0.86 g, 0.61mmol, 38%). El. Anal. Calcd (found) for $C_{85}H_{94}K_2N_6NbO_4$: C 71.15(70.89), H 6.60(5.97), N 5.86(5.33). I.R. [Nujol mull, cm^{-1}] ν: 1594(br), 1484(s), 1319(w), 1270(w), 1243(br), 1214(s), 1182(s), 1133(s), 10959(br), 1079(br), 1047(s), 988(s), 975(vs), 921(w), 898(br), 869(w), 856(w), 792(br), 744(br), 709(s), 698(br), 655(vs), 632(s), 617(w), 607(w). [$\mu_{eff} = 1.38\ \mu_B$].

VII. 3: Results and Discussion

Reaction of $Nb_2Cl_5Li(TMEDA)_3$ with the lithium salts of pyrrole and indole afforded paramagnetic, anionic niobium IV complexes of formula $[(Pyrr)_6Nb][Li(THF)_4]_2$ [pyrr = pyrrolyl, indolyl] (Scheme 7.1). The magnetic moment of these two compounds were slightly lower than expected for a spin-only d^1 electronic configuration. The deviation from the expected spin-only value is likely to be ascribed to spin-orbit coupling as a common feature for 2^{nd} and 3^{rd} row metals. Combustion analysis data in agreement with the proposed formulation were also obtained. The chemical connectivity was elucidated by X-ray crystal structures.

The fact that both complexes contain the metal in the tetravalent oxidation state suggests that the formation of these two species may arise either from a disproportionation pathway or convoluted molecular activation processes. In spite of reiterated attempts, we find no sign for the presence of other species in the reaction mixtures of the mother liquors. Although a one-step disproportionation process involving a variation of oxidation state of two units in unlikely, it is possible that the reaction is in fact the result of two subsequent disproportionations similar to the case of the reaction of $Nb_2Cl_5Li(TMEDA)_2$ complex with tripodal tripyrrolide anions (see Chapter III). Although at this stage we can only speculate, we observe that the behavior is strikingly different from that of similar reactions with other amides and dimethylpyrrolide anions reported in the previous chapters of this thesis which were leading to molecular activation processes. This perhaps indicates that steric hindrance rather than electronic factors play a critical role in determining the fate of the intermediate aggregate or cluster and determine the type of chemical transformation (disproprotionation versus molecular activation).

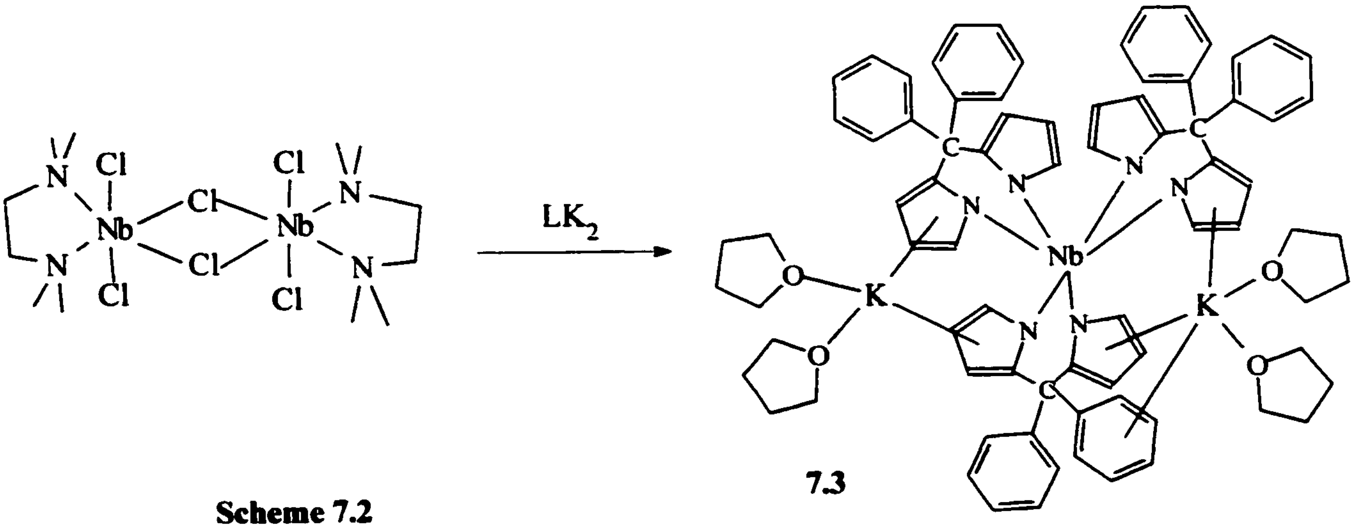
Polypyrrole and porphyrine ligands display a remarkable ability to stabilize low-oxidation states. Highly reactive species displaying unusual reactivity patterns such as low-valent samarium, titanium and vanadium, have been stabilized by using these particular ligand systems. However, in the case of niobium only the oxidation states +4 and +5 have been investigated with these particular ligand systems. This simple observation prompted us to study the reaction of our divalent niobium cluster with the



Scheme 7.1

recently prepared dipyrrolyl dianion which displayed a remarkable versatility in the chemistry of divalent samarium. The most salient characteristic of this particular ligand system can be summarized in an enhanced tendency to assemble di- and polymetallic structures by crossing σ- and π-bonding interactions. Thus, the possibility for the metal center of experiencing the presence of one π-bonded pyrrole ring (similar to a Cp system) and one σ-bonded (as a regular amide) provideds the metal with an unusual stability, steric protection and rigidity which may help the stabilization of exotic oxidation states and preventing unwanted dynamism such as that leading to disproprotionation.

This rationale prompted us to study the reaction of $Nb_2Cl_5Li(TMEDA)_3$, with the diphenylmethane dipyrrolyl anion. Unfortunately, only intractable materials were obtained. Therefore, the far less reactive $Nb_2Cl_6(TMEDA)_2$ was examined as alternative starting material. By using a 2:1 ratio of ligand to niobium, another tetravalent complex $[Ph_2C(C_4H_4N)_2]_3Nb[K(thf)_2]_2$ (**7.3**) was isolated in moderate yield (Scheme 7.2). The magnetic moment and the elemental analysis are in agreement with the formulation as provided by the X-ray crystal structure. The magnetic moment is also in agreement with the d^1 electronic configuration of tetravalent niobium compound.



7.3

Scheme 7.2

In conclusion, the employment of a substantially different pyrrolide-based ligand system, alkali cation, and starting materials containing niobium in different oxidation states, led invariably to the formation of an homoleptic tetravalent and dianionic pyrrolide derivative. Since both di- and trivalent salts invariably disproportionated towards the tetravalent state, it is possible that the initial attack of one or more pyrrolide anion on Nb(II) destabilize the divalent oxidation state and triggers the initial disproprotionation to the trivalent state. These species in turn evolve toward the tetravalent state via another subsequent disproprotionation. Given this behavior, it seems legitimate to conclude that this behavior is rather general. Thus, a fascinating question arises about the factors which promoted the unique case of denitrogenation observed in the case of the dimethylpyrrolide. In fact, the differences in geometry, steric and electronic features with respect to the other pyrrolide ligands hardly justify the remarkable difference in chemical behavior. Further work will be necessary to elucidate this important point which will allow to gain a better grasp in denitrogenation processes.

VII. 4: X-ray Crystallography

Suitable crystals were selected, mounted on thin glass fibers using viscous oil and cooled to the data collection temperature. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω-scans at 0, 90, and 180° in ϕ. Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied for **7.2** and **7.3**; no absorption corrections were required for **7.1**.[7]

No symmetry higher than triclinic was evident from the diffraction data for **7.1**. Solution in *P*-1 yielded chemically reasonable and computationally stable results of refinement. Systematic absences in the diffraction data and the unit-cell parameters are consistent with *R*3, *R*-3, *R*32, *R*3*m* and *R*-3*m* for **7.2** and *Cc* and *C*2/*c* for **7.3**. For **7.2**, only the solution in *R*-3 yielded chemically reasonable and computationally stable results of refinement. For **7.3**, the absence of a molecular center of inversion or two-fold axis and *Z*=2 is consistent with the acentric *Cc* space group. The structures were solved by direct methods, completed with difference Fourier syntheses and refined with full-matrix least-squares procedures based on F^2. Two half anions were each located at an inversion center in **7.1**. The cation is located at a three-fold rotation axis in **7.2** while the anion was located at a three-fold improper rotation axis. Two half-occupied cocrystallized molecules of thf solvent and a molecule of hexane solvent were located in the asymmetric units of **7.1** and **7.3**, respectively. The absolute structure parameter of **7.3** refined to nil indicating that the true hand of the data has been determined. All non-hydrogen atoms, except the isotropically refined carbon atoms of the cocrystallized hexane molecule in **7.3**, were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHEXTL 5.10 program library.[8] Crystal data along with and structure analysis results for **7.1**-**7.3** compounds are given in **Appendix F**.

The structure of **7.1** consists of a symmetry generated monomeric octahedral niobium atom [N(3)-Nb(1)-N(3)a = 180.0°, N(3)-Nb(1)-N(1) = 89.4(2)°] surrounded by six σ-bonded pyrrole rings [Nb(1)-N(3) = 2.144(4)Å, Nb(1)-N(3)a = 2.144(4)Å, Nb(1)-N(1) = 2.140(4)Å, Nb(1)-N(1)a = 2.140(4)Å, Nb(1)-N(2)a = 2.141(4)Å, Nb(1)-N(2) = 2.141(4) Å] (Figure 7.1). For each anionic unit there are also two tetrahedral [Li(THF)$_4$] cations [Li(1)-O(2) = 1.890(12)Å, Li(1)-O(1) = 1.904(11)Å, O(2)-Li(1)-O(1) = 103.2(5)°, O(2)-Li(1)-O(4) = 106.6(5)°] thus doubtlessly assigning the formal oxidation state +IV to the niobium atom. The Nb-N distances fall in the expected range.

Compound **7.2** displays structural features and bond distances and angles which compare very well with those of **7.1**. Even in this case, the complex consists of an octahedral niobium atom [N(1)-Nb-N(1)c = 180.00(12)] (Figure 7.2) with the coordination geometry defined by the nitrogen atoms of six σ-bonded indenyl groups [Nb-N(1)a = 2.177(2)Å, Nb-N(1)b = 2.177(2)Å, Nb-N(1) = 2.177(2)Å, Nb-N(1)c = 2.177(2)Å, Nb-N(1)d = 2.177(2)Å, Nb-N(1)e = 2.177(2)]Å. Two solvated Li(THF)$_4$ groups complete the asymmetric unit. [Li-O(1) = 1.890(4)Å, Li-O(1)a = 1.890(4)Å, Li-O(2) = 1.980(13)Å and O(1)-Li-O(2) = 100.7(3)°, O(1)b-Li-O(1) = 110.4(12)°, O(1)b-Li-O(2) = 112.6(11)°, O(1)b-Li-O(1)a = 110.7(3)°, O(1)a-Li-O(1) = 110.4(12)°, O(1)a-Li-O(2) = 112.6(11)°.

The niobium center in compound **7.3** possesses a distorted octahedral geometry [N(6)-Nb-N(1) = 97.9(2)°, N(6)-Nb-N(5) = 83.8(2)°, N(1)-Nb-N(5) = 92.8(2)°, N(6)-Nb-N(4) = 93.8(2)°, N(1)-Nb-N(4) = 167.7(2)°, N(6)-Nb-N(3) = 172.6(2)°] defined by six nitrogen atoms of three σ-bonded [Nb-N(6) = 2.093(6)Å, Nb-N(1) = 2.088(5)Å, Nb-N(5) = 2.131(6)Å, Nb-N(4) = 2.177(6)Å, Nb-N(2) = 2.181(5)Å, Nb-N(3) = 2.231(6)Å] dipyrrolide units (Figure 7.3). The distortion of the coordination geometry in this particular case is determined by the particular architecture of the dipyrrolide ligands and steric constrain. Each ligand adopts a curiously distorted geometry with the planes of the two pyrrole rings forming obtuse dihedral angles (157.0°, 157.9°, 155.9°). The planes of the two phenyl substituents are nearly perpendicular to each other to minimize steric interactions (with the dihedral angle of 79.9°, 80.7°, 86.0°). Two potassium atoms each bearing two molecules of THF [K(1)-O(1) = 2.668(6)°, K(1)-O(2) = 2.720(6)°, K(2)-O(3) = 2.742(6)°, K(2)-O(4) = 2.812(8)°] are also connected to the Nb(dipyrrolide)$_3$ unit each π-coordinating two pyrrolyl rings from two different dipyrrolide units [distances of K to pyrrole ring centres are 2.857Å, 2.842Å, 3.132Å, 2.920Å]. However, one of the two potassium atoms display an additional π-interaction with one phenyl ring [K(2)-C(37) = 3.088(9)Å, K(2)-C(38) = 3.515(9)Å].

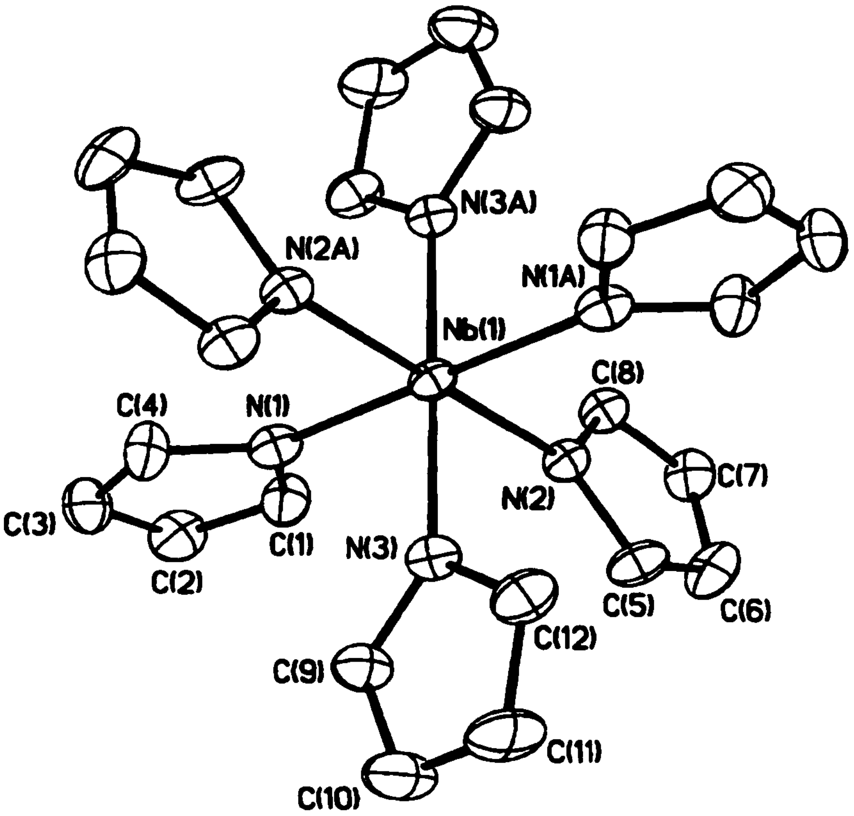


Fig. 7.1: ORTEP drawing of 7.1. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg.): Nb(1)-N(3) = 2.144(4), Nb(1)-N(3)a = 2.144(4), Nb(1)-N(1) = 2.140(4), Nb(1)-N(1)a = 2.140(4), Nb(1)-N(2)a = 2.141(4), Nb(1)-N(2) = 2.141(4), N(3)-Nb(1)-N(3)a = 180.0, N(3)-Nb(1)-N(1) = 89.4(2), Li(1)-O(2) = 1.890(12), Li(1)-O(1) = 1.904(11), O(2)-Li(1)-O(1) = 103.2(5), O(2)-Li(1)-O(4) = 106.6(5).

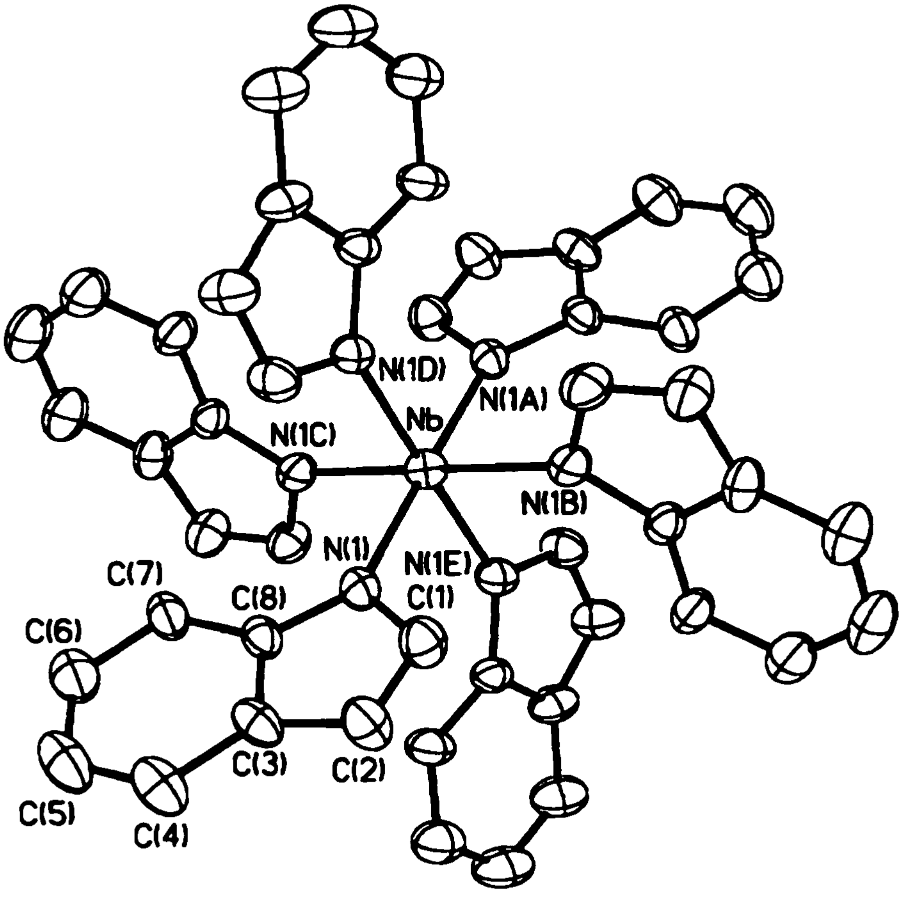


Fig. 7.2: ORTEP drawing of **7.2**. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg.): Nb-N(1)a = 2.177(2), Nb-N(1)b = 2.177(2), Nb-N(1) = 2.177(2), Nb-N(1)c = 2.177(2), Nb-N(1)d = 2.177(2), Nb-N(1)e = 2.177(2), Li-O(1) = 1.890(4), Li-O(1)a = 1.890(4), , Li-O(2) = 1.980(13), O(1)-Li-O(2) = 100.7(3), O(1)b-Li-O(1) = 110.4(12), O(1)b-Li-O(2) = 112.6(11), O(1)b-Li-O(1)a = 110.7(3), O(1)a-Li-O(1) = 110.4(12), O(1)a-Li-O(2) = 112.6(11), N(1)a-Nb-N(1)b = 87.51(10), N(1)a-Nb-N(1) = 87.51(10), N(1)b-Nb-N(1) = 87.51(10), N(1)a-Nb-N(1)c = 92.49(10), N(1)b-Nb-N(1)c = 92.49(10), N(1)-Nb-N(1)c = 180.00(12), N(1)a-Nb-N(1)d = 180.00(12), N(1)b-Nb-N(1)d = 92.49(10), N(1)-Nb-N(1)d = 92.49(10), N(1)c-Nb-N(1)d = 87.51(10), N(1)a-Nb-N(1)e = 92.49(10).

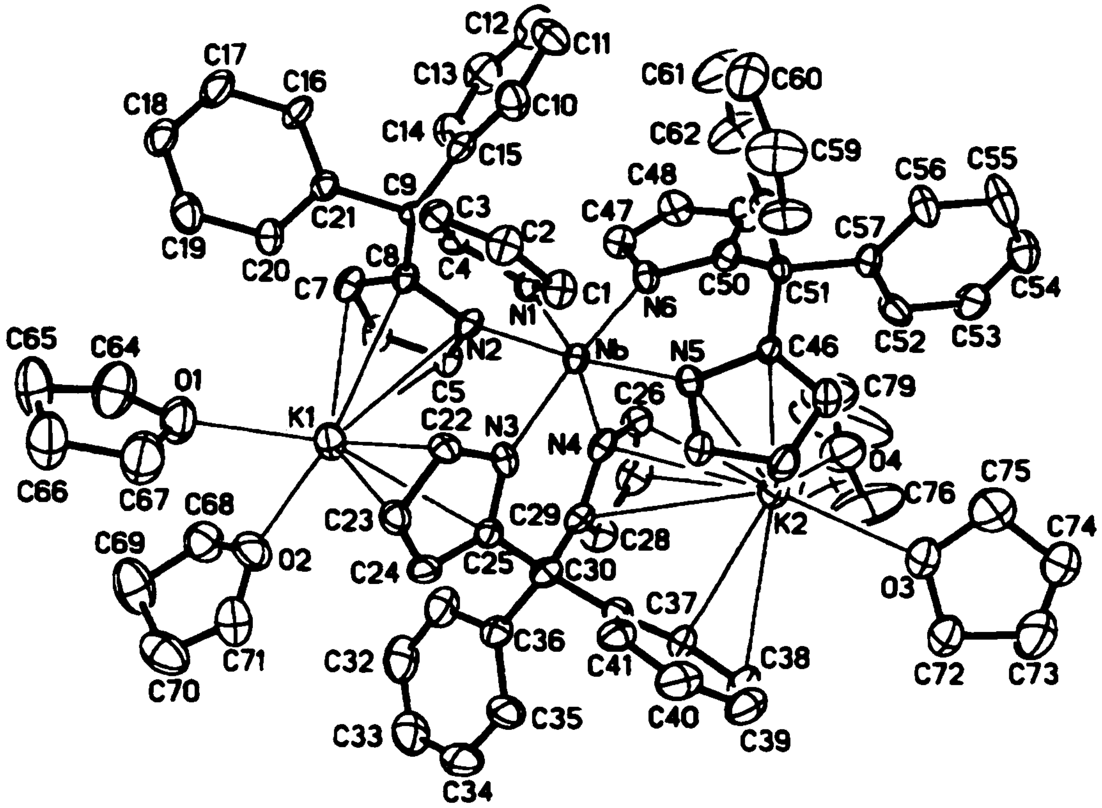


Fig. 7.3: ORTEP drawing of **7.3**. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg.): Nb-N(6) = 2.093(6), Nb-N(1) = 2.088(5), Nb-N(5) = 2.131(6), Nb-N(4) = 2.177(6), Nb-N(2) = 2.181(5), Nb-N(3) = 2.231(6), Nb-K(2) = 4.155(2), K(1)-C(23) = 2.954(9), K(1)-C(6) = 3.012(8), K(2)-N(4) = 3.029(6), K(2)-C(37) = 3.088(9), K(2)-C(26) = 3.097(9), K(2)-C(46) = 3.099(7), K(2)-N(5) = 3.167(6), N(6)-Nb-N(1) = 97.9(2), N(6)-Nb-N(5) = 83.8(2), N(1)-Nb-N(5) = 92.8(2), N(6)-Nb-N(4) = 93.8(2), N(1)-Nb-N(4) = 167.7(2), N(6)-Nb-N(3) = 172.6(2), C(1)-N(1)-Nb = 120.8(5), C(4)-N(1)-Nb = 132.0(4), C(4)-C(9)-C(8) = 112.7(6), C(29)-C(30)-C(25) = 113.6(6), C(46)-C(51)-C(50) = 113.2(6).

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CHAPTER VIII

Preparation and Characterization of Paramagnetic and Diamagnetic Nb(II) Amide Complexes; The Role of Alkali Cation on the Magnetic Properties

VIII. 1: Introduction

In the last few years there has been a dramatic increase in the research interest of the heavier group 5 elements in their lower oxidation states. One of the reasons is formation of M-M bonds along with other interesting topics such as: activation of N_2, CO, H_2 and acetylene and cleavage of C-N and C-H[1-3]. In fact the large range of M-M bonds has been observed for nearly all of the transition metals, forming species with metal-metal single bonds to metal-metal quadruple bonds.[4] In principle, with group 5 metals the d^3 electronic configuration makes these species good candidates for the formation of triply bonded complexes. Among these complexes there is a correlation between the M-M bond distance, the bond order and consequently the magnetism of the complex. For example a Nb^{II} pyrimidinate complex[4c] with the characteristic paddle-wheel shape has the shortest Nb-Nb distance known [2.2035(9) Å]. On the basis of its diamagnetism the existence of an "intrinsically stable" Nb-Nb triple bond was proposed. Also the $Nb_2Cl_5Li(TMEDA)_3$ cluster described in Chapter II, possesses a significantly short Nb-Nb distance [2.400 Å] and is diamagnetic, thus suggesting the presence of a Nb-Nb triple bond. Furthermore, the fact that the isostructural, mixed valence and cationic $[Nb_2Cl_5Li(TMEDA)]^+$ species displays a significantly longer intermetallic separation[5] indicates that the character of the Nb-Nb multiple bond indeed plays an important role in these compounds. We have now attempted the preparation of other paddle-wheel diniobium complexes by using other three-center chelating ligands (7-azaindolyl anion) which, with its coordination mode can provide long intermetallic distances[6].

VIII. 2: Experimental Section

All operations were performed under an inert atmosphere by using standard Schlenck techniques. $Nb_2Cl_5Li(TMEDA)_3$ was prepared according to the procedure described in Chapter III. 7-azaindole was purchased from Aldrich. Solvents were dried with the appropriate drying agents and distilled prior to use. Infrared spectra were recorded on a Mattson 9000 FTIR instrument from Nujol mulls prepared in a drybox. Samples for magnetic susceptibility measurements were prepared inside a drybox and sealed into calibrated tubes. The magnetic moments were calculated by standard methods[7] and corrections for underlying diamagnetism were applied to the data.[8] Elemental analyses were carried out with a Perkin Elmer 2400 CHN analyzer. NMR spectra were recorded with a Bruker AMX 500 MHz spectrometer.

Preparation of $(7\text{-azaindolyl})_4Nb_2[(\mu\text{-}Cl)Li(THF)_3]_2\cdot 2THF$ (8.1):

A solution of 7-azaindole (1.3 g, 11.1 mmol) in ether (70 mL) was treated with a solution of methyllithium in ether (8 mL, 1.4 M) at 0°C. The mixture was stirred for 20 minutes. Ether was removed *in vacuo* and replaced by THF (70 mL). $Nb_2Cl_5Li(TMEDA)_3$ (2.0 g, 2.8 mmol) was added and the mixture stirred overnight. After filtration, and allowing the resulting solution to stand at -30°C, blue crystals of **8.1** separated (1.4 g, 1.1 mmol, 39%). El. Anal. Calcd (Found) for $C_{60}H_{84}O_8N_8Nb_2Li_2Cl_2$: C

54.76(54.33), H 6.43(6.28), N 8.52(8.45). IR (Nujol mull, cm^{-1}) ν: 1591(s), 1556(s), 1417(m), 1334(s), 1199(s), 1147(s), 1113(s), 933(s), 912(s), 889(s), 798(s), 783(s), 757(s). H^1-NMR (d^8-THF, 500 MHz, 23°C) δ: 8.40 (br s, 1H), 7.93 (br m, 2H), 6.75 (br t, 1H), 6.11 (br s, 1H); H^1-NMR (d^6-acetone, 500 MHz, 23°C) δ: 8.20 (d, 1H), 7.93 (dd, 1H), 7.44 (d, 1H), 7.00 (dd, 1H), 6.45 (d, 1H).

Preparation of (7-azaindolyl)$_4$Nb$_2$·2THF (8.2):

A solution of 7-azaindole (1.3 g, 11.1 mmol) in THF (70 mL) was treated with KH (0.44 g, 11.1 mmol). After the initial vigorous gas evolution ceased, the mixture was stirred for additional 30 minutes at room temperature. Solid Nb$_2$Cl$_5$Li(TMEDA)$_3$ (2.0 g, 2.8 mmol) was added and the mixture stirred for 2 hours. The resulting suspension was centrifuged and the solid discarded. The remaining solution was allowed to stand overnight at room temperature upon which red-crystals of **8.2** separated (1.0 g, 1.2 mmol, 43%). El. Anal. Calcd (Found) for $C_{36}H_{36}N_8Nb_2O_2$: C 54.15(53.95), H 4.54(4.43), N 14.03(13.95). IR (Nujol mull, cm^{-1}) ν: 1590(s), 1554(br), 1417(m), 1405(m), 1332(s), 1278(s), 1257(s), 1141(s), 1112(br), 935(m), 910(w), 798(m), 784(m), 763(m), 727(br). H^1-NMR (d^6-acetone, 500 MHz, 23°C) δ: 8.25 (d, CH, 1H), 8.02 (d, CH, 1H), 7.45 (dd, CH, 1H), 7.08 (d, CH, 1H), 6.46 (d, CH, 1H), 3.67 (m, THF, 4H), 1.89 (m, THF, 4H).

VIII. 3: Results and Discussion

Reaction of Nb$_2$Cl$_5$Li(TMEDA)$_3$ with four equivalents of (7-azaindolyl)Li in THF afforded a deep blue solution from which dark-blue crystals of (7-azaindolyl)$_4$Nb$_2$[(μ-

Cl)Li(THF)$_3$]$_2$·2THF (**8.1**) were isolated in good yield (Scheme 8.1). Surprisingly, complex **8.1** which is made of discrete units, is paramagnetic in the solid state and to a small extent in solution in spite of displaying a Nb-Nb distance that is even slightly shorter than the corresponding linear polymeric compound which is reported as a diamagnetic compound.[6h]. A magnetic moment measurement as a function of the temperature (in a sealed quartz tube with a SQUID magnetometer), shows the presence of a residual paramagnetism at 4.5 K (0.6 μ_B per mole) (Figure 8.1). The magnetic moment increases sharply with the temperature to reach a maximum of 1.8 μ_B at 200K and then remains roughly constant up to 300 K. This behavior is most unusual and could infer the presence of an antiferromagnetically coupled dinuclear system. However, the behavior does not conform to that expected for a d^3-d^3, d^2-d^2 or a d^1-d^1 antiferromagnetic system (for such a systems the μ_B value would be much higher). A magnetization study at 3.0 K as a function of field (0-5.0 T) gave a linear response, suggesting the absence of any ferromagnetic coupling. Even though a complete interpretation of the magnetic behavior is not possible at this stage, we can confidently conclude that the sample is paramagnetic, tending towards an $S = 0$ ground state at low temperature. In THF solution, the NMR spectrum showed rather broad lines. A well-solved spectrum was obtained only in acetone solution where, however, the complex changed its color to dark orange-brown.

The paramagnetism of **8.1** might be inconsistent with the presence of a significant Nb-Nb triple bond and is inconsistent with the considerably short Nb-Nb distance. However, a geometry optimization calculation using the atomic coordinates of both **8.1** and the pyrimidinate derivative[4c] and using a force field without electrostatic interactions, predicted Nb-Nb distances of 2.7 and 2.5Å respectively. The value calculated for the 7-azaindolyl derivative is in nice agreement with that observed for the "superlong" quadruply bonded dichromium complex and other derivatives of the same ligand[6a] once the different dimensions of the metal atoms were taken into consideration. Thus the actual presence in both complexes of Nb-Nb distances in the range of 2.2Å clearly indic-

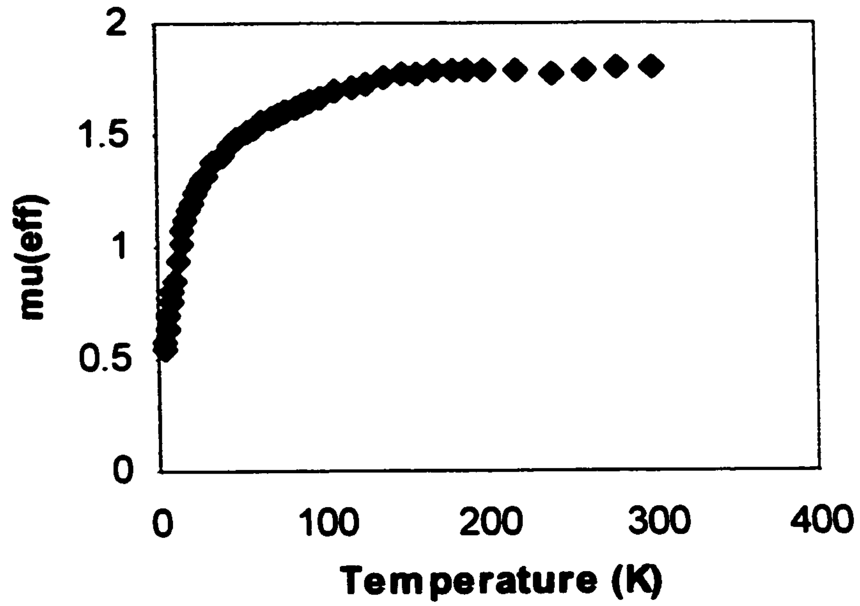


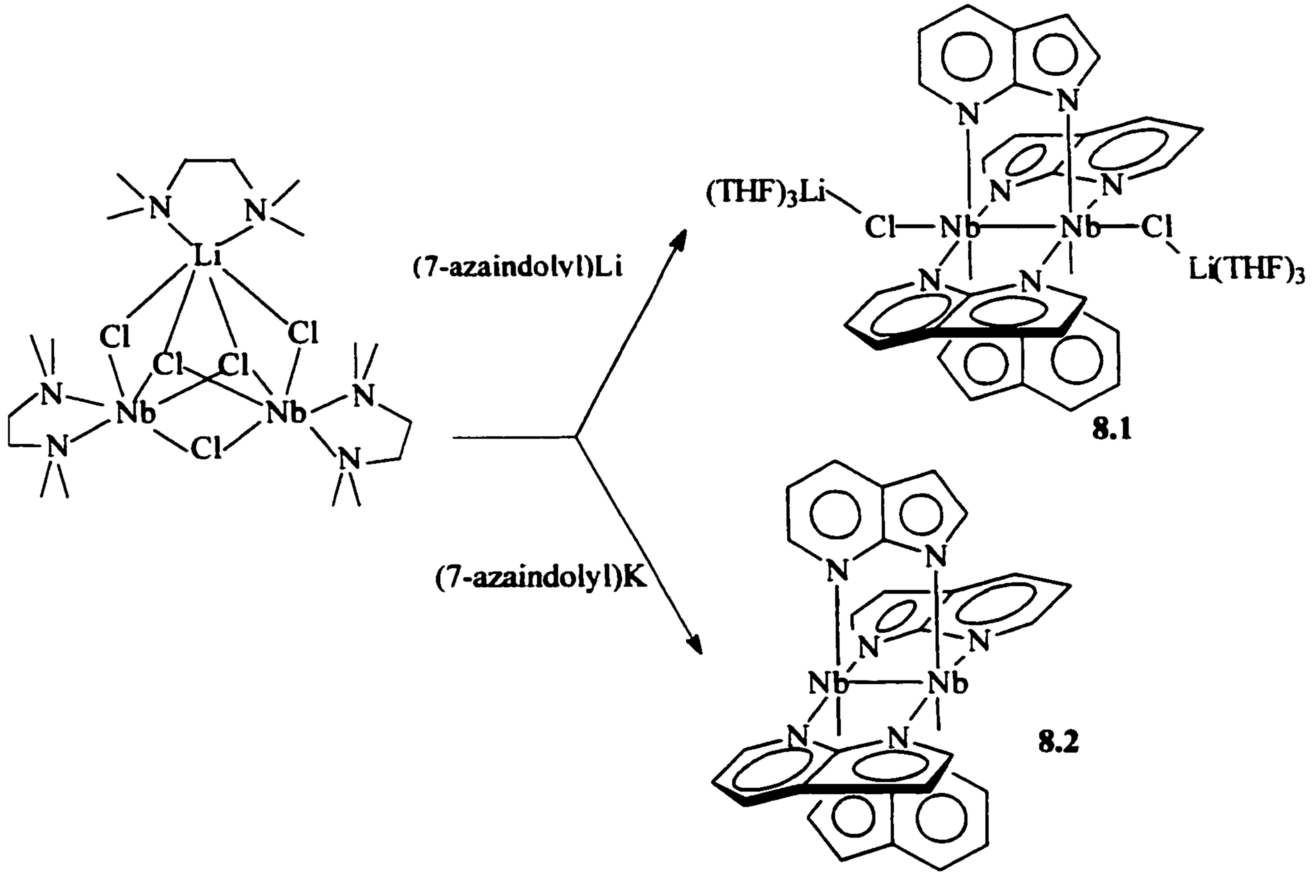
Figure 8.1: Magnetic moment measurement of complex 8.1 as a function of the temperature

ates the presence of a substantial attractive force between the two metals. However, the complex nature of the paramagnetism of **8.1** indicates that other factors in addition to a Nb-Nb bond may contribute to the nature of the intermetallic interaction.

It should be reiterated that the pyrimidinate complex with no LiCl on the axis is indeed diamagnetic.[4c] A question arises about whether or not the small differences in intermetallic distance between the two complexes may be sufficient to determine such a remarkable difference of magnetism. Calculations carried out on the same model compound **8.1** but *without* LiCl and with Nb-Nb distances of both 2.268 and 2.203Å increased the Nb-Nb multiple bond character to 2.97 and 3.02 respectively and showed the presence of a MO with a clear Nb-Nb σ-bond character. This confirms that the presence of LiCl on the intermetallic axis is indeed the factor responsible for decreasing the formal Nb-Nb bond order and implies that the presumably weak coordination of LiCl is preferred to the formation of a presumably strong Nb-Nb σ-bond. These observations remind us of the oddities and intricacies in metal-metal bonding and on the basis of these findings the alleged stability of the Nb-Nb triple bonds should probably be reconsidered.

The reaction of $Nb_2Cl_5Li(TMEDA)_3$ with four equivalents of 7-azaindolyl potassium salt afforded the novel $(7\text{-azaindolyl})_4Nb_2\cdot 2THF$ (**8.2**) which was isolated as red-orange crystals in acceptable yield (Scheme 8.1). Relevant to the present discussion is also the blue-green polymeric $([(7\text{-azaindolyl})_2Nb]_2\{(\mu\text{-}Cl)[\mu\text{-}Li(THF)_2]\}_2)_n$ compound which was obtained via reduction and ligand replacement of $NbCl_3(DME)$ in one-pot synthesis and which is also diamagnetic.[6h]

The difference of magnetic behavior in the three compounds is particularly striking. In the two LiCl adducts, the degree of solvation of the alkali cation is the only factor which apparently determines the linear polymeric versus dimeric structure. Furthermore, this relatively insignificant difference is also the factor which determines the magnetic behavior. On the other hand, the diamagnetism of the polymeric compound, which incidentally has a Nb-Nb distance slightly longer than in the dimeric complex [Nb-Nb = 2.278(2) Å], was established only on the basis of the sharpness of the NMR lines of an acetone solution spectrum.[6h] In addition, the paramagnetic dinuclear LiCl adduct, which displays rather broad NMR lines in THF solution, also gives a well-solved



Scheme 8.1

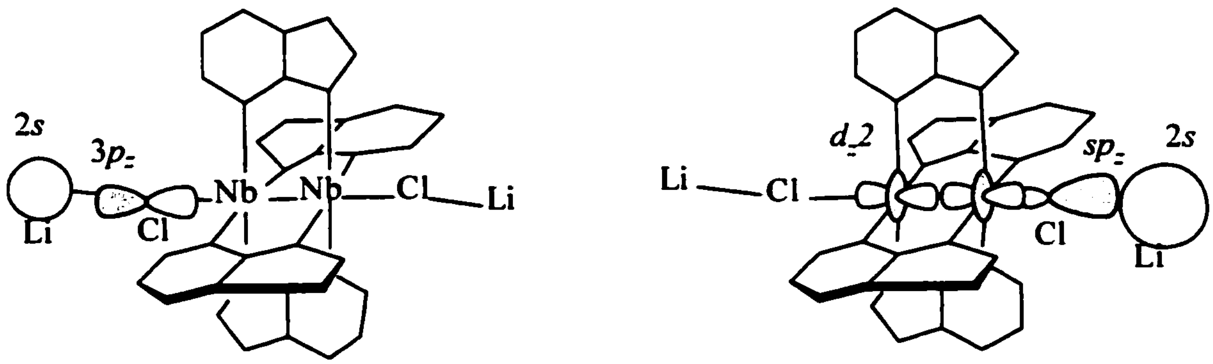
spectrum in acetone solution where, however, the complex changed its color to dark orange-brown. Thus, a LiCl dissociation process is likely to be at the basis of the alleged diamagnetism of the polymeric LiCl adduct. Conversely, complex **8.2** is diamagnetic in both solid state and solution. It also possesses a distinctively different color from the two LiCl adducts (red rather than blue) and, surprisingly, does not coordinate THF which notoriously is a Lewis base stronger than LiCl. Thus questions arise about the nature of the Nb-Nb interaction and about how axial ligation may affect these multiple bonds. The fact that the compounds with LiCl on the axis display completely different colors and magnetic behavior clearly indicates that the axial ligation has substantially modified the electronic configuration of the metal centers. By contrast, the fact that the Nb-Nb distance remains basically unchanged indicates that the axial ligation does not affect the Nb-Nb bond multiplicity.

VIII. 4: Molecular Orbital Calculation

DFT calculations were performed on both the singlet and triplet state of **8.1** and yielded consistent results. The singlet state has a value of the total energy which is smaller than the triplet state by only 1.8 kcal/mol. This small difference, together with the small HOMO-LUMO gap in the singlet state (0.19 eV), accounts for the paramagnetism in terms of low-lying and thermally accessible triplet state. Both the HOMO and LUMO are mainly lithium centered molecular orbitals (Chart 8.1). The LUMO (-2.69 eV) is almost exclusively formed by an out-of-phase combination of one lithium $2s$ (87%) and one chlorine $3p_z$ (10%) atomic orbitals. A similar situation was observed for the HOMO

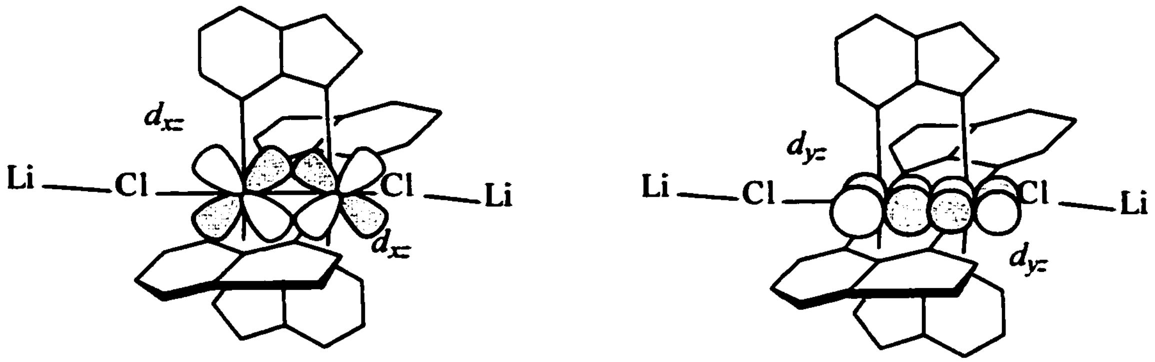
(-2.88 eV) which is also largely contribued by the other lithium atoms' 2*s* orbital (68%) and a chlorine $3s/3p_z$ hybrid (21%) on the second chlorine atom.

However, the two niobium d_{z^2} atomic orbitals also participate in the formation of this orbital with an in-phase combination thus providing an almost negligible Nb-Nb σ-bond character (10%). The next frontier orbitals [HOMO-1 (-3.04 eV) and HOMO-2 (-3.11 eV)] are nearly degenerate Nb-Nb centered π orbitals and are formed by the overlap



LUMO (-2.69 eV)

HOMO (-2.88 eV)



HOMO-1 (-3.04 eV)

HOMO-2 (-3.11 eV)

Chart 8.1

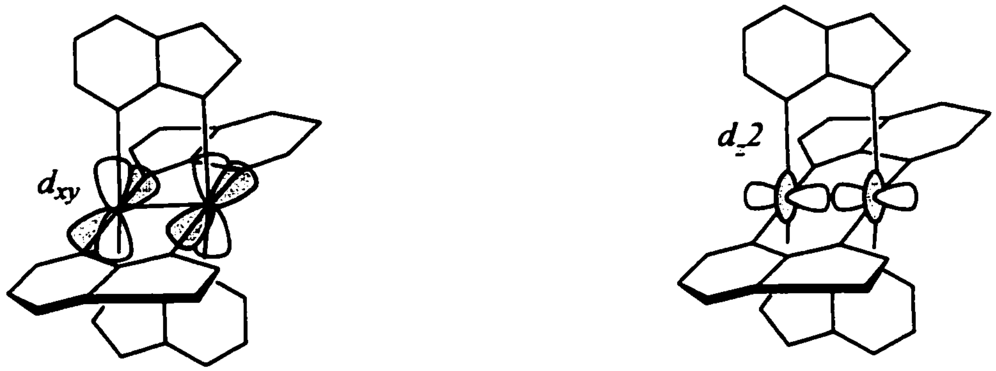
of the d_{xz} and d_{yz} orbitals repectively. The overall calculated Mulliken Nb-Nb bond order was 2.17. The fact that the HOMO and LUMO orbitals are mainly Li-centered suggests that the presence of LiCl on the intermetallic axis is the factor responsible for the destabilization and virtual disappearance of the Nb-Nb σ-bond and, ultimately, for the observed paramagnetism.

For complex **8.2** density functional calculations have carried out on the atomic coordinates of which was provided by the X-ray crystal structure. Given the diamagnetism, calculations were carried out for the singlet state. The three occupied frontier orbitals are Nb-Nb centered with a metal atom contribution of predominantly d-orbital character (Chart 8.2). The HOMO-LUMO gap (0.72 eV) is sufficient to account for the observed diamagnetism in solution. Four frontier orbitals are all Nb-Nb centered. The LUMO (-3.27 eV) is a Nb-Nb δ bond arising from the in phase combination of the two d_{xy} atomic orbitals. The HOMO has the typical shape of a Nb-Nb σ-bond and is generated by the overlap of the d_{z^2} atomic orbitals. The next two occupied molecular orbital (HOMO-1 at -4.44 eV, and HOMO-2 at -4.46 eV) are nearly degenerate Nb-Nb π-orbitals and are respectively formed by the overlap of the d_{xz} and d_{yz} atomic orbitals. The overall calculated Mulliken Nb-Nb bond order is 2.99. Thus the calculation clearly indicates the existence of a Nb-Nb triple bond. In addition geometry optimization calculation using a force field without electrostatic interactions increased the Nb-Nb distance to 2.7Å. This is in nice agreement with the structure of the Cr derivative of the same ligand system and where the Cr-Cr interaction is likely to be insignificant. Therefore, the fact that the Nb-Nb distance of **8.2** is considerably shorter indicates that the Nb-Nb interaction is substantial and sufficient to enforce a distortion from the normal geometry as it would be required by the 7-azaindolyl ligand. The distribution and shape of the frontier orbitals in case of complex **8.1** appears to be very similar to that calculated for **8.2**. However, the presence of the Nb-Cl-Li interactions introduces in the energy level distribution of **8.2** two nearly degenerate MO's which are mainly Nb-Cl-Li centered and which respectively become the HOMO and LUMO. The HOMO has a minor contribution of Nb-Nb σ-bond thus indicating that the introduction of a weak Nb-Cl bonding interaction is done at the expenses of the Nb-Nb σ-bond. The small HOMO-LUMO gap (0.19 eV) is the cause for the paramagnetism observed at room temperature whereas the annihilation of the Nb-Nb σ-bond is responsible for the lower bond order (2.17) that was calculated.

VIII. 5: X-ray Crystallography

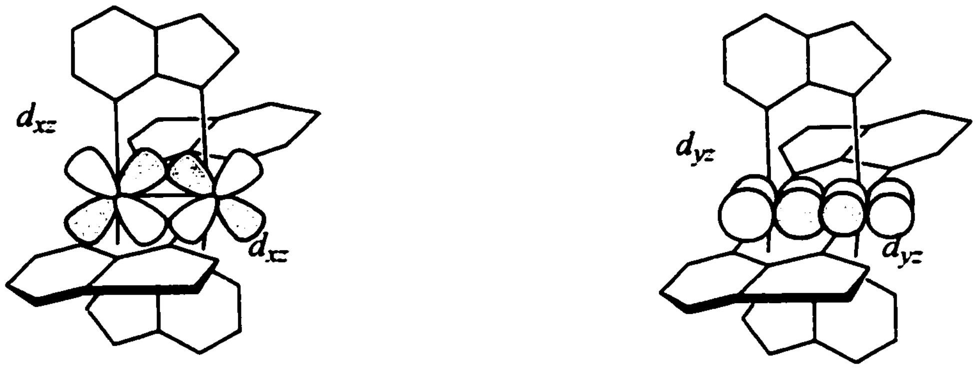
Suitable crystals were selected, mounted on thin, glass fibres using paraffin oil and cooled to the data collection temperature. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω-scans at 0, 90, and 180° in ϕ. Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied .[9]

No symmetry higher than triclinic was observed for **8.2**. Systematic absences in the diffraction data and unit-cell parameters were uniquely consistent with $P2_1/n$ for **8.1**. The structures were solved by direct methods, completed with difference Fourier



LUMO (-3.27 eV)

HOMO (-3.99 eV)



HOMO-1 (-4.44 eV)

HOMO-2 (-4.46 eV)

Chart 8.2

syntheses and refined with full-matrix least-squares procedures based on F^2. The compound molecules were located at inversion centres. A cocrystallized THF solvent molecule was located in each asymmetric unit. One of the two symmetry-unique 7-azaindole ligands were found end-over-end disordered. The close proximity of the atom positions corresponding to the two contributing disordered forms precluded a full modeling of the disorder except for the carbon atom at position 4 which had a refined site disorder distribution of 60/40 for **8.1** and 80/20 for **8.2**. All non-hydrogen atoms were refined with anisotropic displacement parameters except the cocrystallized solvent atoms in **8.1** which were refined isotropically to conserve a favorable data/parameter ratio. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHEXTL 5.10 program library.[10]

The dinuclear complex **8.1** (Figure 8.2) containes four 7-azaindolyl ligands in the form of a paddle-wheel configuration. The molecule has two Li(THF)$_3$ units in *trans* positions bridged to niobium by Cl which provide the niobium atoms with a formal pyramidal coordination geometry. This type of LiCl coordination makes complex **8.1** different from the previously reported pyrimidinate species[5]. The Nb-Nb distance in complex **8.1** [2.2683(13) Å] is longer by only 0.065Å with respect to the pyrimidinate derivative. The long Nb-Cl distance suggests that the coordination of the axial (THF)$_3$LiCl moiety is rather weak.

The crystal structure of **8.2** does not display any particular feature. The characteristic paddle-wheel geometry (Figure 8.3) is defined by four ligands organized in the usual manner around the Nb-Nb vector. Two molecules of THF are present in the lattice with the oxygen atoms oriented towards the Nb atoms and not far from the intermetallic vector [Nb(a)-Nb-O(1) = 168.2(2)°]. However, in spite of the favorable orientation, there is no significant bonding contact since the Nb-O distance [Nb-O = 3.808(13)Å] is clearly outside the bonding range. The only structural feature of interest is the M-M distance [Nb-Nb(a) = 2.263(1)Å] which is surprisingly close to those observed in the paramagnetic and diamagnetic LiCl adducts [2.268(1)Å and 2.278(2)Å respectively].[6h]

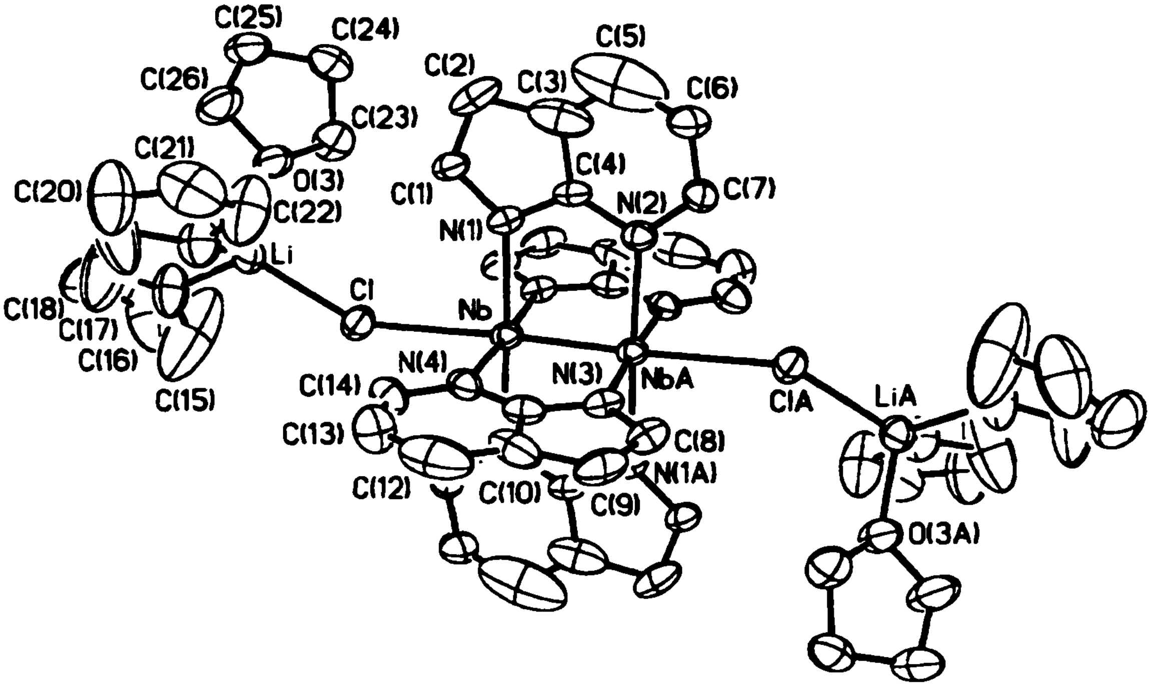


Fig. 8.2: ORTEP drawing of **8.1**. Thermal ellipsoids are drawn at the 30% probability level. Bond distances are in angs (Å) and angles in deg (°): Nb-Nb(a) = 2.2683(13), Nb-Cl = 2.733(2), Nb-N(1) = 2.247(6), Nb-N(4) = 2.266(6), Li-Cl = 2.279(15), N(1)-Nb-N(4) = 90.9(2), N(1)-Nb-N(3a) = 88.3(2), N(1)-Nb-N(2a) = 177.6(2), N(4)-Nb-N(3a) = 177.4(2), N(1)-Nb-Cl = 91.04(17), N(4)-Nb-Cl = 88.37(18), Nb-Cl-Li = 142.2(4), Nb(a)-Nb-Cl = 177.56(6).

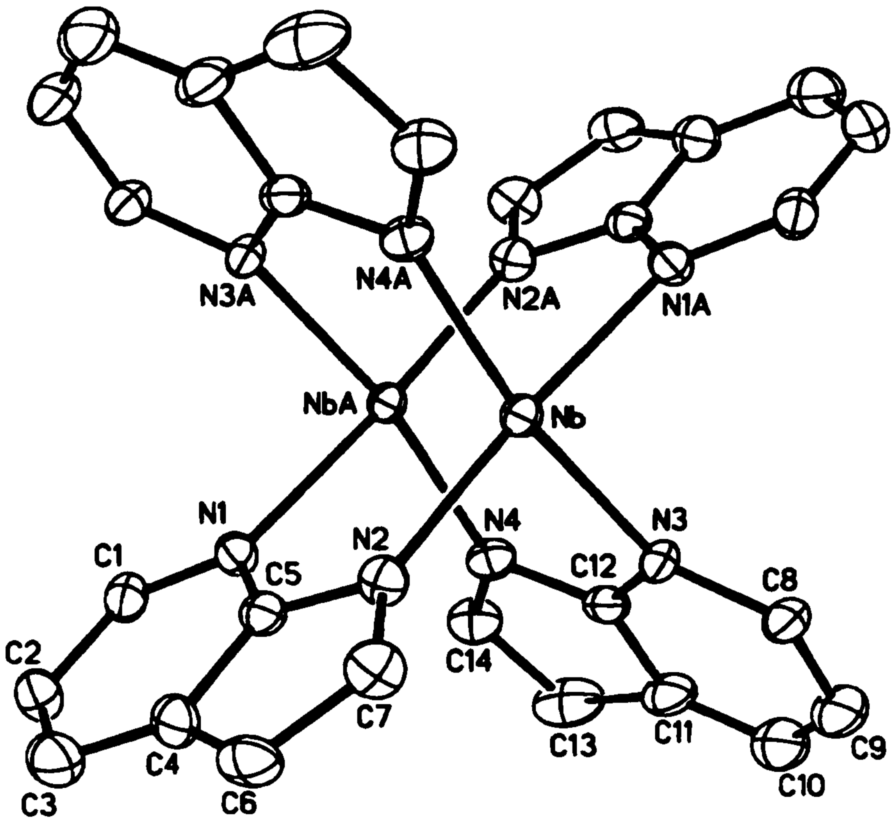


Fig. 8.3: ORTEP drawing of **8.2**. Thermal ellipsoids are drawn at the 30% probability level. Bond distances are in angs (Å) and angles in deg (°): Nb-N(2) = 2.195(5), Nb-N(4a) = 2.198(5), Nb-N(3) = 2.240(5), Nb-Nb(a) = 2.2628(14), Nb-N(1a) = 2.273(5), N(1)-Nb(a) = 2.273(5), N(4)-Nb(a) = 2.198(5), N(2)-Nb-N(4a) = 95.42(19), N(2)-Nb-N(3) = 93.40(19), N(4a)-Nb-N(3) = 170.76(17), N(2)-Nb-Nb(a) = 91.73(14), N(4a)-Nb-Nb(a) = 91.41(14), N(3)-Nb-Nb(a) = 91.08(14), N(2)-Nb-N(1a) = 175.8(2), N(4a)-Nb-N(1a) = 86.77(18), N(3)-Nb-N(1a) = 84.26(18), Nb(a)-Nb-N(1a) = 91.85(14).

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CHAPTER IX

Conclusion

This thesis involves the synthesis, characterization and reactivity of niobium halides in the di- and tri-valent oxidation states.

The main goal of this research was to investigate the reactivity of low and medium valent niobium with different X-donor ligands (X = N, S, O), since most of the documented complexes of niobium with donor ligands of this type were obtained through reduction of suitable complexes in higher oxidation state. The most significant results were obtained in the case where X = N which allowed for the isolation of a series of compounds arising from interesting reaction pathways such as C-N, N-N bond cleavage, C-H bond activation and denitrogenation.

In all these reactions what is noticeable was the role played by the ligand steric hindrance in determining the pathway in which the reaction proceeds to produce the final products:

- direct formation of niobium-amide complexes using Nb (II) and Nb (III) starting material
- formation of short M-M bonds
- reduction of metal center
- formation of cluster complexes

Regarding the use of LDA as a possible ligand for stabilizing Nb (III), steric factors are apparently responsible for the low stability of $[Nb(N^iPr_2)_3]_x$ (X = 1, 2) compounds resulting in the reduced cluster, $Nb_2Cl_5Li(TMEDA)_3$ (**2.1**). However, it is also possible that electronic factors may play an important role in this regard. It is reasonable to suppose that reduction involves the decoupling of electrons in a metal-nitrogen bond with the formation of (i-Pr_2N) radicals. This is based on the assumption that the inductive effect (electron release) of the alkyl groups tends to stabilize the (i-Pr_2N) radical. The same type of reduction was observed using another aliphatic amide, Cy_2NLi, with $NbCl_4(thf)_2$. In the case of the (3,5-Me_2Ph)(Ad)NLi ligand oxidative addition of metal center into the C-N bond of amide occurred.

The Nb(II) cluster, $Nb_2Cl_5(TMEDA)_3Li$, has proven to be a versatile starting material for the preparation of low valent Nb compounds. Reaction of this diamagnetic cluster with (3,5-Me_2Ph)(Ad)NLi ligand resulted in the production of [(3,5-Me_2Ph)(Ad)N]Nb(3,5-Me_2Ph)}$_2$(μ-NAd)$_2$.2(ether) (**2.3**). Conversely, by using the diphenylamide anion the new complex {$[(Ph_2N)_2Nb]_2[\mu$-NPh(μ-η^1:η^2-C_6H_4)]}[Li (TMEDA)$_2$].toluene (**4.2**) was produced. With Cy_2NLi a nitride-bridged, mixed-valence Nb(IV)/Nb(V) species was obtained while bispyridylamide lithium gave $[(py_2N)_2Nb]_2(\mu$-$C_5H_4N)(\mu$-Npy)$[Li(THF)_2](THF)_2[Li_2Cl_2(THF)_4]$ (**5.2**). Each product was a direct result of the cooperative oxidative addition of the two metal centers on either C-N bond, C-H bond or dinitrogen of the amide ligand, respectively. The oxidation of each of the two metal centers provided the electrons necessary for the bond cleavages.

The reaction of trivalent Nb halides with the tripodal tripyrrolyl tri-anion has been investigated. This novel ligand showed an unprecedented ability for capping a dimetallic unit with an unusual bridging mode and providing the first example of M-M bonded stable trivalent Nb amide. Other features of this ligand include an apparent inertness towards the involvement into the reactivity of the trivalent Nb center and the ability of supporting formation of Nb-Nb bonds without the ligand system concurring to the formation of the Nb-Nb MO's. The possibility of coordinating one of the three pyrrolyl ring in a π-bonding fashion is probably the key for understanding the versatility of this ligand and its ability to prevent destructive reactivity patterns such as ring-opening, C-N cleavage or denitrogenation reactions.

Reaction of Nb(II) cluster, $Nb_2Cl_5(TMEDA)_3Li$, with lithium salts of pyrrole and indole shows two subsequent disproportionations similar to the case of the reaction of the $Nb_2Cl_6(TMEDA)_2$ complex with tripodal tripyrrolide anions. Although at this stage we can only speculate, we observe that the behavior is strikingly different from that of similar reactions with other amides and dimethylpyrrolide anions reported in this thesis which afforded instead molecular activation processes. This perhaps indicates that steric hindrance rather than electronic factors play a critical role in determining the fate of the intermediate aggregate or cluster and determine the type of chemical transformation (disproprotionation versus molecular activation).

The reaction of Nb(II) cluster, $Nb_2Cl_5Li(TMEDA)_3$, with the (7-azaindolyl) anions (Lithium and Potassium salts) produced dinuclear species, (7-azaindolyl)$_4$Nb$_2$[(μ-

Cl)Li(THF)$_3$]$_2$ (**8.1**) and (7-azaindolyl)$_4$Nb$_2$.2THF (**8.2**) respectively with a paddle-wheel configuration and with very short Nb-Nb distances (in the range of 2.2 Å). This observation indicates the presence of a substantial attractive force between the two metals due to using this robust ligand which promotes the assembling of a stable Nb$_2$L$_4$ (L = 7-azaindolyl) framework. Surprisingly, the diamagnetism of **8.2** which has no ligand on the intermetallic vector is in sharp contrast with the paramagnetism of the dark-blue **8.1** derivative which retains LiCl on the Nb-Nb axis. Despite that axial ligation considerably which accounts for the difference in magnetic behavior and Nb-Nb bond multiplicity, the Nb-Nb distance remained surprisingly unmodified

In all of the described reactions the strong tendency of niobium to form M-M bonds has been observed. As well, the greater stability of niobium in higher oxidation states has been demonstrated.

APPENDICES

APPENDIX A

Table I. Crystal Data and Structure Analysis Results for **2.1** and **2.2**

	2.1	**2.2**
formula	$C_{18}H_{48}Cl_5LiN_6Nb_2$	$C_{32}H_{64}Cl_{12}Li_2Nb_4O_8$
Formula weight	718.63	1387.75
space group	Cmc2(1)	P2(1)/n
a (Å)	16.896(3)	12.763(2)
b (Å)	15.220(3)	10.989(2)
c (Å)	12.020(2)	18.517(3)
β (deg)	90	91.068(3)
V (Å^3)	3091(1)	2596.6(7)
Z	4	2
Radiation (Kα Å)	0.71073	0.71073
T (°C)	-100	-100
D_{calcd} (g cm^{-3})	1.544	1.775
μ (cm^{-1})	11.91	15.20
R, wR^2, GoF	0.0297, 0.0707, 1.057	0.0625, 0.0675, 1.014

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

Table II. Crystal Data and Structure Analysis Results for **2.3** and **2.4**

	2.3	**2.4**
formula	$C_{80}H_{116}N_4Nb_2O_2$	$C_{12}H_{21}Cl_3N_3Nb$
Formula weight	1351.59	406.58
space group	P 21/c	P21/n
a (Å)	12.5969(2)	7.573(2)
b (Å)	14.3835(1)	17.598(4)
c (Å)	20.3103(3)	12.642(3)
β (deg)	104.22	93.21(3)
V (Å^3)	3567.17(8)	1682.2(6)
Z	2	4
Radiation (Kα Å)	0.70930	0.71073
T (°C)	-70	-70
D_{calcd} (g cm^{-3})	1.258	1.605
μ (cm^{-1})	3.70	11.83
R, wR^2, GoF	0.0461, 0.1334, 1.068	0.0233, 0.0602, 1.065

$R = \Sigma \| F_O | - | F_c \| / \Sigma | F_O |$ $R_w = [(\Sigma(| F_O | - | F_c |)^2 / \Sigma w F_O^2)]^{1/2}$

APPENDIX B

Crystal Data and Structure Analysis Results for **3.1**, **3.2** and **3.3**

	3.1	**3.2**	**3.3**
formula	$C_{58}H_{84}Li_2N_6NbO_8$	$C_{42}H_{52}N_6Nb_2O_4$	$C_{100}H_{152}Cl_{11}K_4N_{20}Nb_6O_6$
Formula weight	1100.10	890.72	2834.23
space group	P-1	P2(1)/c	C2/c
a (Å)	10.562(2)	12.688(2)	44.482(4)
b (Å)	12.247(3)	12.908(2)	12.800(1)
c (Å)	12.799(3)	12.607(2)	26.560(2)
β (deg)	90.288(4)	110.511(3)	125.204(1)
V (Å^3)	1460.1(6)	1933.7(6)	12356(2
Z	1	2	4
Radiation (Kα Å)	-0.70930	0.71073	0.71073
T (°C)	-153	-95	-95
D_{calcd} (g cm^{-3})	1.251	1.530	1.524
μ (cm^{-1})	2.62	6.44	96.7
R, wR^2, GoF	0.0709,0.1612, 1.030	0.0609,0.1203, 1.020	0.0873, 0.2237, 1.084

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

APPENDIX C

Crystal Data and Structure Analysis Results for **4.1**, **4.2** and **4.3**

	4.1	**4.2**	**4.3**
formula	$C_{12}H_{32}Cl_5N_4Nb_2$	$C_{79}H_{90}N_9Nb_2Li$	$C_{52}H_{50}N_4Nb_2O$
Formula weight	595.49	1358.36	932.78
space group	Pna2(1)	P21/n	P2(1)2(1)2(1)
a (Å)	19.843(9)	13.4635(8)	14.1827(7)
b (Å)	8.509(9)	39.259(2)	15.5713(8)
c (Å)	13.218(7)	14.4635(9)	19.2238(9)
β (deg)		94.936(1)	
V ($Å^3$)	2232(3)	7597.0(8)	4245.4(4)
Z	4	4	4
Radiation (Kα Å)	0.70930	0.70930	0.70930
T (°C)	-153	-153	-153
D_{calcd} ($g\ cm^{-3}$)	1.772	1.188	1.459
μ (cm^{-1})	16.28	3.48	5.84
R, wR^2, GoF	0.022, 0.046, 1.05	0.091, 0.250, 1.01	0.021, 0.056, 1.01

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

APPENDIX D

Crystal Data and Structure Analysis Results for 5.1 and 5.2

	5.1	**5.2**
formula	$C_{40}H_{58}N_2NbO$	$C_{66}H_{71}ClLi_2N_{15}Nb_2O_4$
Formula weight	675.81	1373.53
space group	P21/c	P-1
a (Å)	12.5969(2)	13.9589(7)
b (Å)	14.3835(1)	14.2761(7)
c (Å)	20.3103(3)	18.778(1)
α (deg)		96.992(1)
β (deg)	104.223(1)	93.911(1)
γ (deg)		118.336(1)
V ($Å^3$)	3567.17(8)	3235.1(3)
Z	4	2
Radiation (Kα Å)	0.70930	0.71073
T (°C)	-153	-70
D_{calcd} ($g\ cm^{-3}$)	1.258	1.410
μ (cm^{-1})	3.7	0.456
R, wR^2, GoF	0.045, 0.057, 1.05	0.0512, 0.1316, 1.057

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

APPENDIX E

Crystal Data and Structure Analysis Results for **6.1** and **6.2**

	6.1	**6.2**
formula	$C_{62}H_{105}Cl_5LiN_{11}Nb_4$	$C_{24}H_{40}N_5Nb_2$
Formula weight	1560.40	584.43
space group	P-1	C2/c
a (Å)	12.295(3)	18.387(4)
b (Å)	14.916(3)	15.314(3)
c (Å)	20.818(5)	18.971(4)
α (deg)	96.763(4)	90.00
β (deg)	91.542(4)	110.377(3)
γ (deg)	107.375(4)	90.00
V ($Å^3$)	3610(1)	5007(2)
Z	2	8
Radiation (Kα Å)	0.71073	0.71073
T (°C)	-20	-70
D_{calcd} (g cm^{-3})	1.435	1.550
μ (cm^{-1})	8.48	9.36
R, wR^2, GoF	0.0455, 0.1094, 1.058	0.0350, 0.0882, 1.192

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

APPENDIX F

Crystal Data and Structure Analysis Results for 7.1, 7.2 and 7.3

	7.1	**7.2**	**7.3**
formula	$C_{60}H_{96}Li_2N_6NbO_9$	$C_{80}H_{100}Li_2N_6NbO_8$	$C_{85}H_{94}K_2N_6NbO_4$
Formula weight	1152.22	1380.45	1434.77
space group	P-1	R-3	Cc
a (Å)	13.050(2)	12.591(1)	18.673(9) A
b (Å)	13.206(2)	12.591(1)	22.149(9)
c (Å)	18.325(2)	12.591(1)	18.866(9)
α	84.886	75.633(2)	90
β (deg)	87.905(1)	75.633(2)	105.826(9)
γ	84.242(1)	75.633(2)	90
V ($Å^3$)	3128.5(7)	1835.8(3)	7507(7)
Z	2	1	4
Radiation (Kα Å)	0.71073	0.71073	0.71073
T (°C)	-100	-70	-70
D_{calcd} (g cm^{-3})	1.223	1.249	1.270
μ (cm^{-1})	2.49	2.23	3.26
R, wR^2, GoF	0.0668, 0.1636,1.023	0.0558, 0.0600, 1.013	0.0510, 0.1232, 1.020

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

APPENDIX G

Crystal Data and Structure Analysis Results for 8.1 and 8.2

	8.1	**8.2**
formula	$C_{60}H_{84}Cl_2Li_2N_8Nb_2O_8$	$C_{36}H_{36}N_8Nb_2O_2$
Formula weight	1315.95	798.55
space group	P2(1)/n	P-1
a (Å)	14.280(1)	9.079(3)
b (Å)	12.9435(9)	9.551(3)
c (Å)	18.307(1)	10.571(4)
α (deg)	90	83.476(6)
β (deg)	108.264(1)	89.613(6)
γ (deg)	90	69.641(5)
V (Å^3)	3213.4(4)	853.3(5)
Z	2	1
Radiation (Kα Å)	0.71073	0.71073
T (°C)	-70	-70
D_{calcd} (g cm^{-3})	1.360	1.554
μ (cm^{-1})	4.97	7.17
R, wR^2, GoF	0.0572, 0.1730, 1.028	0.0679, 0.1447, 1.005

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