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UNIVERSITY OF OTTAWA

Abstract

This thesis deals with the syntheses and characterization of a novel series of Cr(II), as well as V(II) complexes.

The strength of Cr-Cr quadruple bonds has been investigated experimentally. The Cr-Cr multiple bond of the dimeric $[TAACr]_2$ [TAA = tetramethyldibenzotetraaza[14]annulene] (**2.1**) is reversibly cleaved by pyridine to form monomeric paramagnetic octahedral $[TAACrpy_2]$.py (**2.2**), and Reaction of the quadruply- bonded $[Me_8Cr_2][Li(THF)]_4$ (**3.1**) with TMEDA in ether led to facile cleavage of the dimeric structure and formation of an unprecedented high-spin monomeric square-planar $[Me_4Cr][Li(TMEDA)]_2$ (**3.2**). The reaction can be reversed by treating complex **3.2** with THF and Et_2O. The structures of **2.2** and **3.2** has been demonstrated by X-ray analysis.

The synthesis, characterization and stability properties of a novel series of Cr(II) alkylchromates together with their transformation into unprecedented alkylidene (Schrock-type) Cr(III) species, and Cr(II) and Cr(III) metallacycles is described in chapter 4. Reaction of $CrCl_2(THF)_2$ with 4 equivalents of RLi [R=Me, $PhCH_2$, $(CH_3)_3CCH_2$, $(CH_3)_2C(Ph)CH_2$] led to the initial formation of the corresponding $R_8Cr_2Li_4(THF)_4$ (**4.1**) which were isolated as thermally labile and almost diamagnetic crystalline solids. Treatment of these complexes with TMEDA gave different species containing either Cr(II) or Cr(III), depending on the nature of the alkyl. While in the case of the methyl derivative the monomeric $Me_4Cr[Li(TMEDA)]_2$ (**4.2**) was reversibly formed, another diamagnetic Cr(II) complex $[(PhCH_2)_6Cr_2[Li(TMEDA)]_2$ (**4.3**), likely dimeric, was obtained in the case of the benzyl

derivative. Addition of TMEDA to the *in situ* prepared diamagnetic $[(CH_3)_3CCH_2]_8Cr_2[Li(THF)]_4$ gave the chromacyclobutane species $[(CH_3)_3CCH_2]_2$-$[CH_2C(CH_3)_2CH_2]Cr[Li(TMEDA)]_2$ (**4.4**). In the case of the corresponding neophyl derivative a Cr(III) complex $[o\text{-}C_6H_4(C(CH_3)_2CH_2]_2Cr(TMEDA)][Li(TMEDA)_2]$ (**4.5**) was obtained via an unexplained oxidation reaction. The utilization of a RLi:Cr stoichiometric ratio of 2:1, in the presence of TMEDA, led to the formation of the corresponding paramagnetic dialkyl species $(TMEDA)CrR_2$ [R = CH_2Ph (**4.7**), $CH_2C(CH_3)_3$ (**4.8**), $CH_2C(Ph)(CH_3)_2$ (**4.9**)]. In these three cases there is evidence that the reaction proceeds via formation of the intermediate monosubstitution product $(TMEDA)CrR(\mu\text{-}Cl)[LiCl(TMEDA)]$. In the case of the crystalline benzyl derivative (**4.6**) the product was isolated in analytically pure form. Finally, the employement of a $PhCH_2Li$:Cr stoichiometric ratio of 3:1 formed a Cr(III) complex, probably an alkylidene species $(TMEDA)Cr(CHPh)CH_2Ph$ (**4.10**). The structures of **4.4, 4.5, 4.6, 4.7, 4.9** and **4.10** were clarified by X-ray analysis.

The ability of three center chelating ligands to form dichromium units and to enforce short and very short Cr-Cr contacts is examined in a consistent series of cyclohexyl amidinate chromium complexes, with the aim of understanding the factors intrinsic in the nature of the bridging ligands which are able to promote or disfavor dinuclear aggregation and to determine the extent of intermetallic separation. The reaction of lithium amidinate $(R'NCRNR')^-Li^+$ with $CrCl_2(THF)_2$ produced dinuclear $[(CyNC(H)NCy)_2Cr]_2.C_7H_8$ (**5.1**) and monomeric $(CyNC(CH_3)NCY)_2Cr$ (**5.2**), $\{CyNC[Ph\text{-}(o\text{-}CH_2NMe_2)]NCy\}_2Cr$ (**5.3**) and $[(Me_3Si)NC(Ph)N(SiMe_3)]_2Cr$ (**5.4**) depending on the steric interaction between the lateral cyclohexyl and the central amidinate group. The structures of **5.1, 5.2, 5.3,** and **5.4** were characterized by X-ray analysis.

Reaction of Li-dppm [dppm = bis(diphenylphosphino)methane] with $CrCl_2(THF)_2$ and with $SmCl_3(THF)_3$ led to the formation of an unprecedented dinuclear mixed-coordination complex $[Cr(Ph_2PC(H)PPh_2)](\mu\text{-}Cl)(\mu\text{-}C(H)(PPh_2)_2)[Cr(Ph_2PC(H)PPh_2)]$ **(6.1)** and mononuclear $Sm[\eta^3\text{-}Ph_2PC(H)PPh_2]_3$ **(6.2)**. The structures of **6.1** and **6.2** were demonstrated by X-ray analysis.

The synthesis and characterization of a new series of mono-, di- and trinuclear Cr(II) borohydride compounds is described in chapter 7. The reaction of $CrCl_2(TMEDA)$ with two equivalents of $NaBH_4$ afforded the thermally unstable $(TMEDA)Cr(BH_4)_2$ **(7.1)** which was converted by treatment with pyridine into the octahedral monomeric $(Py)_4Cr(BH_4)_2$ **(7.2)**. The reaction proceeds via formation of an intermediate trinuclear complex $\{[(TMEDA)(Py)Cr(\eta^1\text{-}BH_4)]_2[(Py)_2Cr(\eta^2\text{-}BH_4)_2]\}(\mu,\eta^1\text{-}BH_4)_2$ **(7.3)** which was isolated and characterized by X-ray crystallography. Reaction of **7.1** and **7.2** with both CO_2 and RN=C=NR [R = Cy, i-Pr] afforded hydride insertion and formation of the corresponding diamagnetic lantern-type Cr(II) formate $(HCO_2)_4Cr_2Py_2$ **(7.4)** and formamidinate compounds $[RNC(H)NR]_3Cr_2(\mu\text{-}BH_4)$ [R = Cy **(7.5a)**, i-Pr **(7.5b)**] respectively, with supershort Cr-Cr quadruple bonds. The structures of **7.1, 7.2, 7.3** and **7.5b** were elucidated by X-ray analysis.

Reaction of V(II) and V(III) salts with lithium amidinates formed a series of compounds where both the nuclearity and the oxidation state of the final complex were determined by the steric bulk of the substituents of the amidinate ligand. While dinuclear compounds with and without short V-V contacts have been obtained in the case of formamidinate anions, monomeric complexes and a dinuclear end-on dinitrogen complex were

formed with the more bulky acetamidinate and trimethylsilyl benzamidinate. The reaction of $VCl_2(TMEDA)_2$ and of $VCl_3(THF)_3$ with two equivalents of formamidinate lithium salts respectively yielded dimeric $\{[CyNC(H)NCy]_2V\}_2$ (**8.2**), with a very short V-V multiple bond, and $\{[CyNC(H)NCy]_2VCl\}_2$ (**8.4**) which is also dimeric. The formation of **8.2** proceeded through the intermediate monomeric $[CyNC(H)NCy]_2V(TMEDA)$ (**8.1**) which was isolated and fully characterized. The dinuclear structure was reversibly cleaved by treatment with pyridine forming the monomeric $[CyNC(H)NCy]_2V(Py)_2$ (**8.3**). Conversely, similar reactions with acetamidinate anion gave only the monomeric $[CyNC(Me)NCy]_2V$- $(THF)_2$ (**8.5a**) and $[CyNC(Me)NCy]_2VCl$ (**8.7**) respectively. Attempts to form a dinuclear structure by either removal of THF from **8.5a** or reduction of **8.7** gave only the V(III) compound $[CyNC(Me)$-$NCy]_3V$ (**8.6**). In the case of the very bulky benzamidinate ligand, similar monomeric complexes $[Me_3SiNC(Ph)NSiMe_3]_2V(THF)_2$ (**8.5c**) and $[Me_3SiNC(Ph)NSiMe_3]_2VCl$(**8.10**) were obtained. However, attempts to form dinuclear species via THF dissociation from **8.5c** or reduction of **8.10** gave a novel dinitrogen complex $\{[Me_3SiNC(Ph)NSiMe_3]_2V\}_2(N_2)$ (**8.8**).

Finaly, reaction of $VCl_2(TMEDA)_2$ with two equivalents of carboxylic acid in THF in the presence of a slight excess of TMEDA at room temperature, afforded the large scale preparation of the linear V(II) trimer $V_3(R_2CHCOO)_6(TMEDA)_2$ [R=Ph_2CH (**9.1**), $PhCH_2$ (**9.2**)]. Cleavage of the trimeric unit and formation of a high-spin monomeric species $[(R_2CHCOO)_2V(pyridine)_4]$ (**9.3**) was achieved upon simple treatment of **9.1** with pyridine at room temperature. The structures of **9.1** and **9.2** are demonstrated by X-ray analysis.

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List of Abbreviations

Å	Angstrom
Ar	aryl
bipy	2,2'-dipyridine
Bu	n-, s-, i-, or t-butyl
Bz	benzyl
cm^{-1}	wavenumbers
Cp	cyclopentadienyl
Cy	cyclohexyl
δ	chemical shift
dppe	bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
esr or epr	electron spin (or paramagnetic) resonance
Et	ethyl
F_c	calculated structure factor
F_o	observed structure factor
g	grams
h	hours
IR	infrared
L	ligand
μ_{eff}	effective magnetic moment in Bohr magnetons

M	central(usually metal) atom in compound
Me	methyl
mmol	millimoles
NMR	nuclear magnetic resonance
Np	neopentyl
Ph	phenyl
ppm	parts per million
Pr	normal, or isopropyl
Py	pyridine
Pz	pyrazolyl
R	alkyl
SCF-Xα-SW	self-consistent field, Xα, scattered wave
T	temperature
TAA	tetramethyldibenzotetraaza[14]annulene
THF	tetrahydrofuran
TMEDA	N,N,N',N'-tetramethylethylenediamine
tol	tolyl
X	halogen or pseudohalogen
Z	number of molecules in the unit cell

Chapter 1

Introduction

1.1 Introduction

Multiple bonds between transition metals are one of the most important functional groups in inorganic chemistry.[1-3] The recognition of the existence of a M-M multiple bond in $[Re_2Cl_8]^{2-}$ by Cotton et al. in 1964[4] is acknowledged as a true landmark in the development of transition metal chemistry. This discovery not only opened new avenues and perspectives in inorganic chemistry for the preparation and understanding of important new families of compounds, such as the clusters, but also showed that chemical bonds of multiplicity higher than three may be formed between two metal atoms. Initially, a theory of metal-metal bonding was developed to explain why $[Re_2Cl_8]^{2-}$ has a very short Re-Re intermetallic distance and an eclipsed, rather than a staggered structure, as well as to account for the diamagnetism of this d^4 species. The basic assumption of this simple but effective theory is that transition metal cations utilize partially-populated d-orbitals for the formation of one σ, two π and two δ bonding (and the corresponding antibonding) orbitals (Fig. 1-1). Given that one of the two δ orbitals has the proper orientation and symmetry to interact with four or more ligands, the quadruple bond results to be the highest possible multiplicity. In agreement with this hypothesis, no example of multiple bonds between two atoms exceeding a bond order of four has ever been reported in the literature. Since the discovery and the understanding of the Re-Re quadruple bond, a very large number of complexes[1,2] containing metal-metal bonds have been synthesized and characterized, and metal-metal bonding is accepted as a major bonding pattern in the chemistry

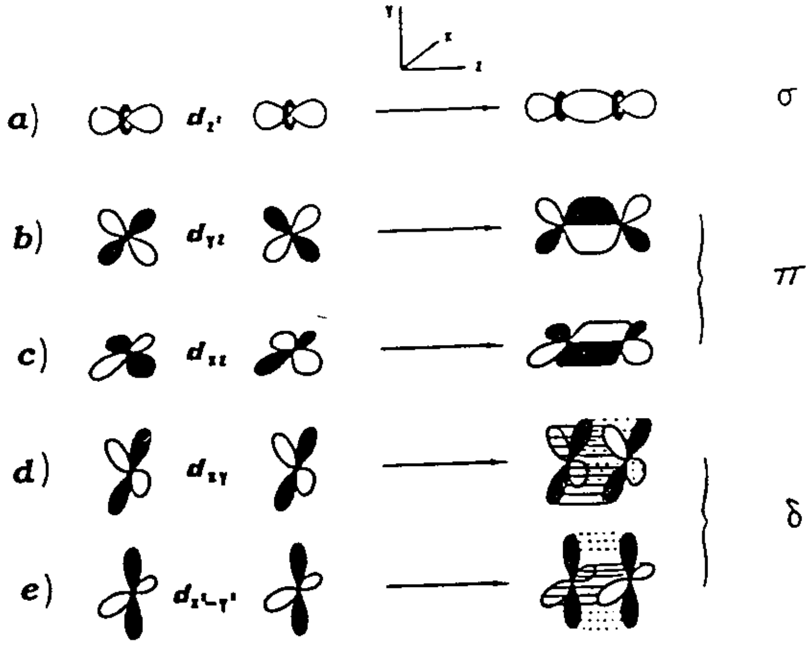


Fig. 1-1 The σ, π, and δ overlaps between two sets of d orbitals on adjacent metal atoms of low-valent transition metals.

It was with the discovery of the isostructural $[Mo_2Cl_8]^{4-}$ which has a $\sigma^2\pi^4\delta^2$ electronic configuration that the decade of exponential growth in the field of metal-metal multiple bond chemistry started.[5] Fig. 1-2 shows the annual number of articles concerning metal-metal multiple bonds for the period 1964-1993 and demonstrates the growth of this field. More than a thousand research papers have been published in this field since 1964. Fig. 1-2 also clearly indicates that after the induction period, the research activity in this area has reached a steadily high level. Recently M-M bonding has become an attractive and challenging research field not only for the synthesis and characterization of new compounds, but also for theoretical calculations.

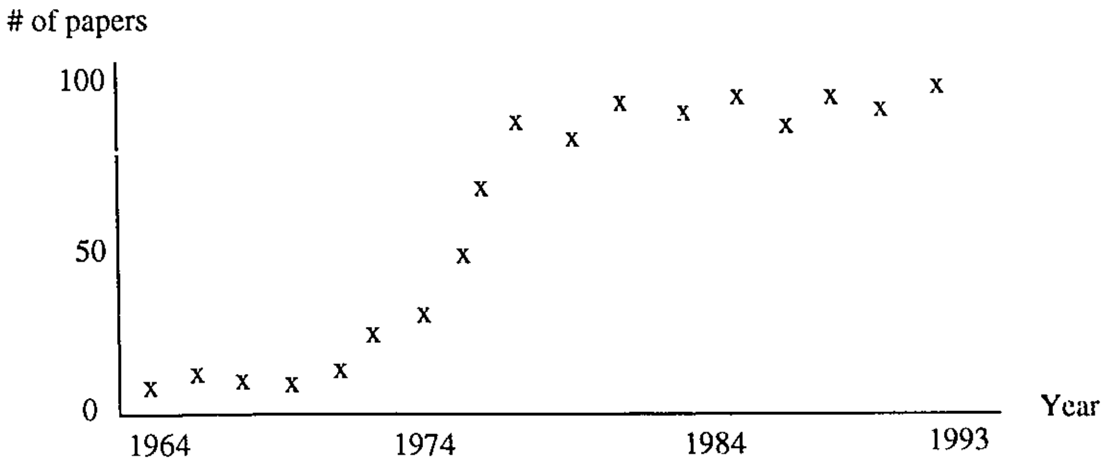
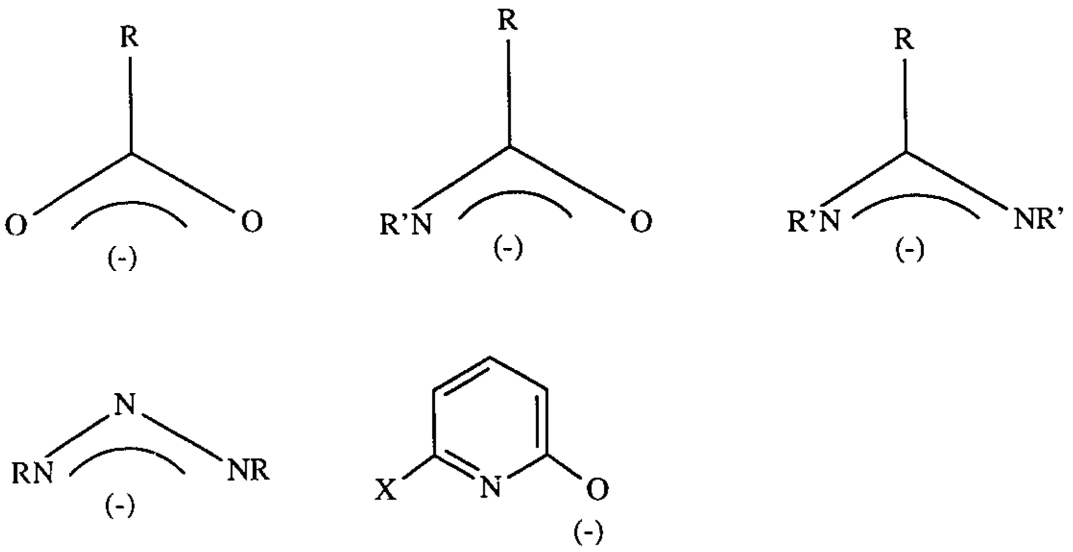


Fig. 1-2 The development of M-M multiple bond chemistry

1.2 M-M multiple bonds in the second and third row transition metal complexes

Very short metal-metal multiple bonds are commonly encountered with or without bridging ligands for second and third row transition metals such as Mo, W, Tc and Re.[1,2] In the case of Mo, a large number of quadruply bonded complexes with bridging ligands have been synthesized and characterized. The most common bridges used are carboxylates or allylic-like three-center chelating ligands. The salient characteristics of these ligands are a wide variety of combinations of donor atoms, the presence of one negative charge and four π-electrons (Scheme 1-1). Other dimolybdenum(II) complexes without bridging ligands have also been reported, such as anionic $[X_4Mo\text{-}MoX_4]^{4-}$, neutral $X_2L_2Mo\text{-}MoX_2L_2$ and macrocyclic $N_4Mo\text{-}MoN_4$ [X = Cl, Br, I, NCO, NCS or CH_3; L = a monodentate ligand (e.g., NR_3, PR_3, $P(OR)_3$, AsR_3); N_4 = tetraazaannulene and porphyrins]. In addition, there are numerous triply-bonded dimolybdenum species of type R_6Mo_2[1] and $Mo_2X_2R_4$[1] with an "ethane-like"



Scheme 1-1

structure [X = Cl, Br or I; R = CR_3, NR_2, OR, SR or SeR]. The great variety of these compounds speaks for a tendency of these metals to form M-M bonds, and suggests that these bonds might be fairly strong. This is also in line with the results of theoretical calculations, which predict that the M-M bonding provides a major contribution to the stabilization energy of the dimetallic unit.

1.3 M-M multiple bonds in the Cr(II) complexes

With the exclusion of clusters of zero and negative valent metals, M-M bonds are widely present amongst the second and third row transition series; the greatest number of complexes being originated by Mo, W, Re and Rh.[1,2] However, for the first row transition series there are considerably less examples cited: a few dozen of Cr(II) complexes and several V(II) compounds. The reason for this difference in trend is not clear. One possibility is that the smaller and more compact M^{n+} (n = 2, 3) ions of the first transition series can not give quite as good d-d orbital overlap as do the larger metals in the second and third transition series.

As mentioned above, multiple bonds between first-row medium-valent transition metals are very rare and mainly present in chromium and vanadium chemistry. The most striking feature of these systems is their ability to form the shortest ever found intermetallic contacts, suggesting that these divalent metals might possess a great ability to form M-M bonds and that M-M multiple bonds might be reasonably strong in these dimetallic units. However, a literature survey of this chemistry at the time when this project started pointed out a few striking features. Despite the fact that these metals may form exceedingly short intermetallic distances, the occurrence of M-M multiple bonds is invariably observed in the presence of bridging three-center chelating ligands. Only in one case, a quadruply bonded dichromium complex $(PMe_3)RCr(\mu\text{-}R)_2CrR(PMe_3)$ (R = Me_3SiCH_2) was formed with a monodentate bridging ligand.[6] For a long time the complexes $Cr_2Me_8Li_4L_4$ (L = THF, Et_2O),[7] $Cr_2(C_4H_8)_4Li_4(Et_2O)_4$[8] and $Cr_2(C_3H_5)_4$,[9] which contain a very short Cr-Cr intermetallic contact (~ 2 Å), have been regarded as the sole examples of Cr-Cr multiple bonds without bridging ligands. However, the crystal structures of these compounds have shown that four Li countercations form a square plane located perpendicularly to the intermetallic axis, and their close proximity to the Cr centers suggests that the role of these alkali cations might be more complicated than simply electrostatic.

Macrocyclic ligands such as tetradentate Schiff bases, porphyrins and tetraazaannulenes have been widely used in the chemistry of group 6 metals. While with the heavier Mo and W these complexes are always dimeric with short unsupported M-M bonds, the Cr analogues are invariably monomeric.[10,11] The only exception is $(TAACr)_2$,[12] which was prepared a few years ago in our laboratory and whose crystal structure provided the first example of a short Cr-Cr multiple bond without bridging ligands or countercations in the intermetallic region.

The strength of the Cr-Cr quadruple bonds is a very puzzling and controversial feature. Supershort Cr-Cr quadruple bonds possess unusually short internuclear distances, which may suggest that similar to the case of the isostructural Mo and W compounds, the intermetallic interaction is rather strong. However, both theoretical and some spectroscopic data have suggested that these bonds are so weak that they are unlikely able to hold together the dinuclear frame in the absence of bridging interactions. The paradox between extreme shortness and weakness has ignited a theoretical controversy[20-24,115] about the real nature of these bonds and whether or not the definition of the chemical bond is appropriate for these M-M interactions. The first indication of the weakness of these multiple bonds was provided by the experimental work of Cannon and coworkers. Studies carried out on $Cr_2(O_2CCH_3)_4(H_2O)_2$ in aqueous solution have shown that these species originate a series of spontaneous dissociation equilibria (25 °C, for the concentration range 0 - 1.0 M)(equation 1, 2, 3).[13,14] Later they also found that the above equilibria may be completely shifted to the right in the presence of polydentate ligands to give mononuclear products.[15-17] The rate-determining step for this cleavage reaction is the dissociation of the dimeric $Cr_2(O_2CCH_3)_4$ to originate a monomeric species. Its dissociation energy was estimated to be only about 45 KJ mol^{-1} larger than that of $Cu_2(CH_3COO)_4$ where the Cu-Cu interaction is limited to a simple antiferromagnetic exchange.[18,19] This implies that the energy of the Cr-Cr quadruple bonds is

$$Cr_2(O_2CCH_3)_4 \rightleftharpoons 2\,Cr(O_2CCH_3)_2 \qquad pK = 4.35 \qquad (1)$$

$$Cr(O_2CCH_3)_2 \rightleftharpoons Cr(O_2CCH_3)^+ + CH_3CO_2^- \qquad pK = -0.8 \qquad (2)$$

$$Cr(O_2CCH_3)^+ \rightleftharpoons Cr^{2+} + CH_3CO_2^- \qquad pK = -0.9 \qquad (3)$$

only about 45 KJ mol^{-1}, thus giving the first indication that these bonds might be surprisingly weak.

Theoretical calculations have played a fundamental role in understanding the nature of the quadruple bond in second and third row transition metal complexes. Therefore, the failure of these calculations to correctly predict the stability and the electronic configuration of the quadruply bonded dichromium systems is at least surprising. Comparative calculations at the SCF level have been performed for Cr_2^{4+}, Mo_2^{4+}, $[Cr_2(CH_3)_8]^{4-}$, and $Cr_2(O_2CH)_4{\bullet}2H_2O$ systems.[20] For Mo_2^{4+} the SCF ground state corresponds to the expected $\sigma^2\pi^4\delta^2$ electronic configuration which is commonly used to rationalize and describe the M-M quadruple bonds. By contrast, the ground state for the metal-metal interaction of Cr_2^{4+} is the $\sigma^2\delta^2\delta^{*2}\sigma^{*2}$ non-bonding configuration. Since this surprising result clashes with the remarkable shortness of the intermetallic contacts, it was argued that such a description of Cr-Cr bonding could be incomplete. The major argument used to dismiss the results of these calculations was provided by the molecular structure of the $[Cr_2(CH_3)_8]^{4-}$ complex which has shown a dinuclear frame without bridging ligands and with quite a short Cr-Cr bond length (1.98 Å). The effect of the four lithium cations has been regarded as purely electrostatic. Therefore, more sophisticated calculations have been attempted such as including correlation effects, which allow bonding configurations of higher energy to mix into the ground state.[21] However, the metal-metal bond order at the shorter Cr-Cr intermetallic separation (1.98 Å) approaches two rather than four, and it is significantly reduced at the longer Cr-Cr separation (2.36 Å). A moderate theoretical success was obtained by introducing a large number of configuration interactions (CI) into the calculations.[22] The results of these calculations performed on $Cr_2(O_2CH)_4$ and related systems have confirmed that the leading configuration is indeed $\sigma^2\pi^4\delta^2$. However, this description is the lowest in energy only at Cr-Cr distances less than 1.8 Å, while at Cr-Cr distances in the 2.25 - 2.50 Å range the $\sigma^2\delta^2\delta^{*2}\sigma^{*2}$ configuration is lower in energy. In any case the quadruply bonded configuration $\sigma^2\pi^4\delta^2$ is not dominant and makes up less than 20% of the wavefunction and therefore its contribution to the description of the Cr-Cr quadruple bond is minimal. The fact that the leading configuration's contribution is so small may be responsible for the anomalous behavior of the Cr-Cr quadruple bond. In "typical" molecules the leading configuration normally makes up more than 80% of the wavefunction at the equilibrium distance and only as the bond lengthens does the importance of the leading configuration decrease.

Recent calculations by the generalized molecular orbital method (a Hartree-Fock type with some configuration interaction built in) on $Cr_2(O_2CH)_4$ and $Cr_2[(HN)_2CH]_4$ showed that Cr-Cr bonding in the latter is much stronger.[23] In each case the $\sigma^2\pi^4\delta^2$ configuration was the most important contributor to the ground state, but it was much more important in $Cr_2[(HN)_2CH]_4$ (48%) than in $Cr_2(O_2CH)_4$ (12%). Although the result was not consistent with experimental data, it indicated that the nature of the bridging ligands is a very important factor in affecting the nature of the Cr-Cr interaction.

Generalized valence bond (GVB) calculations have been carried out on the model compounds $Cr_2(O_2CH)_4$, $Cr_2(O_2CH)_4(H_2O)_2$, $Cr_2[(HN)OCH]_4$, $Cr_2[(HN)_2CH]_4$, and $Cr_2[(HN)_2CH]_4(H_2O)_2$.[24] In all cases, the Cr-Cr distances calculated are far too great compared to the observed values (Table 1-1). Despite GVB calculations not providing correct absolute values for Cr-Cr bond length, the calculated values do show that the Cr-Cr distances increase as the ligands change from HCO_2 to HCO(NH) to $HC(NH)_2$, and with the attachment of axial water molecules. Some workers concluded that Cr_2^{4+} compounds are so highly correlated that no simple, one configuration description of the bond is possible. For these reasons, the existence of a Cr-Cr quadruple bonds was viewed by Hall as a question of *semantics*[25] (i.e. the Cr-Cr interaction is a bond depending on one's definition of a chemical bond).

Table 1-1 Some calculated and observed Cr-Cr distances (Å)

Calculated		Observed	
Compound	Cr-Cr	Compound	Cr-Cr
$Cr_2(O_2CH)_4$	2.49	$Cr_2(O_2CH)_4$ (g)	1.97
$Cr_2(O_2CH)_4(H_2O)_2$	2.60	$Cr_2(O_2CH)_4(H_2O)_2$	2.36
$Cr_2[(HN)OCH]_4$	2.38	several	~1.95
$Cr_2[(HN)_2CH)_4$	2.30	several	~1.85
$Cr_2[(HN)_2CH)_4(H_2O)_2$	2.48	no	

Another abnormal characteristic of dinuclear chromium carboxylates $Cr_2(O_2CR)_4L_2$

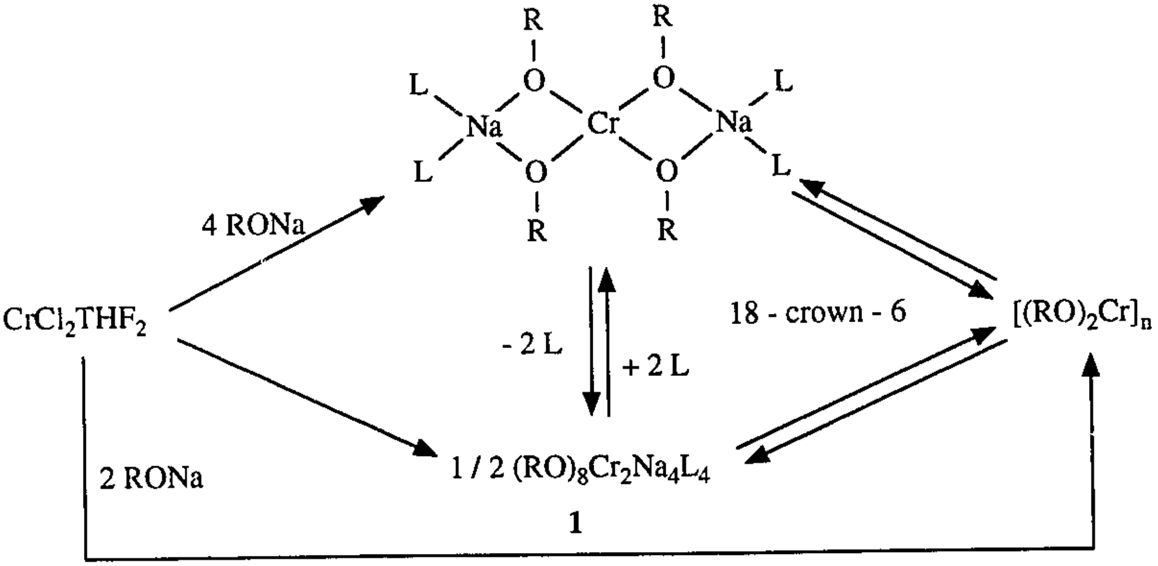
(L = MeOH, H_2O, Py, MeCN etc.) is provided by their weak, residual paramagnetism.[26] There are two possible explanations of this feature. Firstly, the partial paramagnetism of Cr(II) carboxylate samples may arise from traces of impurities such as Cr(II) or Cr(III) monomers. Secondly, these complexes may have inherent partial paramagnetism arising from a slight population of the triplet state (2J = 400 - 1000 cm^{-1}) at higher temperature. The separation in energy of a low-lying triplet state from a diamagnetic ground state can be estimated by magnetic or spectroscopic measurements.[27] Recent results have shown that the singlet-triplet separation not only varies as the axial ligand changes but also can be markedly affected by changing the nature of the bridging ligands. (e.g. from RCO_2^- to $R_2NCO_2^-$.) This result suggests, from a different point of view, that ligand plays very important role in Cr-Cr contacts.

When a dinuclear frame is supported by bridging ligands it is always difficult to establish the existence of the metal- metal bond and to evaluate its contribution to the stabilization of the dinuclear frame. In other words, it is impossible to establish the precise contribution of these bridging ligands to the stabilization of the dinuclear frame, to determine the length of the intermetallic contacts and to establish efficient magnetic couplings between the two metals. The bridging three- center chelating ligands, which have been widely employed for the preparation of quadruply bonded dichromium systems, undoubtedly possess a unique ability to function as binucleating ligands. They can form very short metal-metal contacts even in the cases where no direct metal-metal bond exists, such as in the case of tetrameric $[Li(DMOB)]_4$[28-32] and dimeric Cu(I) complexes. The existence of artificially short Li-Li contacts provide the best indication that these particular ligands are indeed capable of enforcing short intermetallic contacts by prevailing over electrostatic repulsions. As mentioned above, similar situation occurs in Cu(I) chemistry. In accordance to metal-metal bonding theory, d-orbitals or at least unpaired electrons are required in order to form M-M bonds. For this reason, no direct M-M bond exists in dinuclear Cu(I) complexes despite that very short M-M distances have been determined in $Cu_2(form)_2$ (form = p-$MeC_6H_4NCHNC_6H_4$-p-Me),[33] $Cu_2(PhNNNPh)_2$,[34] $[Cu(MeNNNMe)]_2$,[35] $Cu_2(O_2CCH_3)_2$,[36] $Cu_2[o\text{-}(Me_3Si)_2CC_5H_4N]_2$,[37] and $(o\text{-}Me_2N\text{-}C_6H_4)_4Cu_6Br_2$.[38] Although theoretical calculations on Cu(I) complexes have initially shown the existence of a certain degree of Cu-Cu bonding,[39] it is well-recognized that these interactions are very weak and unlikely able to hold the dinuclear frame together in the absence of bridging ligands. More recently, calculations carried out on $Cu_2(form)_2$ also ruled out the existence of direct Cu-Cu bonding.[33] Therefore, the dimeric structure and the short intermetallic contact of Cu(I) complexes is just the result of the bridging ability of these ligands. Several other examples of this type of behavior may be found in the chemistry of Ni(II) and Pd(II) complexes.[40,41]

In order to evaluate the ability of divalent chromium to form significant M-M bonds, it is important to study the chemistry of divalent chromium complexes of monodentate ligands without special bridging abilities. It is worth reminding that many examples of dimolybdenum and ditungsten complexes of monodentate ligands with and without additional monodentate bridging ligands have been reported.

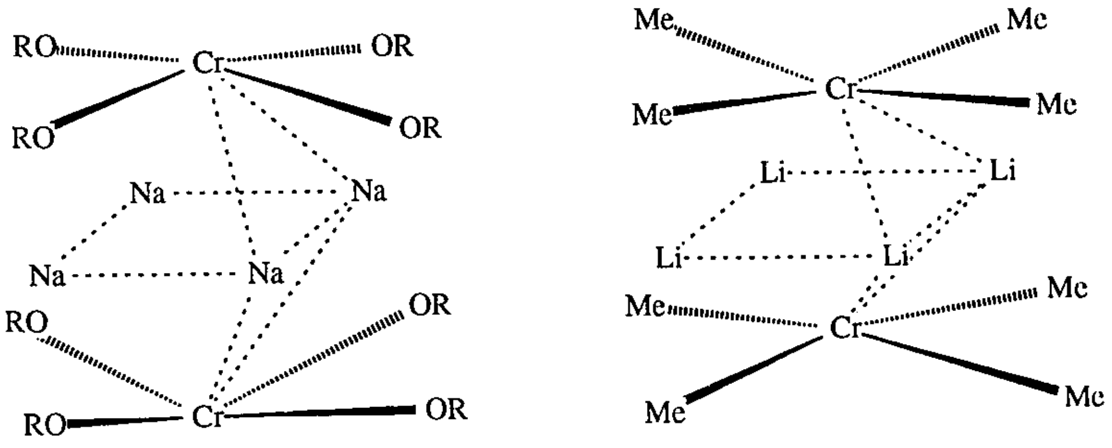
The molecular structures of a number of ternary halides containing Cr(II) and alkali metals such as $MCrCl_3$, M_2CrCl_4, etc. have been determined.[42-45] These species invariably contain high spin d^4 Cr(II). Available structural data have ruled out the presence of M-M bonds. All anhydrous and hydrated Cr(II) halides are mononuclear, dimeric or polymeric with high spin d^4 electronic configuration.[46,47] The polymeric aggregation of Cr(II) halides is easily disrupted via coordination of Lewis bases to form discrete mononuclear or dinuclear compounds, such as $CrCl_2(THF)_2$, $CrCl_2(PR_3)_2$, $CrCl_2(dmpe)_2$ (dmpe = bis-dimethyl-phosphano-ethane)[48,49] and $[CrCl(dppe)_{1/2}(CH_3CN)_2]_2(\mu\text{-}Cl)_2$.[50] In striking contrast, Mo analogues are almost always di- or tetra-nuclear with strong Mo-Mo bonds.

The structural features of Cr(II) alkoxides provide a good example of the poor ability of divalent chromium to form Cr-Cr multiple bonds. A series of monomeric and dimeric Cr(II) alkoxides have been synthesized and characterized (Scheme 1-2).[51-54] The structure of the final



Scheme 1-2

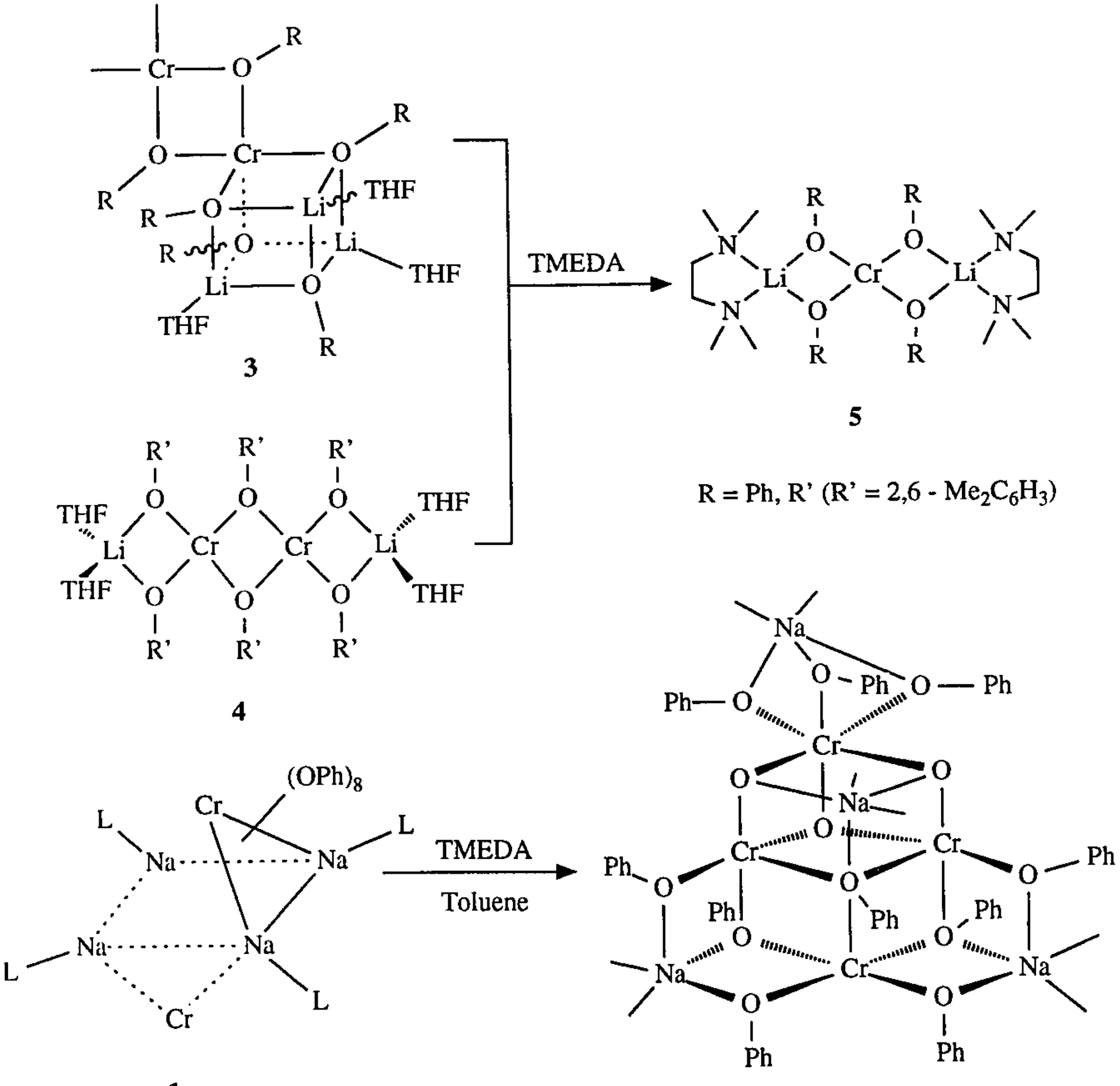
products strongly depends on both the nature of the ligands used and the stoichiometric ratio between the reagents. Square planar monomeric complexes were obtained in the case of bulky aryloxides. Although the dimeric complexes $(RO)_8Cr_2Na_4(THF)_4$ (R = **1a** Ph, **1b** ^{i}Pr) have been synthesized by reaction of $CrCl_2THF_2$ with an excess of NaOR. X-ray structural analysis shows that no direct Cr-Cr bond exists in these compounds (Cr-Cr distances = 3.634 to 3.739 Å). This is quite surprising when considering the close similarity with $Me_8Cr_2Li_4(THF)_4$ (Scheme 1-3). Although **1** and **2** have a similar structural framework, they remarkably differ in their Cr-Cr intermetallic separations. In the case of **1**, it is the alkali cation that holds the two monomeric 'Cr(OR)$_4$' fragments together as indicated by the facile cleavage obtained upon solvation of Na^+. On the other hand, unlikely the different size of the alkali metal cations (Li versus Na) may be responsible for this remarkable difference. Therefore, the nature of the donor atom (oxygen instead of carbon) may be pointed out as the factor which determines the absence of Cr-Cr bond. Attempts to synthesize Cr(II) alkoxides by using ROLi in place of RONa yielded the dimeric species **3** and **4** with totally different molecular frames (Scheme 1-4).[55]



1 Cr - Cr = 3.63 Å **2** Cr - Cr = 1.98 Å

Scheme 1-3

The simple modification of the coordination sphere of the alkali cation led to the

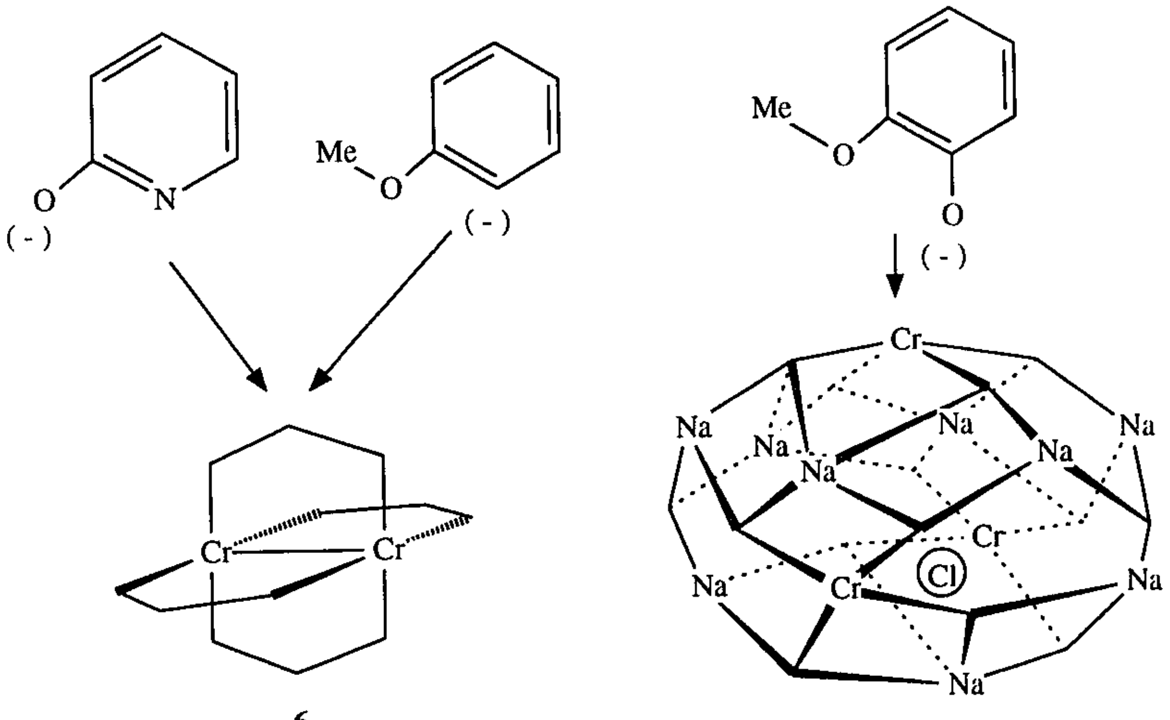


R = Ph, R' (R' = 2,6 - $Me_2C_6H_3$)

Scheme 1-4

cleavage of the $Cr_2(OR)_2$ unit in the case of Li aryloxides, whilst caused an increase in the nuclearity in the case of the corresponding Na derivatives (Scheme 1-4).[56] These results perhaps indicate that the alkali metals may play a role in the formation of the dinuclear frame of $Me_8Cr_2Li_4(THF)_4$ and in forcing the formation of the very short Cr-Cr contact, for reasons other than simply electrostatic.

Cotton et. al. reported that the reaction of three-center chelating ligands such as 2-hydroxopyridinate and 2-methyloxophenyl with $CrCl_2THF_2$ produced the quadruply-bonded dichromium complexes **6** with a supershort Cr-Cr contact.[57] However, results recently obtained in our lab have shown that replacement of three-center chelating ligands with guaiacol, where the bite of the three-center chelating ligand has been modified without significantly modifying the overall shape of the ligand, disrupts the lantern-type structure (Scheme 1-5).[55] X-ray structural analysis showed absence of Cr-Cr bonds while the trinuclear



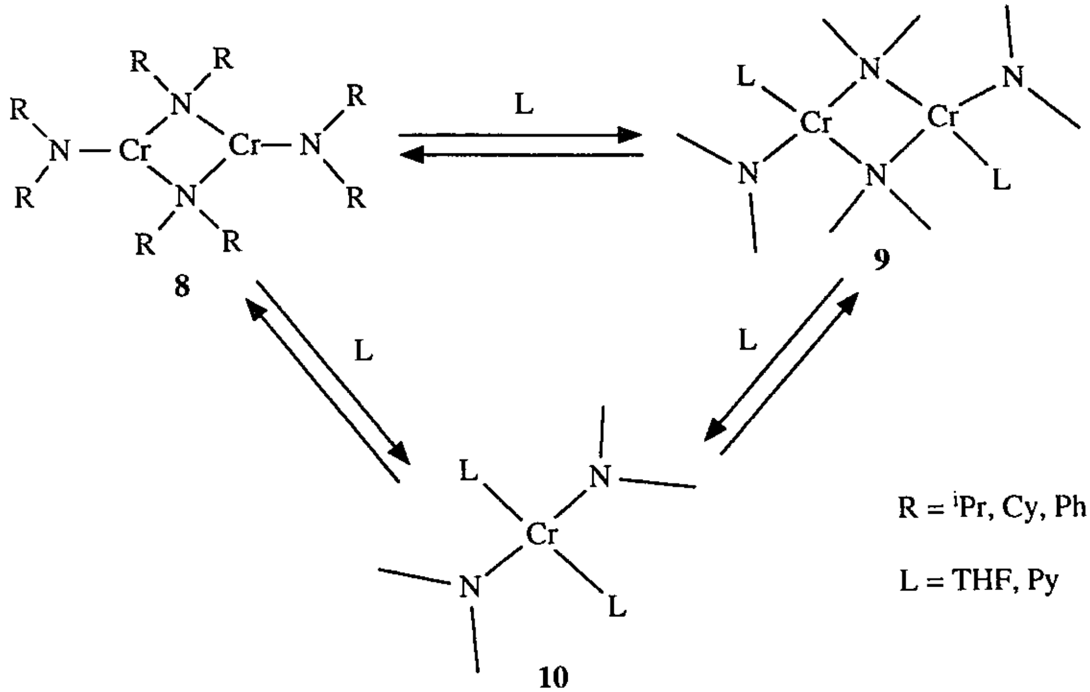
6

7

Scheme 1-5

structure is assembled by a network of bridging Cr-OR-Na-OR-Cr arrays. Once again the modification of the coordination sphere of the alkali cation in **7** cleaves the trinuclear structure **7**. These results clearly indicate that the ligand's "bite" determines the extent of Cr-Cr intermetallic separation.

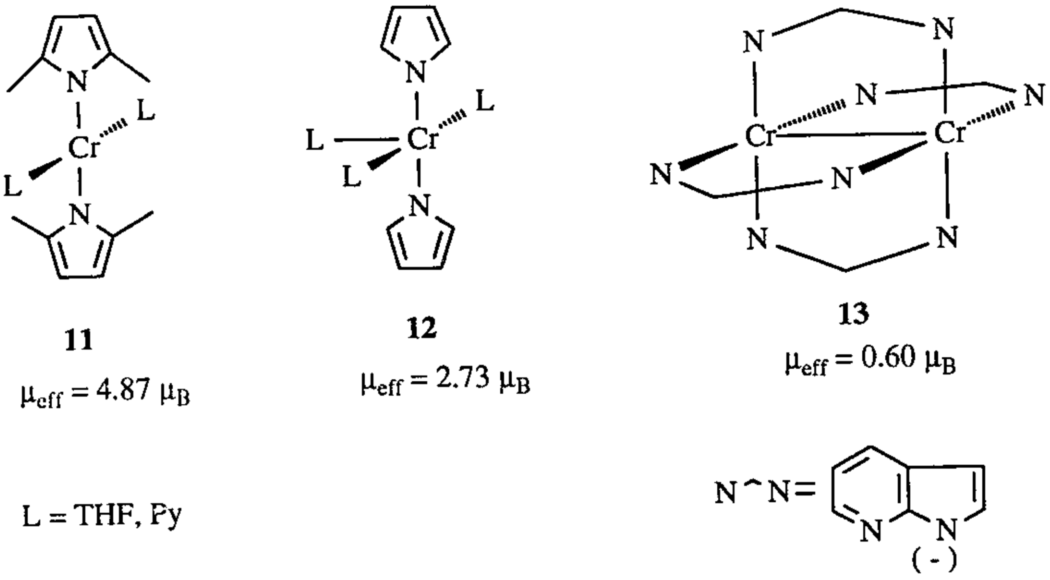
The systematic failure of oxygen donor based ligands to support Cr-Cr bonds may be explained by the ability of the oxygen donor atom to populate the Cr-Cr antibonding orbitals with its non-bonding electron pairs. Therefore, it was interesting to analyze the behavior of anionic organic amides whose nitrogen donor atom posses fewer non-bonding electrons than oxygen and might allow the formation of Cr-Cr multiple bonds. To this end several dinuclear Cr(II) amides $[(R_2N)_2Cr]_2$ (R = **8a** ^{i}Pr, **8b** Cy, **8c** Ph) have been synthesized.[58] The use of both monomeric and dimeric Cr(II) compounds as starting materials for the preparation of Cr(II) amides did not affect the nature of the reaction products. In all cases a dinuclear complex was found with short Cr-Cr distance (2.866 Å in **8a** and 2.834 Å in **8b**) and low paramagnetism, which may suggest the presence of some Cr-Cr bonding interaction. However, the temperature dependence of the magnetic properties, the increase of intermetallic distance (up to 3.152 Å) upon addition of coordinating solvents (THF or Pyridine), and the complete cleavage of the $Cr_2(NR_2)_2$ core by treatment with an excess of coordinating solvents (Scheme 1-6), strongly indicate the absence of a significant attractive force between the two centers. These results also show that the magnetic properties of the metal depend on the intermetallic separation imposed on the Cr_2N_2 core by the bridging ligands. As well, when the particular geometry of the three-center chelating ligand is restored in $(Ph_2N)^-$, by placing a donor atom (nitrogen) in the ortho position of the aromatic rings (bis-pyridylamine) and therefore introducing a minimal alteration in the steric and electronic configuration of the ligand, a supershort Cr-Cr



Scheme 1-6

intermetallic contact (1.937 Å) and the classical frame of the quadruply- bonded system were found in the dimeric Cr(II) amide derivative $Cr_2[(C_5H_4N)_2N]_4$. This behavior gives a strong indication that indeed the geometry of the three center chelating ligand is a determining factor for the formation of Cr-Cr quadruple bonds.

A similar trend was observed in the structural and magnetic properties of a series of Cr(II) pyrrolyl complexes[59] (Scheme 1-7). The square planar geometry of **11** and the pyramidal geometry of **12** are closely reminiscent of the hypothetical "monomeric units" which compose the quadruply-bonded dichromium complexes of three-center chelating ligands, where an additional axial donor atom plays the important role in determining the extent of intermetallic separation.[1,2] Compounds **11** and **12** are monomers because of the poor ability of



11 $\mu_{eff} = 4.87\ \mu_B$

12 $\mu_{eff} = 2.73\ \mu_B$

13 $\mu_{eff} = 0.60\ \mu_B$

L = THF, Py

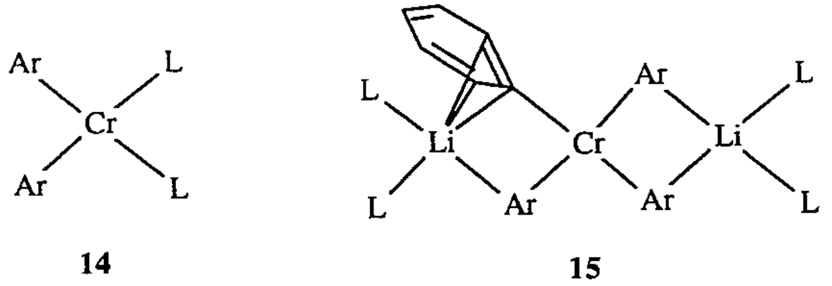
Scheme 1-7

pyrrole to bridge two metal centers. When the unique geometry of the three-center ligand is restored by placing a donor atom in one of the α positions of the pyrrolyl ring (such as in the case of 7-azaindole), the usual lantern-type quadruply-bonded dichromium complex **13** was obtained. However, the Cr-Cr distance in **13** (2.604 Å) is the longest ever found in lantern-type Cr(II) complexes and is hardly in agreement with the existence of a Cr-Cr quadruple bond. By contrast, the low residual paramagnetism is consistent with that of the other quadruplybonded Cr(II) systems with supershort intermetallic distances. This implies that three- center chelating ligands not only work as binucleating ligands but may also determine efficient electronic pairing between the two metals (probably through ligand-mediated superexchange). These results provide additional evidence about the primary role played by the bite of the three-center chelating ligand in determining: 1) the nuclearity; 2) the extent of intermetallic separation; and

3) the magnetic properties of the complexes.

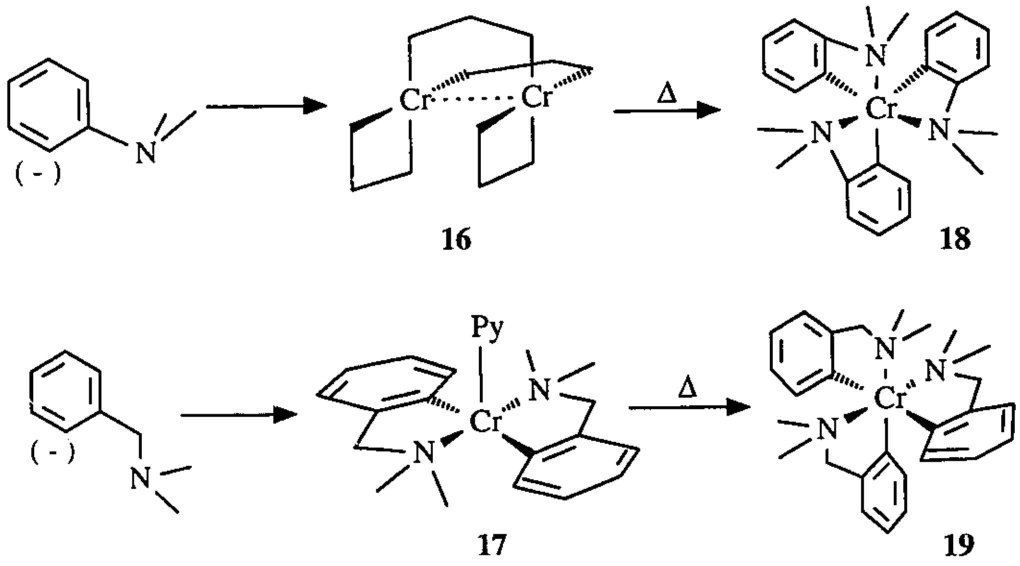
The above results convinced us that the Cr-Cr distance alone is not a good criterion to assess the existence of a Cr-Cr bond in the presence of bridging ligands. For dichromium(II) complexes of the general formula: $Cr_2(bridge)_4L_n$ with n = 0, 1, or 2, large variations in the metal-metal bond length (from the supershort 1.83 Å to a very long bond length of 2.60 Å) are commonly encountered. While the possibility that these variations may be associated with the size and shape of the ligand's bite did not encounter the favor of some scientists, it was argued that the length of the Cr-Cr bond might be the function of the basicity of both the bridging three-center chelating anion and the presence of additional ligands on the intermetallic axis.[60,61] Empirical relationships have been developed which apparently show that an increased basicity of the axial ligand L_{ax} will remove electronic charge from the intermetallic region, thus being responsible for the observed lengthening. Once more this behavior, which intuitively suggests that the Cr-Cr interaction cannot be strong, contrasts with the behavior of the quadruply-bonded dimolybdenum complexes where the metal-metal bond length (typically in the range 2.1 ± 0.1 Å for a wide range of ligands) is relatively insensitive to the nature of the ligand.

Another strategy to make dinuclear Cr(II) complexes with short Cr-Cr intermetallic contact may be based on the employment of alkyl or aryl ligands which use carbon as a donor atom. In fact, supershort Cr-Cr contacts have been found mainly in the Cr(II) alkyl and allyl derivatives. By contrast, the crystallographic characterization of both neutral and anionic Cr(II) aryl complexes has shown only monomeric structures (Scheme 1-8).[62,63] The failure of **15** to dimerize may be ascribed to the π-interaction of Li with the aromatic rings. Once again, when



Scheme 1-8

a three-center chelating geometry in the aryl ligand was reinstalled by placing a dimethylamino group in the *ortho* position of the phenyl ring, a dinuclear chromium complex **16** with a supershort Cr-Cr intermetallic contact was isolated[64] (Scheme 1-9). If the bite of the



Scheme 1-9

above three-center chelating ligand is enlarged, such as by inserting a CH_2 between the phenyl ring and the N donor atom, a pentacoordinated complex **17** was obtained. The square pyramidal geometry and the low spin d^4 electronic configuration of chromium in **17** are also reminiscent of those observed in the pyrrolyl complex $(Pyrr)_2CrPy_3$. The fact that complex **17** failed to form a dinuclear Cr(II) complex provided additional support to the idea that the ligand's bite is a very important factor in determining the Cr-Cr intermetallic separation and the nuclearity of Cr(II) complexes. Both dimeric **16** and monomeric **17** have a moderate thermal stability and, upon thermolysis, formed the corresponding monomeric Cr(III) species **18** and **19**, respectively. Once again, this result indicated that the presence of a three-center chelating ligand is a driving force for dimeric aggregation. However, other factors (e.g. electronic configurations of metal center), in addition to ligand geometry, may prevail over the binucleating ability of the three-centre chelating ligands.

1.4 Proposed research on Cr(II)

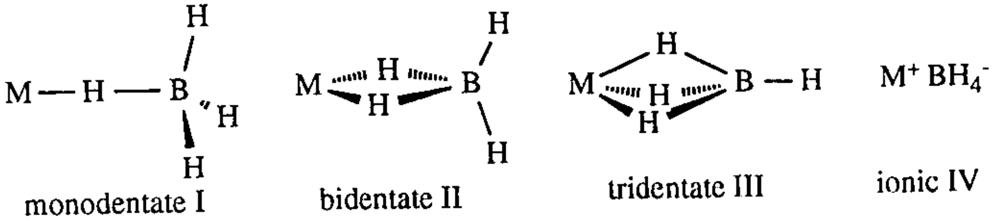
$[(TAA)Cr]_2$ (TAA = tetramethyldibenzotetraaza[14]annulene)[12] is the only Cr(II) dinuclear complex so far reported which does not contain any bridging ligands. The very short Cr-Cr distance (2.096 Å), the absence of bridging ligands and its almost diamagnetic nature suggest that a Cr-Cr quadruple bond possibly exists in this case, and that the Cr-Cr multiple bond may be strong enough to hold together the dimetallic unit. However, the $[(TAA)Cr]_2$ complex has the characteristic residual paramagnetism, and in addition, theoretical calculations indicate the presence of a Cr-Cr triple bond rather than a quadruple one.[65] This prompted us to carry out a study to evaluate the strength of the Cr-Cr multiple bond in $[(TAA)Cr]_2$. Our finding are reported in chapter 2.[66]

As mentioned above, the preparation and crystal structure of $[Me_8Cr_2][Li(THF)]_4$ marked a milestone in the development of the chemistry of Cr-Cr quadruple bonds. For a long time $[Me_8Cr_2][Li(THF)]_4$ **2** has been regarded as a rare example of a supershort Cr-Cr quadruple bond without bridging three-center chelating ligands. Furthermore, the two Cr atoms in **2** are slightly intruded into the plane described by the four μ^3-CH_3 ligands. So it is suggested that a supershort Cr-Cr quadruple bond may exist in complex **2**. However, theoretical calculations carried out by several methods agree that the non-bonding configuration is the leading one.[20] On the basis of the finding described above on the chemistry of Cr(II) aryloxides, it seemed likely that the presence of Cr-Me-Li-Me-Cr bridges may be a crucial factor to support the dinuclear frame. Since in the chemistry of Cr(II) alkoxides the modification of the alkali cation coordination sphere has a spectacular effect on determining both the nuclearity and the structure, we have studied the same effect on a new series of Cr(II) alkyls. Details about the preparation and characterization of novel Cr(II) alkyls are reported in chapter 3[67] and 4.[68]

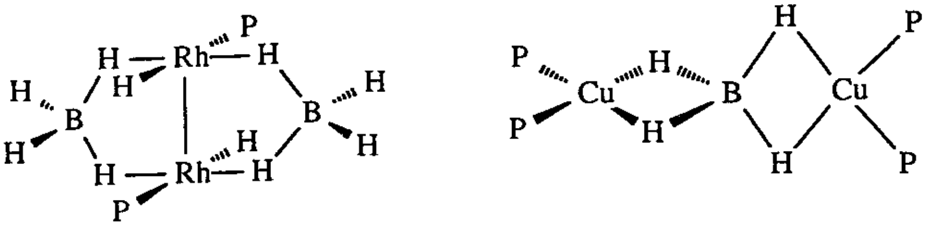
In order to identify the factors which are responsible of the ability of three center chelating ligands to form exceedingly short Cr-Cr contacts, we have investigated selected lantern-type systems where the bite, steric hindrance and electronic configurations of three-center chelating ligands and donor atoms were systematically varied. Chapter 5 will discuss how the ligand's steric bulk is capable of determining the nuclearity (dimeric vs monomeric) of Cr(II) complexes.[69] Since arylformamidinates have proven to be particularly versatile to form very short M-M distances with several different metals,[70-74] a series of amidinate ligands have been employed for this study.

We have also examined the role of both the electronic configuration of three-center chelating ligand and the donor atom in affecting the nuclearity. There are some cases reported in the literature where chelating ligands with the three center geometry failed in forming Cr-Cr bonds. This is the case, for example, of the dinuclear complex $Cr_2Cl_4(dmpm)_2$ (dmpm = bis-dimethylphosphano-methane)[75] which was formed by using the neutral ligand dmpm (where no π-electrons are present and only two pairs of non-bonding electrons are available). The absence of Cr-Cr bond in $Cr_2Cl_4(dmpm)_2$ was evidenced by the long Cr-Cr distance (3.24 Å) and the high paramagnetism. A possible explanation for this behavior may reside in the fact that there is no conjugation between the two terminal donor atoms. Therefore, the deprotonation of the CH_2 group such as in $(Ph_2PCHPPh_2)^-$ anion might restore the communication between the two phosphorous atoms. The results of this study are reported in chapter 6.[76]

The tetrahydroborate anion, BH_4^-, does not have π-electrons or non-bonding electronic pairs and usually works as a mononucleating ligand with four possible ligation patterns[77] (Scheme 1-10). However, in some cases this anion has shown to be able to work as a bridging ligand between two transition metals. In these cases the BH_4^- anion adopted a three center chelating geometry even though the anion does not possess a π system. Some dinuclear tetrahydroborates, formulated on the basis of magnetic and infrared measurements, are reported in Scheme 1-11.[78,79] This behavior suggests that it may be possible to prepare dinuclear Cr(II) borohydrides. Another reason to select BH_4^- ligand was provided by the



Scheme 1-10



Scheme 1-11

observation that, although transition metal tetrahydroborates are widely studied across the periodic table, no Cr(II) borohydride derivatives have been characterized. The preparation and characterization of a novel series of Cr(II) borohydrides are reported in chapter 7.[80]

1.5 M-M multiple bonds in V(II)

For the divalent divanadium compounds, most of the characterized complexes are mononuclear species with octahedral geometry [such as *trans*-$VCl_2(TMEDA)_2$, *trans*-VCl_2Py_4,[81] $V(TMEDA)R_2$ [R = $(2\text{-MeN-}C_5H_4N)^-$, $(PhNNNPh)^-$, 7-azaindolyl, $(PhNCHNPh)^-$, $(C_5H_4N)_2N^-$],[82] only a very few species with short V-V bonds have been prepared and characterized.[83-85] As in the case of Cr(II) derivatives, three-center chelating ligands, such as 2,6-dimethoxyphenyl, di-p-tolylformamidinato, were used. The major difference lies in the fact that in the case of V(II), in order to obtain the lantern-type structure the metal has to adopt a square-planar coordination geometry. While this geometry is normal for a d^4 Cr(II), it turns out to be very unusual for d^3 V(II) and d^2 V(III) which by far prefer octahedral structures. Therefore, the formation of dimers with short M-M bonds may be achieved only through either enforcement of an unusual square planar coordination geometry of the metal center (which, although very rare, has been documented in the case of bulky aryloxides)[285] or through formation of bioctahedral edge-sharing structures (which require considerable ligand distortion of the three-center chelating bridging ligand). On the other hand, there are no examples of dimeric vanadium(II) species with a very short V-V bond in the presence of monodentate ligands. Unsupported V-V multiple bonds are yet to be discovered. By contrast, there are several dinuclear organometallic V(III) complexes with bridging ligands where the short intermetallic distances have initially suggested the occurrence of V-V multiple bonds.[86-90] Further experimental studies on the magnetic properties of these systems and theoretical calculations have pointed out that no direct V-V bond exists in these systems, but only antiferromagnetic exchange.[90]

The sole theoretical work on a triply bonded divanadium system using the model compound $V_2(O_2CH)_4$ was reported in 1985.[91] The results from both Hartree-Fock-Roothan and Fenske-Hall calculations were well consistent with each other. Authors confidently predicted that $V_2(O_2CR)_4$ molecules should exist in a singlet state with V-V triple bonds. However, similar to the Cr(II) case, the single-bond configuration, $\sigma^2\delta^2\delta^{*2}$, was determined to contribute more significantly than the triply bonded to the overall stabilization energy.

1.6 Proposed research on V(II)

During our studies in the Cr(II) chemistry it was found that although very short and supershort Cr-Cr intermetallic contacts suggest Cr-Cr quadruple bonds, these bonds are very weak, easily cleaved, and controlled by the ligand's electronic configuration, steric hindrance, donor atoms, bite, etc. In order to probe the nature and the strength of V-V multiple bond, amidinate ligands were again chosen for the same reasons which made them valuable in the case of chromium. Details about this study are discussed in chapter 8.[92]

Since carboxylate anions have been proven to be versatile bridging three-center chelating ligands and many group 6 metal carboxylate complexes with very short M-M quadruple bonds have been structurally characterized, the synthesis of dinuclear V(II) carboxylates with short V-V intermetallic contacts was attempted. The surprising results of this study are reported in chapter 9.[93]

Chapter 2

Reversible Cleavage of Cr-Cr Multiple Bond in $[TAACr]_2$ [TAA = tetramethyldibenzotetraaza[14]annulene].

2.1 Introduction

Until the recent discovery that a dichromium moiety with a very short Cr-Cr distance may exist in $[TAACr]_2$ (TAA = tetramethyldibenzotetraaza[14]annulene) in the absence of any bridging interaction,[12] extremely short Cr-Cr contacts have been found in a particular class of compounds containing bridging three-center chelating ligands,[2,60,61,94-97] and in a few organometallic dimers with bridging carbon donor atoms.[7,8,98,99] The extremely short M-M distances and the magnetic properties of the complexes initially suggested that a strong M-M multiple bond[100] (thought to be quadruple) was the thermodynamic driving force for the dimer formation. However, more recent experimental[18,19,101-103] and theoretical[25] work has established that Cr-Cr quaduple bonds are paradoxically weak. We even question whether or not these Cr-Cr interactions are sufficient to be termed a chemical bond.[104]

The crystal structure of $[TAACr]_2$[12] (**2.1**) has shown that it is possible to form Cr-Cr bonds sufficiently strong to hold together the dimetallic unit, when the metal is "pyramidalized"[105] by a "small-hole" macrocyclic ligand. Since complex **2.1** has a very short Cr-Cr distance and the characteristic residual low paramagnetism, questions again arise about how strong this M-M bond should be. Theoretical calculations[65] carried out on **2.1** have indicated the presence of a Cr-Cr triple bond. Conversely, a quadruple bond has been calculated in the diamagnetic and isostructural di-molybdenum derivative, although the energy levels of the M-M bond orbitals are comparable in the two complexes.

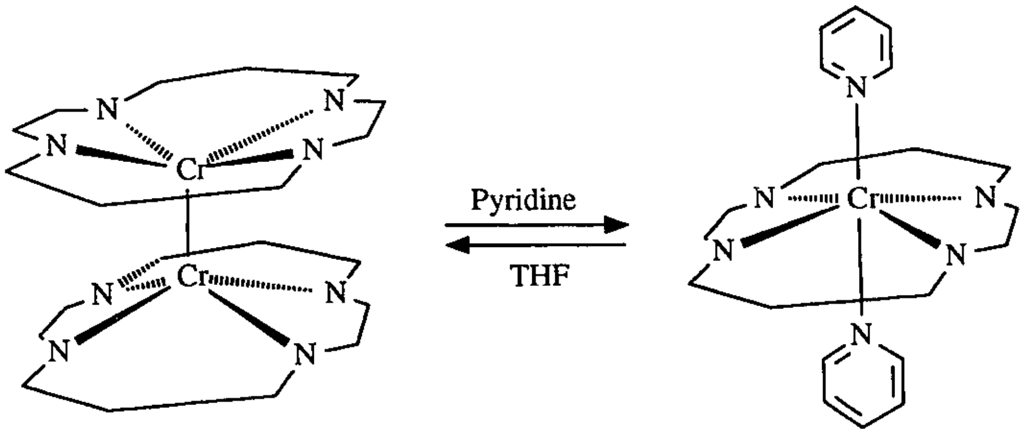
We felt that it was important to try to evaluate experimentally the strength of the Cr-Cr multiple bond of **2.1** and to provide a comparison with the isostructural molybdenum derivative. In this chapter we describe the reversible cleavage of $[TAACr]_2$ by pyridine to form an octahedral, low-spin monomeric $[TAACr(py)_2]py$ complex.

2.2 Results and Discussion

When the deep-red dimeric $[TAACr]_2$ (**2.1**) was recrystallized from pure pyridine, a black-brown needle-shaped crystalline solid was formed. Analytical results were consistent with the formulation $[TAACrpy_2].py$ (**2.2**). The paramagnetism of **2.2**, consistent with a low-spin d^4 electronic configuration, $[\mu_{eff} = 2.79\ \mu_B]$ strongly suggests that a major molecular reorganization occurred in pyridine solution. Conversely, when complex **2.2** was redissolved in either hot toluene or THF, the deep-red dimer **2.1** was reformed in moderate yield and analytically pure form (Scheme 2-1). This result indicates that a chemical equilibrium exists between the two species, and its position is probably determined by the amount of pyridine in solution. Unfortunately, attempts to grow suitable crystals of **2.2** failed, due to unfavorable crystal shape. However, a curious phenomenon of co-crystallization was observed when a pyridine solution of **2.2** was layered with a mixture of THF/hexane. The I.R. spectrum of the resulting large brown lozenges showed the same spectrum as it could be obtained by the overlap of the spectra of the pure **2.1** and **2.2**.

The X-ray crystal structure revealed one dimeric $[TAACr]_2$ and two monomeric octahedral $TAACrPy_2$. Two molecules of THF and one disordered molecule of pyridine were

Scheme 2-1



2.1

2.2

found also in the lattice. The dimeric unit is identical to that of the previously reported dimer[12] with the expected geometrical parameters and very similar Cr-Cr distance [Cr(1)-Cr(1a) = 2.075(7)Å]. The monomeric molecule is somewhat surprising. The octahedral geometry of chromium (Figure 2-1) with the two pyridine *trans* with respect to the macrocycle plane is unusual[48,49,106] for a Cr(II) d^4 electronic configuration, which usually prefers square-planar or square pyramidal geometries.[51,54-56,59,63, 107-109] Moreover, this octahedral geometry is unique among the TAA- transition metals derivatives, where the characteristic saddle-shape of the ligand imposes pyramidal geometries on the transition metal, with or without an additional ligand on the apical position. The deviation of the macrocycle from the planarity is probably responsible for the small difference in the Cr-N distances [Cr(1)-N(5) = 2.138(18), Cr(1)-N(6) = 2.059(19)Å] formed by the two axial pyridine molecules.

The facile dimer dissociation, the paramagnetism of the monomeric complex and its ability to co-crystallize with the dimer prompted us to reconsider the residual paramagnetism

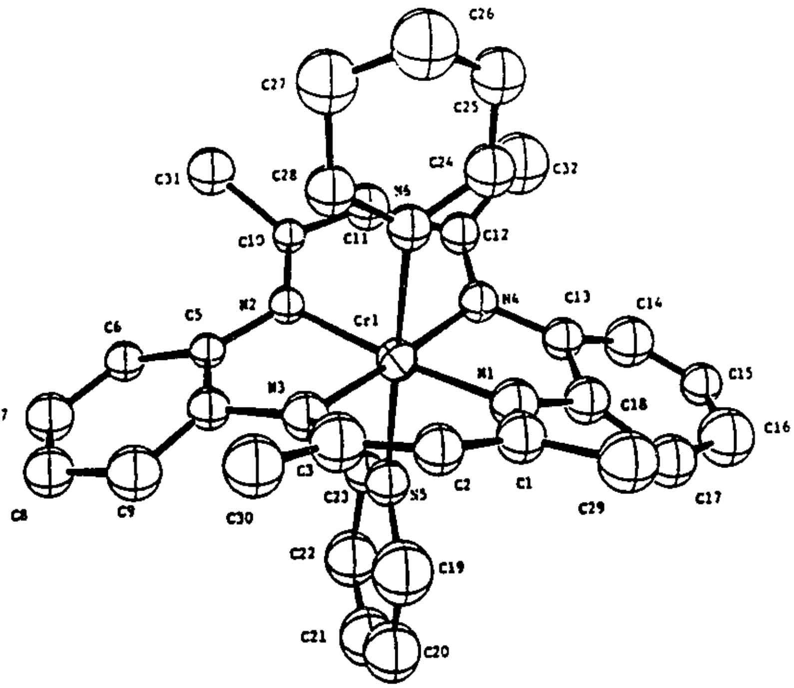


Figure 2-1. ORTEP plot of monomeric unit of **2.2**, showing the labeling scheme.

of **2.1** [μ_{eff}= 0.49 μ_B per chromium atom] observed in the temperature dependence of $1/\chi_g$.[12] Theoretical calculations[65] have indicated that a poor Cr-Cr δ overlap is the cause of the residual paramagnetism. However, it is not possible, on the basis of the results reported in this chapter, to exclude the possibility that the low residual paramagnetism might, in fact, be caused by a small amount of co-crystallized monomer, undetected by the single crystal X-ray analysis and by elemental analysis (the dimer always retains molecules of solvent in the lattice). Therefore, there is a possibility that the pure dimer could in reality be diamagnetic.

While we did not find evidence that the same cleavage may occur in the isostructural dimeric [TAAMo]$_2$,[65] the existence of the monomer/dimer equilibrium in the case of the chromium derivative indicates that the energy of a Cr-Cr multiple bond cannot be greater than four times the energy of a Cr-pyridine bond.

2.3 X-ray crystallography

X-ray diffraction experiments throughout this thesis were performed on a Rigaku AFC6 diffractometer. Crystal structures were solved by both Dr. C. Bensimon and S. Gambarotta. Data were collected at low T (~-160 °C) using the ω-2θ scan technique, to a maximum 2θ value of 50.0°, for suitable air-sensitive crystals mounted on glass fibers. Cell constants and orientation matrices were obtained from the least-squares refinement of 25 carefully centered high-angle reflections. The intensities of three representative reflections were measured after every 150 reflections to monitor crystal and instrument stability showing no significant decay. Data were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by either Patterson or direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were located in the difference Fourier maps and refined isotropically in the case of favorable observation/parameter ratio. The final cycle of full-matrix least-squares refinement was based on the number of observed reflections with $[I > 2.5\sigma(I)]$. Neutral atomic scattering factors were taken from Cromer and Waber.[110] Anomalous dispersion effects were included in Fcalc. All calculations were performed using the TEXSAN software package on a Digital VAX station. Details on data collection and structure refinement for **2.2** are reported in Table 2-1. Selected bond distances and angles are given in Table 2-2.

Table 2-1 Crystal Data and Structural Analysis Results

formula	$Cr_4N_{21}C_{121}H_{153}O_2$
formula weight	1241.66
crystal system	monoclinic
Space Group	C2
a (Å)	27.089(16)
b (Å)	15.125(5)
c (Å))	14.449(5)
α (deg)	
β (deg)	103.35(4)
γ (deg)	
V ($Å^3$)	5760(4)
Z	2
Radiation (MoKα Å)	0.70930
T (°C)	25
R	0.117
R_w	0.132

Table 2-2 Selected Bond Distances (Å) and Angles (deg)

Cr1-N1 = 1.95(3)	N5-Cr1-N6 = 176.9(18)
Cr1-N5 = 2.138(18)	N1-Cr1-N5 = 86.0(12)
Cr1-N6 = 2.059(19)	N1-Cr1-N6 = 91.9(12)

2.4 Experimental Section

All operations were performed under inert atmosphere in a dry-box (Vacuum Atmosphere) or using standard Schlenk techniques. $[Cr(TAA)]_2$[12] was prepared according to published procedures. Infrared spectra were recorded on a Mattson 9000 FT-IR instrument from Nujol mulls prepared in a dry-box. Samples for magnetic susceptibility measurements were weighed inside a dry-box equipped with an analytical balance, and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature. The magnetic moment was calculated according to standard methods,[111] and corrections for underlying diamagnetism were applied to data.[112] Combustion analysis data were obtained which satisfactorily verified the composition of the complexes.

Preparation of $[TAACrPy_2]$.py

$[TAACr]_2$ (2.0 g, 2.5 mmol) was added to freshly distilled dry pyridine (50 mL). The resulting suspension was boiled and filtered hot. Black-brown very fine needles were separated upon slow cooling at room temperature (1.3 g, 2.1 mmol. yield 42 %). El. Anal. Calcd (found) for $C_{37}H_{37}N_7Cr$: C 70.35(70.06), H 5.90(5.89), N 15.52(15.01), Cr 8.23(7.97). I.R. [KBr, nujol mull, cm^{-1}]: 1570(m), 1540(m), 1450(s), 1390(vs), 1270(w), 1195(s), 1180(s), 1030(m), 980(s), 725(m), 640(s), 610(s), 515(w), 490(w). [$\mu_{eff} = 2.79\ \mu_B$].

Preparation of [TAACrPy$_2$][TAACr]$_2$.Py.THF

A saturated solution of [TAACrPy$_2$].py in pyridine (15 mL) was layered with THF and hexane in a 70 cm Schlenck tube. Large brown lozenges were obtained upon slow diffusion (two months).

Chapter 3

Reversible cleavage of Cr-Cr quadruple bond of $[Me_8Cr_2][Li(THF)]_4$ via modification of the coordination sphere of the alkali cation.

3.1 Introduction

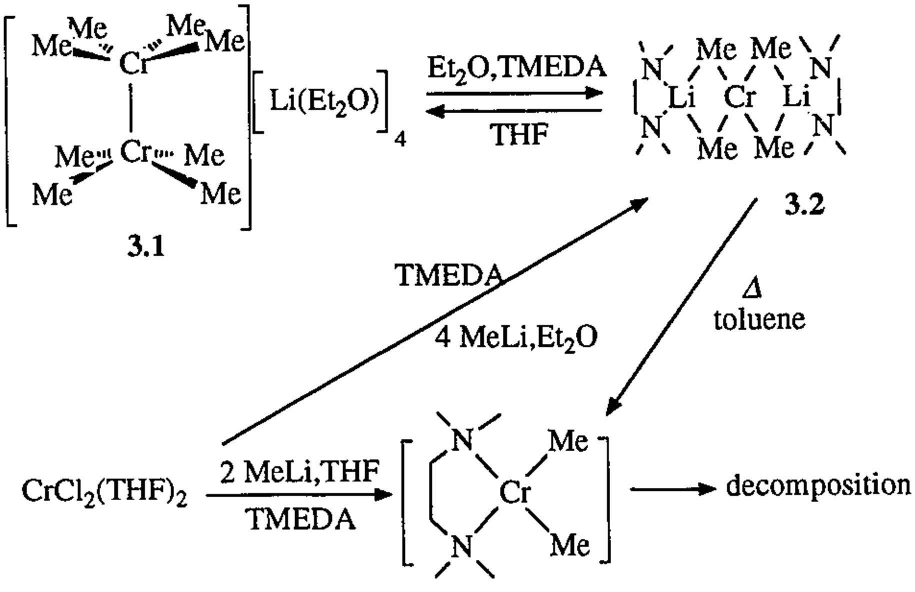
The preparation and crystallographic characterization of $[Me_8Cr_2][Li(THF)]_4$, reported by Krausse more than twenty years ago,[7] marked a milestone in the development of the chemistry of Cr-Cr quadruple bonds, by posing a puzzling problem for both synthetic and theoretical chemists. This complex is one of the very few cases[8,12,113] in which an extremely short Cr-Cr distance [Cr-Cr = 1.980Å] is formed in the absence of bridging three-center chelating ligands.[2,61] The distorted coordination geometry (the two chromium atoms are intruded into the coordination polyhedron), the small residual paramagnetism, the *supershort* intermetallic distance, and the absence of bridging ligands, all indicate the existence of a Cr-Cr quadruple bond[100] capable of a significant attractive force. By way of contrast, theoretical calculations predicted that the Cr-Cr interaction should be limited, in spite of the very short Cr-Cr distance, to either an efficient antiferromagnetic exchange[21,114,115] or a weak Cr-Cr quadruple bond.[22]

It was initially recognized that the four lithium cations exert a certain stabilizing role on the Cr-Cr quadruple bond.[7] Nevertheless, their interaction is commonly regarded as mainly electrostatic and it is common belief[22,116-118] that the Cr-Cr quadruple bond (either weak or strong) is the primary driving force for the formation of this dimer. However, the observation that Cr-(RO)-Na-(OR)-Cr bridges are capable of holding together a $[(RO)_8Cr_2]^{4-}$ frame in the absence of a direct Cr-Cr bond [Cr..Cr = 3.6 Å],[51,54-56] suggests the possibility that similar Cr-Me-Li-Me-Cr bridges might contribute significantly to stabilizing the dinuclear frame of **3.1**. The obvious consequence would be that, in spite of the supershort Cr-Cr distance and the efficient magnetic coupling, the Cr-Cr quadruple bond might not be the primary factor for holding together the dimetallic frame.

3.2 Results and Discussion

The reaction of $[Me_8Cr_2][Li(Et_2O)]_4$ (**3.1**) with TMEDA in ether solution proceeds rapidly at room temperature to form extremely air-sensitive orange-yellow crystals of $[Me_4Cr][Li(TMEDA)]_2$ (**3.2**) (Scheme 3-1). The same compound can be conveniently prepared in large scale and analytically pure form by reaction of $CrCl_2(THF)_2$ with four equivalents of MeLi in Et_2O containing an excess of TMEDA, and further recrystallization from pure

Scheme 3-1



TMEDA. Complex **3.2** is surprisingly stable in neat TMEDA, from which it can be recrystallized at about 80°C, without appreciable signs of decomposition. Conversely, decomposition and formation of black tarry material was observed in hot toluene. Similar decomposition products were observed upon treating $CrCl_2(THF)_2$ with two equivalents of MeLi in the presence of TMEDA. The formation of **3.2** can be reversed and complex **3.1** can be reformed just by dissolving **3.2** in THF, evaporating the solvent to dryness and recrystallizing the residual solid from ether. Complex **3.2** is paramagnetic with a magnetic moment consistent with a monomeric square-planar d^4 Cr(II) complex [$\mu_{eff} = 4.98\ \mu_{BM}$].

The monomeric structure of **3.2** has been demonstrated by X-ray analysis. The molecule is composed of a square-planar central monomeric Me_4Cr core [C(7)-Cr(1)-C(7a)=180.0(1)°, C(7)-Cr(1)-C(8)=93.8(2)°] connected to each of the two LiTMEDA fragments through two bridging methyl groups (Figure 3-1). The two identical $CrLiMe_2$ moieties are folded in a butterfly conformation with the lithium atom elevated above the Me_4Cr plane [C(7)-Cr(1)-Li(1)-C(8)=131.3(3)°]. The angles subtended at the bridging carbon atoms [Cr(1)-C(7)-Li(1)=72.4(2)°, Cr(1)- C(8)-Li(1)=72.6(2)°] are considerably narrow and, together with the short Cr-Li distances [Cr(1)-Li(1)=2.589(6)Å], might suggest some extent of Cr-Li bonding interaction. The Cr-C distances are elongated [Cr(1)-C(7)=2.204(5)Å, Cr(1)-C(8)=2.213(4)Å] with respect to other neutral Cr(II) alkyls[48,62] and are comparable to those found in complex **3.1** and other bridged Cr(II) aryls.[63,99] The lithium atoms possess a normal tetrahedral geometry with the coordination tetrahedron defined by two carbon and two TMEDA nitrogen atoms [Li(1)-C(7)= 2.176(7)Å, Li(1)-N(1)= 2.136(6)Å].

The cleavage of the Cr-Cr quadruple bond, obtained by replacing a Lewis base

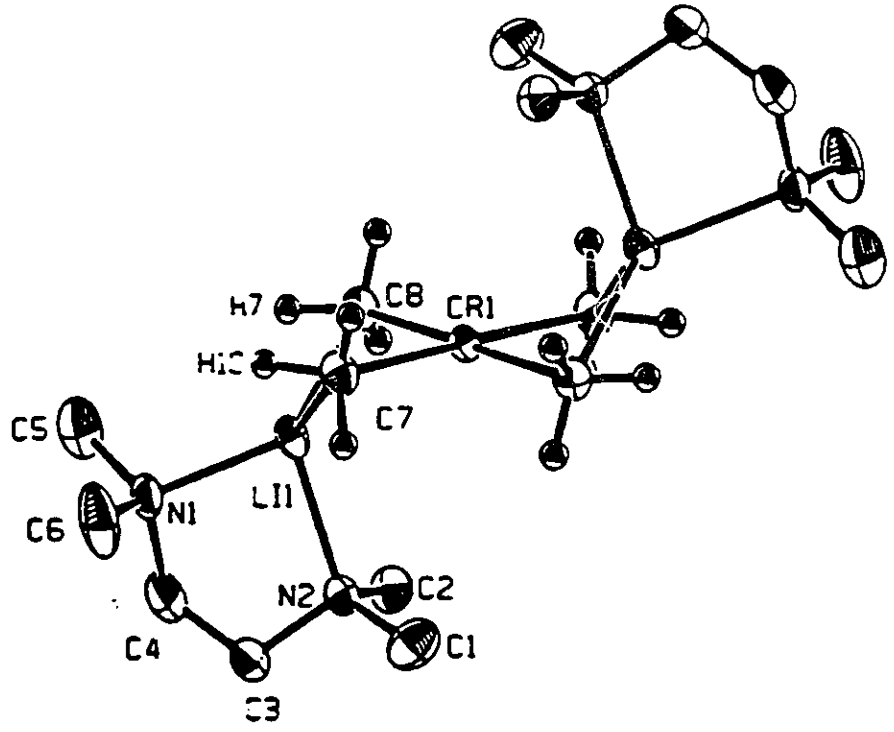


Figure 3-1. ORTEP drawing of **3.2**, showing the labeling scheme.

coordinated to the alkali cation, and without altering the coordination environment of the transition metal, is surprising. It demonstrates that: *i*) the role of the alkali cation is vital to the stability of the Cr-Cr interaction of complex **3.1** and *ii*) the Cr-Cr interaction (if any) cannot hold together the dinuclear frame in the absence of Cr-Me-Li- Me-Cr bridges. Therefore, the question again arises as to whether or not the definition of chemical bond is appropriate for the Cr-Cr interaction[25] in complex **3.1**, in spite of the very short intermetallic distance and the efficient magnetic coupling. Interestingly, we have found that the isostructural $Me_8Mo_2Li_4(THF)_4$[119] cannot be cleaved in similar or harder reaction conditions, in agreement with theoretical calculations which predict the existence of a significant Mo-Mo quadruple bond.[12] Another fascinating question arises from the nature of bonding in the Cr-Me-Li-Me-Cr bridges, thus expected to be responsible for holding together the dinuclear frame of **3.1**.[7] Although indication of the nature of this interaction cannot be provided by the poor quality structure of **3.1**, it might be suggested by the bonding mode of lithium with the Me_4Cr moiety of **3.2**. The data set of **3.2** was of sufficient quality to locate and refine the hydrogen atoms. The hydrogens of each bridging methyl group define a slightly distorted tetrahedron centered on carbon with the fourth position occupied by chromium. Each lithium atom is placed side-on and perpendicularly with respect to one of the three C-H bonds of each of two bridging methyl groups [Li(1)-H(7)-C(8)=88.67, Li(1)-H(10)-C(7)=82.27], forming considerably short Li...H distances [Li1-H(10)=2.064Å, Li(1)-H(7)=1.992Å]. These geometrical features suggest, as long as we consider the hydrogen atom positions as significant, that the sp^3 orbital of the bridging carbon atom is oriented mainly towards the transition metal. Thus, the short Cr-Li distance of **3.2**, the folding of the Me_2CrLi core and the narrow angle subtended at the carbon atom might be regarded as the optimal distance imposed by the two Li-H agostic interactions, rather than as an improbably strong Cr→Li bond.

3.3 X-ray crystallography

Refer to Section **2.3**. Details on data collection and structure refinement for **3.2** are reported in Table 3-1. Selected bond distances and angles are given in Table 3-2.

Table 3-1 Crystal Data and Structural Analysis Results

formula	$CrC_{16}H_{44}N_4Li_2$
formula weight	458
crystal system	orthorhombic
Space Group	Pcab
a (Å)	12.707(5)
b (Å)	15.600(6)
c (Å))	11.829(6)
V (Å^3)	2345(3)
Z	4
Radiation (MoKα Å)	0.71069
T (°C)	-173
R,	0.049
R_w	0.047

Table 3-2 Selected Bond Distances (Å) and Angles (deg)

Cr1-Li1 = 2.589(6)	C7-Cr1-C7a = 180.0(1)
Cr1-C7 = 2.204(5)	C7-Cr1-C8 = 93.8(2)
Cr1-C8 = 2.213(4)	C7-Cr1-Li1 = 131.3(3)
Li1-C7 = 2.176(7)	Cr1-C7-Li1 = 72.4(2)
Li1-N1 = 2.136(6)	Cr1-C8-Li1 = 72.6(2)
Li1-H10 = 2.064	L1-H7-C8 = 88.67
Li1-H7 = 1.992	Li1-H10-C7 = 82.87

3.4 Experimental Section

All operations were performed under inert atmosphere in a dry-box (Vacuum Atmosphere) or using standard Schlenk techniques. $Me_8Cr_2Li_4L_4$ (L = THF, Et_2O)[7] was prepared according to published procedures. Infrared spectra were recorded on a Mattson 9000 FT-IR instrument from Nujol mulls prepared in a dry-box. Samples for magnetic susceptibility measurements were weighed inside a dry-box equipped with an analytical balance, and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature. The magnetic moment was calculated according to standard methods,[111] and corrections for underlying diamagnetism were applied to data.[112] Combustion analysis data were obtained which satisfactorily verified the composition of the complexes.

The preparation of $[Me_4Cr][Li(TMEDA)]_2$ (3.2).

Method A: A light-yellow solution of **3.1** (0.8 g, 1.5 mmol) in Et_2O (200 mL) was treated with neat TMEDA (20 mL). The resulting orange solution was concentrated to small volume and the little amount of insoluble material, separated during the concentration, was removed by filtration. Extremely air- sensitive orange-yellow crystals of **3.2** (0.6 g, 1.7 mmol, 57% yield) were obtained upon standing overnight at -30°C. Satisfactory analytical results were obtained. I.R. [nujol mull, cm^{-1}, KBr] ν: 1360(s), 1295(s), 260(m), 1180(m), 1160(s), 1135(s), 1100(m), 1070(s), 1040(s), 1020(s), 950(s), 840(w), 790(s), 770(s), 720(w), 615(s), 590 (sh). [$\mu_{eff} = 4.98\ \mu_B$]. Anal. (Calcd) found for $C_{16}H_{44}N_4CrLi_2$: C (53.62), 53.44; H (12.37), 12.28; N (15.63), 15.44; Cr (14.51), 14.35.

Method B: A suspension of $CrCl_2(THF)_2$ (12.4 g, 46 mmol) in neat TMEDA (400 mL) was refluxed overnight originating a blue insoluble solid. The resulting mixture was cooled to -50°C and a solution of MeLi in Et_2O (130 mL, 1.4 M) was added dropwise by syringe. A green solid initially formed and disappeared upon stirring at room temperature originating an orange suspension. The solid was isolated by filtration and recrystallized from neat TMEDA (80°C), yielding bright-orange octahedral crystals (10g, 28mmol, 61% yield).

Chapter 4

Cr(II) Organochromates. Preparation, Characterization and Stability.

4.1 Introduction

Metallacycle[120-122] and Schrock-type carbenes[123-131] of Mo and W play a fundamental role in a series of synthetically useful transformations[132-140] and some important catalytic processes.[141-148] By way of contrast, chromacyclobutane species and chromium alkylidenes remain almost unknown[149,150] despite of the remarkable development of the chemistry of Fisher-type chromium(II) carbenes.[151-158] Since these species are currently used in quite a number of stoichiometric metal-promoted transformations,[159-169] we became interested in the preparation of low- and medium-valent chromium alkylidenes (Schrock-type). An electron-rich configuration of the chromium atom is in fact expected to offer a variety of reactivity patterns due to the ability of the low-valent metal to perform oxidative addition reactions, thus further extending the range of reactivity and catalytic performances. Since Cr(II) alkyls are the most obvious precursors for the preparation of Cr(II) carbenes and metallacycles, and since examples of divalent chromium organometallics remain relatively rare[8,48,49,63,64,113,170-174] (apart from the quadruply bonded systems), we have recently undertaken a systematic synthetic study to clarify the structure, synthesis and stability features of these species.

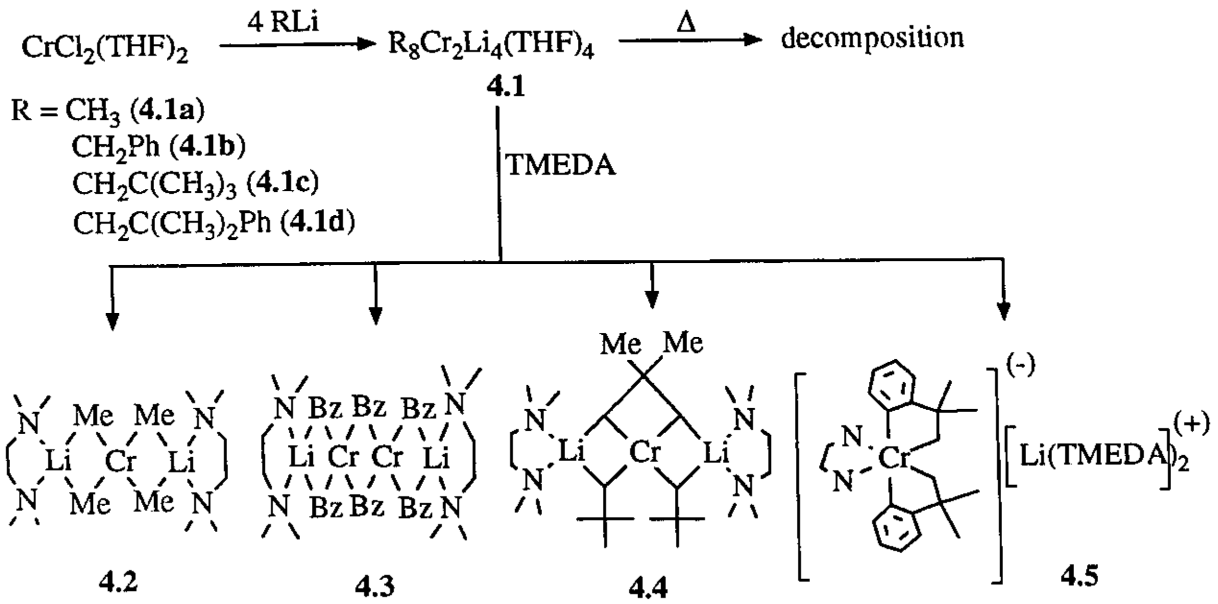
Last but not least, interest in the chemistry of divalent chromium alkyls is attracted by the behavior of the few existing dinuclear Cr(II) complexes of non-chelating alkyls. A literature survey suggested that monodentate alkyls might possess a unique ability to bridge dichromium species, thus favoring the occurrence of short or extremely short Cr-Cr contacts.[113,172-175] In an attempt to understand this important characteristic, we have recently revisited the chemistry of $Me_8Cr_2[Li(THF)]_4$[7] finding, despite the presence of a very short intermetallic contact, that no significant Cr-Cr bond exists in this species.[67] While the factors which are capable of enforcing the remarkably short Cr-Cr distance remain to be identified, the crystal structure of the monomeric $Me_4Cr[Li(TMEDA)]_2$[67] suggests the attractive possibility that Li..H(Me) agostic interactions might be capable of assembling dimeric structures and enforcing very short Cr-Cr contacts. Therefore, since the presence of α-hydrogen atoms seems to be a prerequisite for the occurrence of bonding interaction with the alkali cation, we have selected for this preliminary study alkyls such as $-CH_2Ph$, $-CH_2(t\text{-}Bu)$ and $-CH_2C(Ph)Me_2$. The most attractive characteristic of these alkyls, however, is provided by their well-known ability to undergo α-hydrogen abstraction to form alkylidene and/or metallacyclobutane species, as indicated by the chemistry of high-valent Mo and W congeners.

In this chapter, we describe the synthesis, characterization and stability properties of a novel series of alkyl Cr(II) complexes together with their transformation into unprecedented alkylidene Cr(III) derivatives, and Cr(II) and Cr(III) metallacycles.

4.2 Results and Discussion

As illustrated in Schemes 4-1 and 4-2, the result of the reaction of $CrCl_2(THF)_2$ with RLi [R = CH_2Ph, Me, $CH_2C(CH_3)_3$, $CH_2C(CH_3)_2Ph$] was determined by both the RLi/Cr stoichiometric ratio and the presence in the reaction mixture of a chelating Lewis base (TMEDA = N,N,N',N'-tetramethylethylenediamine). In the cases where a molar ratio of 4 was employed (Scheme 4-1), the reactions led to the initial formation of bright-yellow/ orange,

Scheme 4-1



poorly-soluble and almost diamagnetic materials. Unfortunately, in contrast to $Me_8Cr_2Li_4(THF)_4$ (**4.1a**), which is thermally stable, the benzyl (**4.1b**), neopentyl (**4.1c**) and neophyl (**4.1d**) analogues are very labile thus preventing analytical determinations. In all cases, the complexes had to be isolated from reaction mixtures kept at temperatures below -40°C to avoid a rapid decomposition with formation of deeply-colored intractable solutions. Similar behavior was also observed in solid state where crystalline samples of **4.1b** and **4.1d** decomposed within a few hours at temperatures about -20°C. Although the formulation is not proven, we speculate that these complexes are isostructural with $Me_8Cr_2Li_4(THF)_4$, since they showed the same residual paramagnetism which has been determined in the dimeric $Me_8Cr_2Li_4(THF)_4$, and in general for the quadruply bonded systems.

The behavior of the diamagnetic and dimeric $R_8Cr_2Li_4(THF)_4$ (**4.1**) with respect to the coordination of Lewis bases is somewhat surprising. In the case of the methyl derivative **4.1a**, displacement of THF from the coordination sphere of lithium takes place with monodentate ligand such as pyridine, without significant modification of the molecular structure and of the magnetic properties of the product. Only a slow decomposition was observed upon heating **4.1a** in the presence of a large excess of pyridine. In contrast, treatment with a chelating diamine such as TMEDA, gave a reversible reaction where the dinuclear frame was cleaved to form the monomeric and paramagnetic $Me_4CrLi_2(TMEDA)_2$ (**4.2**). The isolation and crystal structure determination of this complex has been described previously[67] (see chapter 3).

Similar attempts to cleave the dinuclear structures of **4.1b**, **4.1c** and **4.1d** via reaction with TMEDA gave an unpredictable trend of reactions. The addition of TMEDA to **4.1b** or reaction of $CrCl_2(THF)_2$ with 4 equivalents of $PhCH_2Li(TMEDA)$ complex gave the moderately stable $(PhCH_2)_6Cr_2Li_2(TMEDA)_2$ (**4.3**) as a diamagnetic reddish-brown crystalline solid. The dimeric structure is indicated by the diamagnetism observed in both solid state and solution, while the formulation is suggested by the integration of the NMR resonances. This type of dinuclear structure is also suggested by the analogy with the chemistry of dinuclear Cr(II) aryloxo lithium chromates.[55]

In the case of the $[(CH_3)_3CCH_2]_8Cr_2Li_4(THF)_4$ derivative, the reaction proceeded in a similar manner when either the preformed complex was resuspended in THF containing TMEDA, or neat TMEDA was added to the crude reaction mixture from the preparation of **1c** maintained at -50°C. After the addition of TMEDA, the reaction was allowed to reach room temperature. Subsequent cooling gave a poor yield of deep-orange crystals of the metallacycle derivative $[(CH_3)_3CCH_2]_2[CH_2C(CH_3)_2CH_2]Cr[Li(TMEDA)]_2$ (**4.4**).

The complex is monomeric and consists of one chromium atom bound to two neopentyl groups and to the two terminal carbon atoms of a $CH_2C(CH_3)_2CH_2$ unit, forming a chromacyclobutane ring (Figure 4-1). Two Li(TMEDA) moities are connected to the central

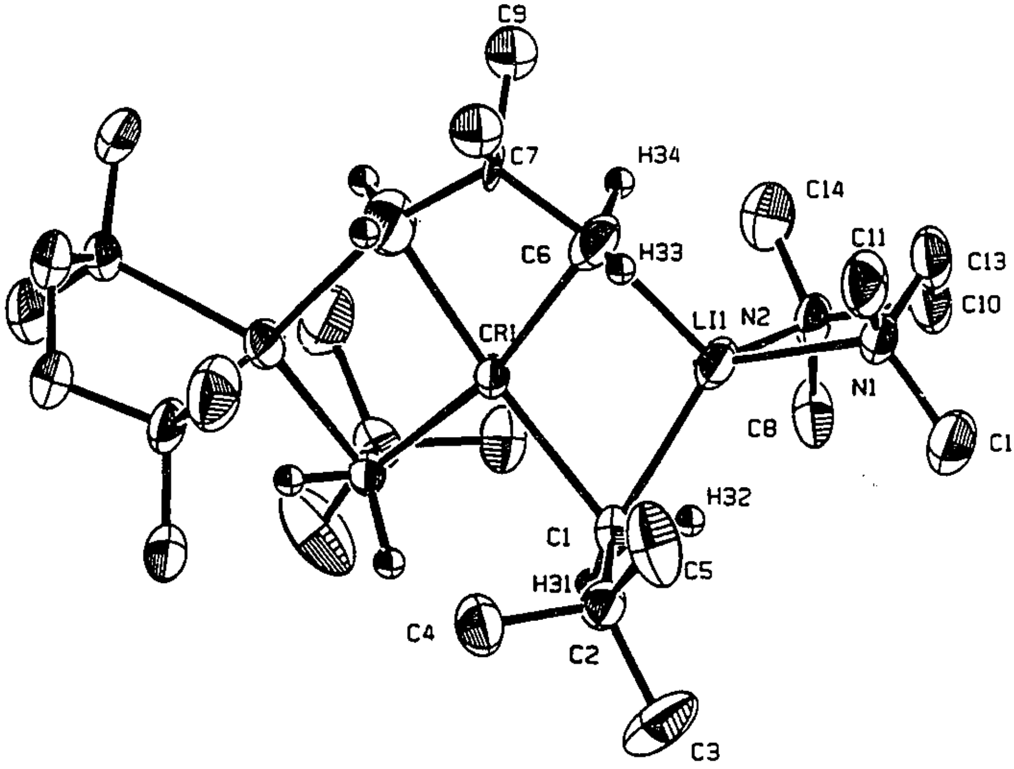


Figure 4-1. ORTEP plot of **4.4**

organochromium core by the bridging carbon atoms of the neopentyl and cyclobutane ring. The backbone of the molecule is formed by an almost linear Li-Cr-Li array [Li1-Cr1-Li1a = 167.9(5)°] with the chromium atom placed in the center of a distorted square-plane defined by four bridging carbon atoms. Of these four bridging carbon atoms, two are provided by two bridging neopentyl groups placed in *cis* position with respect to the square-planar chromium and with the bulky t-Bu moieties pointing in opposite directions with respect to the molecular plane [Cr1-C1-C2 = 113.9(4)°]. The remaining two bridging carbon atoms are provided by one metallacyclobutane moiety. The plane defined by the four bridging carbon atoms [Cr1-C1 = 2.267(6)Å, Cr1-C6 = 2.198(7)Å], the two lithiums [Li1-C1 = 2.29(1)Å, Li1-C6 = 2.12(1)Å] and chromium is rather twisted. In contrast to the crystallographically imposed planarity of the central metallacyclobutane core [Cr1-C6-C7-C6 = 0.0°, Cr1-C6-C7 = 91.6(4)°, C6-C7-C6 = 108.2(7)°], the two $LiCrC_2$ cores are significantly folded, [Cr1-C1-Li1-C6 = 20.4(4)°, Cr1-C6-Li1 = 77.4(4)°, C6-Li1-C1 = 102.3(5)°, Cr1-C1-Li1 = 72.5(3)°] forming a rather short Cr-Li non bonding distance [Cr1-Li1 = 2.70(1)Å]. The coordination geometry of the chromium atom is distorted square-planar [C1-Cr1-C6 = 164.2(3)°, C1-Cr1-C1a = 92.1(3)°, C6-Cr1-C6a = 68.5(4)°] while that of the two alkali cations is distorted tetrahedral [N1-Li1-N2 = 84.5(4)°, N1-Li1-C1 = 113.2(5)°]. Similar to the case of the monomeric $Me_4CrLi[(TMEDA)]_2$, short contacts have been found between one of the two α-hydrogens of the neopentyl group (the position of which was isotropically refined) and the alkali cation [Li1-H32 = 1.93Å]. This contact is also significantly shorter than the Li-C distance of the corresponding carbon atom [Li1-C1 = 2.29(1)Å]. This suggests that a fairly strong Li-H agostic interaction may be the factor which holds together the heterodimetallic frame and which also folds the $CrLiC_2$ core. Conversely, the hydrogen atoms of the two bridging carbons of the metallacyclobutane moiety are almost equidistant from the lithium atom [Li1-H33 = 2.24Å, Li1-H34 = 2.39Å] while the distance from the corresponding carbon atom [Li1-C6 = 2.12(1)Å] appears to be the shortest contact. The methyl group of the metallacyclobutane group displayed large thermal parameters, possibly indicating some disorder. The disorder has been modeled by assigning an occupancy of 33% of the carbon atom over three positions, (C9, C15, C16) as revealed by the difference Fourier maps. The significant improvement of the residual values supports the accuracy of the model.

In the initial step, the reaction probably formed anionic metallates analogous to the cases of **4.2** or **4.3**, which produce the metallacyclobutane via γ-hydrogen abstraction and consequent elimination of neopentane. The divalent oxidation state of the chromium atom of complex **4.4** is indicated by both the solid state crystal structure and confirmed by the magnetic moment which is as expected for a Cr(II) d^4 high-spin electronic configuration. This species is a rare example of a metallacyclobutane species and a very unique case in the chemistry of Cr(II).

In the case of the neophyl derivative $[(CH_3)_2PhCCH_2]_8Cr_2Li_4(THF)_4$ (**4.1d**), the reaction with TMEDA led to the formation of anionic Cr(III) species $[o\text{-}C_6H_4(C(CH_3)_2CH_2]_2Cr(TMEDA)][Li(TMEDA)_2]$ (**4.5**) where the two aromatic rings of both neophyl groups have been metallated in the *ortho* position. The octahedral coordination geometry, characteristic of Cr(III), is completed by one molecule of TMEDA. A lithium cation coordinated to two molecules of TMEDA was found in the crystal structure in a stoichiometric ratio of 1/1 with chromium, thus indicating a formal oxidation state of (+III) for the metal. The oxidation state of the transition metal has been further confirmed by the measurement of the magnetic moment which is consistent with a Cr(III) d^3 high-spin electronic configuration. Although it is unclear how the oxidation of the metal center occurs in this case, a disproportionation reaction is the most likely possibility. This is also suggested by the rather poor yield, which indicates the likelihood of more products being present in the reaction mixture.

The structure of **4.5** consists of two separate ionic fragments. The anion (Figure 4-2)

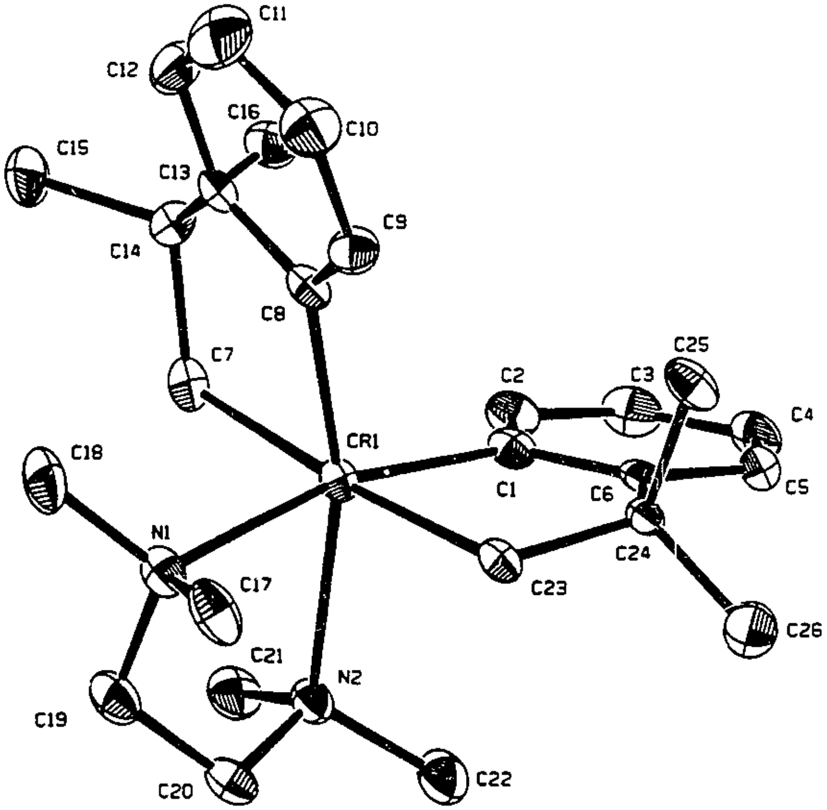
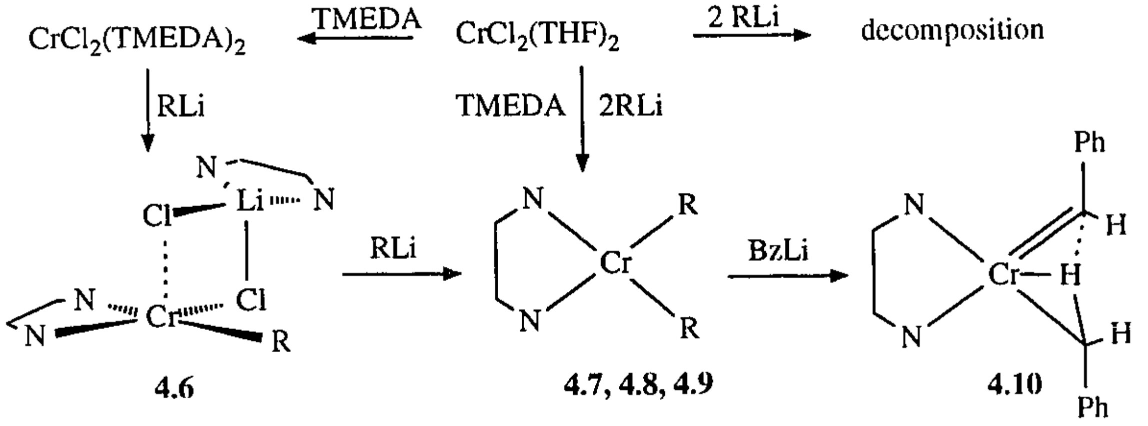


Figure 4-2. ORTEP plot of **4.5**

is composed of a slightly distorted octahedral Cr(III) atom with the coordination octahedron defined by the two nitrogen atoms of one chelated TMEDA molecule (Cr1-N1 = 2.335(4)Å, Cr1-N2 = 2.328(4)Å] and four carbon atoms of two neophyl groups [C1-Cr1-N1 = 166.0(2)°, C7-Cr1-C23 = 175.4(2)°, C8-Cr1-N2 = 165.4(2)°]. Each neophyl group is bound to chromium through the methylene carbon atom and one *ortho* carbon atom of each phenyl group [Cr1-C1 = 2.083(5)Å, Cr1-C23 = 2.172(5)Å]. Each neophyl group works as a chelating ligand forming slightly twisted five-membered rings with the central metal atom [C1-C6-C24-C23 = 17.2(6)°]. The metallocycles are coplanar with the corresponding phenyl ring of the neophyl group. The two methyl groups borne by the two neophyl β-carbon atoms point in opposite directions with respect to the metallocycle plane. The methylene carbon atoms are in *trans* positions with respect to each other, while the two aromatic carbons occupy the *cis* positions probably to minimize steric repulsions. The cationic fragment is formed by one tetrahedral lithium cation sorrounded by two chelating TMEDA molecules. No significant intermolecular contacts have been found between the two ionic units.

The utilization of RLi:Cr stoichiometric ratio of 2:1 in the reaction of $CrCl_2(THF)_2$ with RLi [R = $PhCH_2$, $(CH_3)_3CCH_2$, $Ph(CH_3)_2CCH_2$] gave a substantially different reactivity pattern (Scheme 4-2). While only decomposition was obtained from the reaction carried out at

Scheme 4-2



-60°C in the absence of TMEDA, clean and reproducible reactions were obtained when reaction with RLi [R = $CH_2C(CH_3)_3$, $CH_2C(CH_3)_2Ph$, CH_2Ph] were carried out on the preformed $(TMEDA)CrCl_2$ complex. The reaction led to the initial formation of an intense deep-green color. With the exception of **4.8**, the color did not change upon reaching room temperature and crystals of $(TMEDA)CrR_2$ [R = $PhCH_2$ (**4.7**), $(CH_3)_3CCH_2$ (**4.8**), $(CH_3)_2PhCCH_2$ (**4.9**) were isolated at -30°C from the corresponding toluene solutions. All these complexes have magnetic moments that are consistent with a high spin Cr(II) d^4 electronic configuration.

The structure of **4.7** and **4.9** have been demonstrated by X-ray analysis. In complex **4.7** the tetrahedrally-distorted square-planar coordination geometry of chromium [N1-Cr1-N2 = 80.15(6)°, N1-Cr1-C1 = 95.58(7)°, C1-Cr1-C8 = 165.10(8)°, N2-Cr1-C8 = 91.02(7)°, N1-Cr1-C8 = 165.10(8)°] (Figure 4-3) is defined by two nitrogen atoms of one chelated TMEDA molecule [Cr1-N1 = 2.227(2)Å, Cr1-N2 = 2.225(2)Å] and by two methylene groups of each benzyl group [Cr1-C1 = 2.185(2)Å, Cr1-C8 = 2.177(2)Å]. The angles subtended at the methylene carbon atom are rather different in the two groups [Cr1-C8-C9 = 111.9(1)°, Cr1-C1-C2 = 120.5(1)°] and are a probable result of steric interactions and crystal packing.

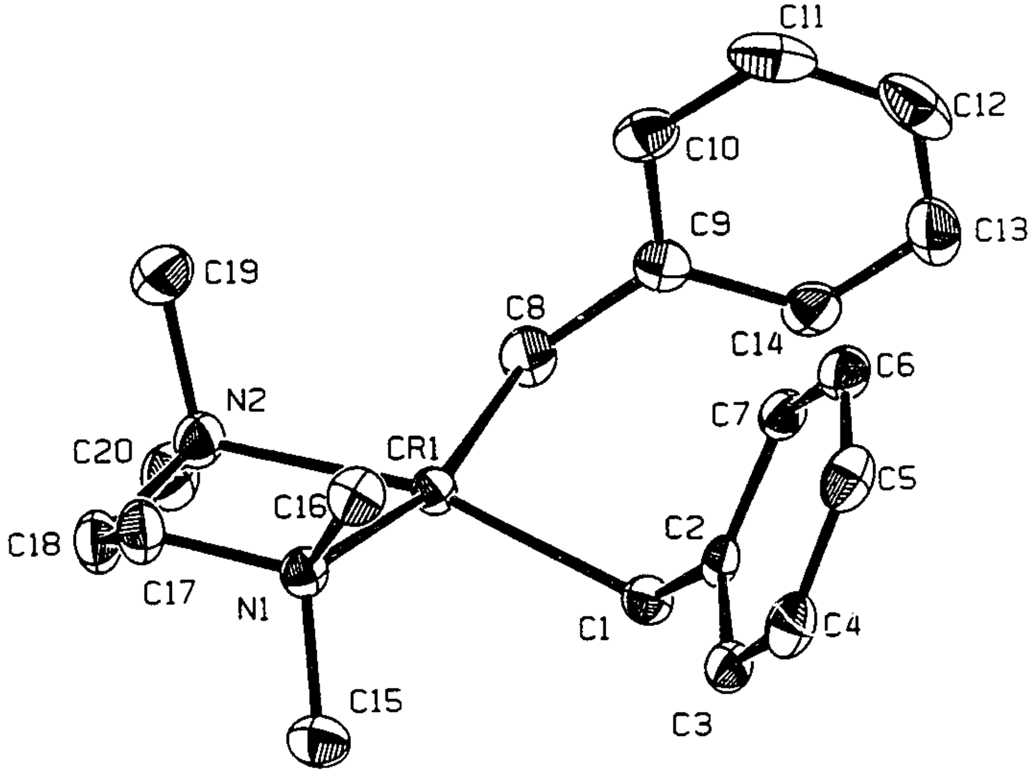


Figure 4-3. ORTEP plot of **4.7**

Complex **4.9** is basically isostructural with complex **4.7** (figure 4-4). Two nitrogen atoms of

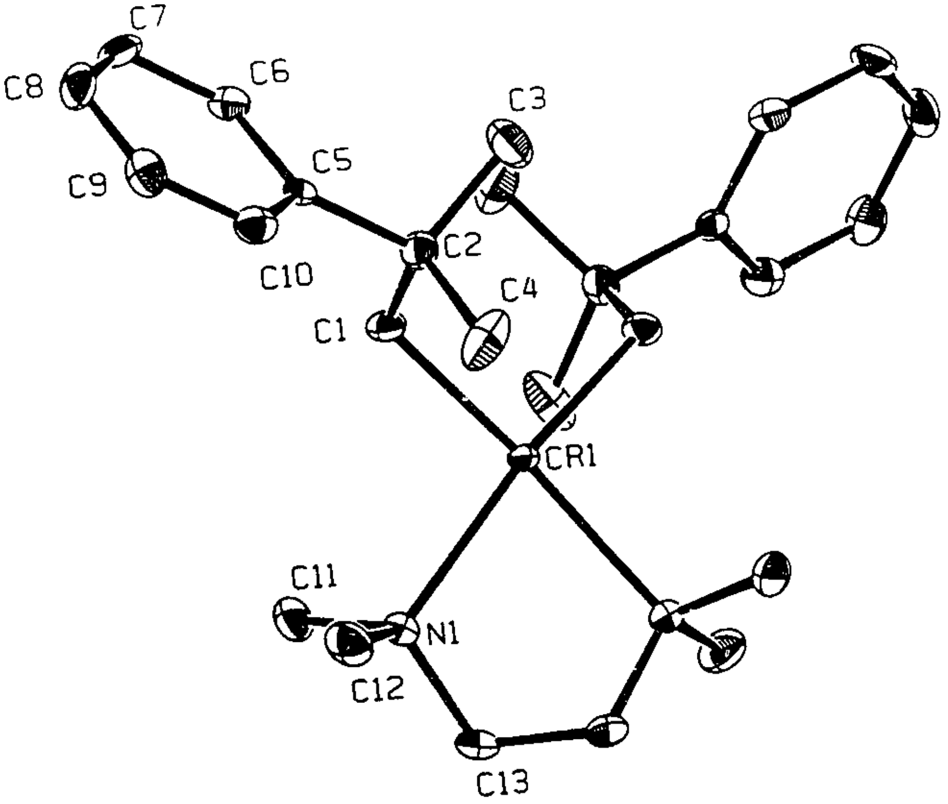


Figure 4-4. ORTEP plot of **4.9**

one chelated TMEDA molecule [Cr1-N1 = 2.249(3)Å] and two methylene carbon of two neophyl groups define the tetrahedrally-distorted square-planar coordination geometry of the chromium atom [N1-Cr1-C1 = 92.8(1)°, N1-Cr1-C1a = 158.0(1)°, N1-Cr1-N1a = 79.6(1)°]. The two bulky moieties of the two neophyl groups are oriented in the two opposite directions with respect to the Cr1-N1-N1a plane. The Cr-C distance [Cr1-C1 = 2.146(3)Å] is only slightly shorter than in the dibenzyl analogue **4.7**. The angle subtended at the methylene carbon atom [Cr1-C1-C2 = 118.2(2)°] is rather wide, likely as a result of the steric interaction of the two bulky $Ph(CH_3)_2C$ groups.

In the case of the benzyl derivative it was possible to isolate deep-blue crystals from the initial deep-green solution simply by using a stoichiometric ratio $PhCH_2Li$:Cr of 1:1 thus clarifying the structure of the intermediate (TMEDA)CrBzCl(μ-Cl)(LiTMEDA) (**4.6**) adduct. Attempts to isolate analytically pure complexes in the cases of the neopentyl and neophyl derivatives were unsuccessful, since the reactions gave mixtures of final product, unreacted starting material and dialkyl species.

The structure of complex **4.6** consists of one square-planar (TMEDA)Cr(CH_2Ph)Cl moiety where the chlorine atom bridges between the chromium and the lithium atom of a tetrahedral (TMEDA)LiCl unit (Figure 4-5). A molecule of [(TMEDA)Li(μ-Cl)]$_2$ was also found co-crystallized in the unit cell in the stoichiometric ratio 2:1 with the chromium unit. The square plane centered on the chromium atom [N1-Cr1-N2 = 81.8(2)°, C1Cr1-N2 =

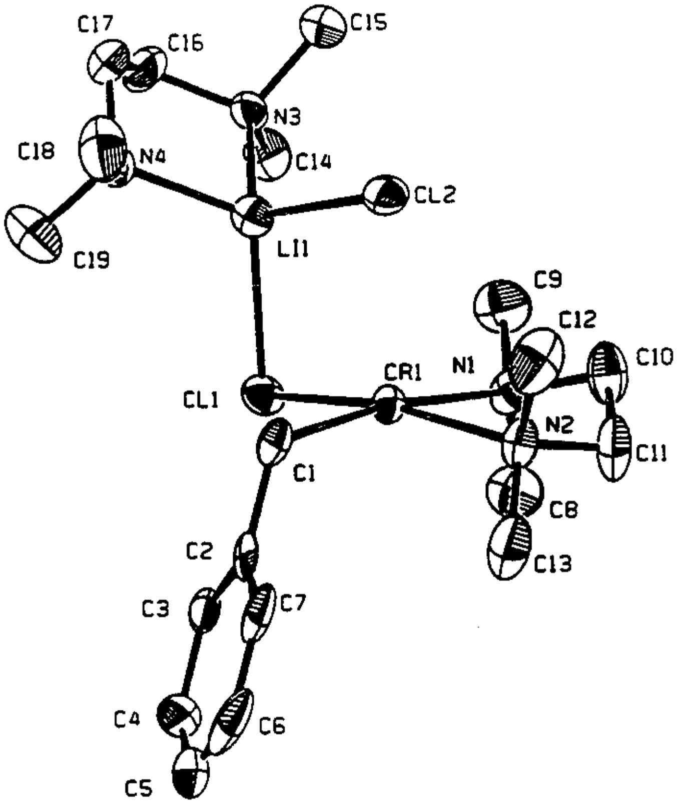


Figure 4-5. ORTEP plot of **4.6**

95.8(2)°, C1-Cr1-Cl1 = 92.1(2)°, C1-Cr1-N1 = 170.9(3)°, Cl1-Cr1-N2 = 165.1(2)°] is defined by the two nitrogen atom of one chelating TMEDA molecule [Cr1-N1 = 2.209(6)Å, Cr1=N2 = 2.184(6)Å], the methylene carbon atom of the benzyl group [Cr1-C1 = 2.141(7)Å, Cr1-C1-C2 = 116.5(4)°] and the bridging chlorine atom [Cr1-Cl1 = 2.425(2)Å, Cl1-Li1 = 2.34(1)Å, Cr1-Cl1Li1 = 85.3(3)°]. The chromium atom is only slightly elevated above the basal plane [distance from the plane 0.21(3)Å]. The second chlorine atom borne by lithium is positioned on the apex of an ideal square pyramid based on the chromium atom [C1-Cr1-Cl2 = 97.6(2)°, Cl1-Cr1-Cl2 = 91.40(7)°, N1-Cr1-Cl2 = 91.4(2)°, Cl2-Cr1-N2 = 100.0(2)°], forming a fairly short Cr-Cl non-bonding distance [Cr1..Cl2 = 2.671(2)Å]. No intermetallic contacts were observed with the [TMEDA)Li(μ-Cl)]$_2$.

Variable amounts of bright orange crystals were found in the deep-red crystalline mass of **4.7**. This orange complex (**4.10**) turned out to be the only stable product when the ligand replacement reaction was carried out on $CrCl_2$(TMEDA) by using a stoichiometric ratio $PhCH_2Li$/Cr of 3/1. In one case, the crystals were of sufficient quality to undertake an X-ray crystal structure determination in spite of an unfavorable flat shape. The results of this determination show a chemical connectivity remarkably similar to **4.7** (Figure 4-6). Apart from the different orientation of the two phenyl rings and the geometry of the chromium atom (square-planar rather than flattened tetrahedral), the bond distances and angles are very comparable in the two complexes. Different from **4.7** however, the coordination geometry of chromium, as defined by the two nitrogen of the chelating TMEDA and the two carbon atoms of the benzylidene and benzyl units, is square-planar [C6-Cr1-N2 = 173.9(2)°, N1-Cr1-C13 = 174.6(3)°, N1-Cr1-C6 = 94.0(2)°]. The benzylidene and benzyl groups form identical Cr-C

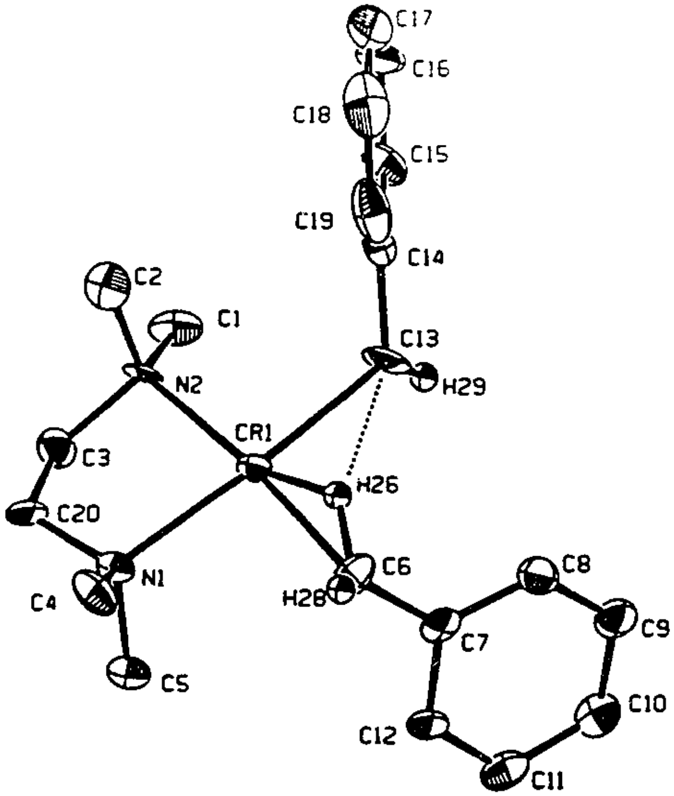


Figure 4-6. ORTEP plot of **4.10**

distances [Cr1-C6 = 2.170(7)Å, Cr1-C13 = 2.169(7)Å] which also compare well with those of complex **4.7**. The orientation of the two phenyl rings marks the most significant difference between the two complexes (on the same side of the molecule instead of transoid with respect to the molecular plane, as might be expected). Different from complex **4.7**, the angle subtended at the methylene carbon atoms are similar [Cr1-C6-C7 = 115.7(4)°, Cr1-C13-C14 = 120.9(5)°]. This is likely the result of the position of one hydrogen atom of the benzyl group, which was located and refined in a position intermediate between chromium and the corresponding carbon atom [Cr1-H26 = 1.31Å, C6-H26 = 1.14Å], and not far from the carbon atom of the benzylidene group [C13-H26 = 2.10Å].

The steric hindrance of **4.7** and **4.10** does not appear a sufficient reason alone to justify a rotameric phenomenon, since the two complexes crystallize in different crystal systems (monoclinic and orthorhombic) with remarkably different colors, magnetic properties and coordination geometries of the metal atom. The possibility that either **4.7** or **4.10** might be a terminal hydrido species (TMEDA)Cr(H)$(CH_2Ph)_2$ cannot be excluded by the absence of hydrogen observed during chemical degradation experiments carried out with 2 equivalents of dry HCl in a closed vessel connected to a Toepler pump. The cyclic voltammograms of the two compounds, obtained under identical conditions, show two completely different patterns. Complex **4.10** displays a reversible one-electron reduction wave at -2.37 V (E_{pa}-E_{pc} = 63 mV) and an additional irreversible reduction at -3.50 V (200 mV/sec, V vs ferrocenium/ferrocene) (Figure 4-7). Unfortunately, comparison with data available for other Cr(III) complexes[179,180] is not appropriate due to the diversity of the substrates. Nevertheless, the $E_{2nd\ red}$ - $E_{1st\ red}$ = 1.13 V is in good agreement with that determined in the case of some monocyclopentadienyl Cr(III) complexes[179] thus giving some indication that **4.10** might be a Cr(III) species. The voltammogram also shows two irreversible features at +0.42 and +0.97 V. Conversely, the cyclic voltammogram of complex **4.7** only shows an electrochemically irreversible reduction at -1.90 with return peak wave at -1.20 V. Although these data are not conclusive for the assignment of the metal oxidation state, they clearly indicate that complexes **4.7** and **4.10** *are chemically different species* in spite of the remarkably similar ligand environment.

Further indication about the different nature of the two complexes is offered by EPR spectroscopy. While the intensely blue-green toluene solutions of the two complexes are EPR silent, probably due to signal saturation, the solid state spectra are totally different. Complex **4.7** shows the same intense and non-resolved band commonly observed for Cr(II) complexes,

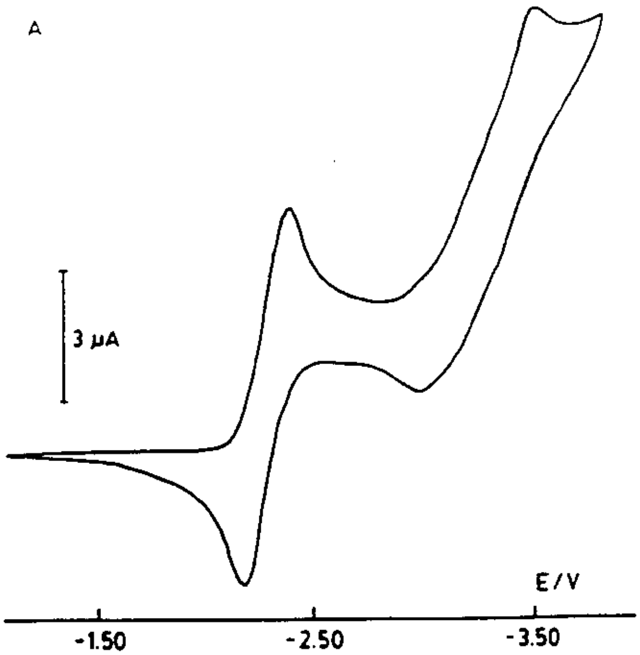


Figure 4-7. Cyclic voltammogram of **4.10** in THF at room temperature (supporting electrolyte Bu_4NBF_4 0.2 M, scan rate 200 mV/sec, potential relative to Cp_2Fe).

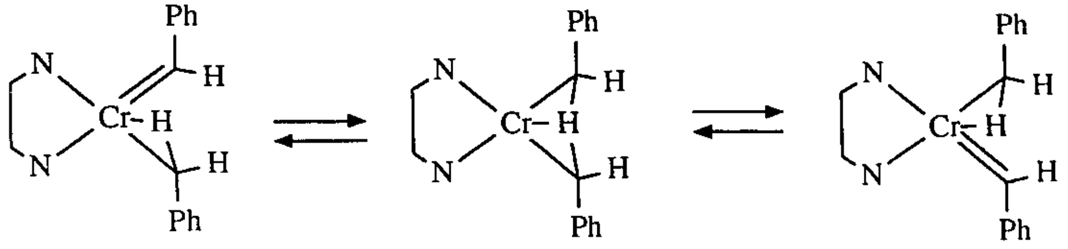
while **4.10** displays a complicated spectrum reminiscent of those observed for the Cr(III) Cp'CrMeCl derivatives.[181]

The values of the magnetic moments of **4.7** an **4.10** [μ_{eff} = 4.68 μ_B and μ_{eff} = 3.96 μ_B respectively] are consistent with a d^4 and d^3 electronic configurations and support the proposed assignment of the oxidation states. Since chemical degradation experiments do not provide evidence that complex **4.10** might be a terminal hydride, we tentatively propose a Cr(III) carbene formulation (TMEDA)Cr(=CHPh)(CH_2Ph).

The similarity of the Cr-C distances formed by the benzyl and benzylidene groups in complex **4.10** suggests that the two groups might interconvert via simple hydrogen transfer

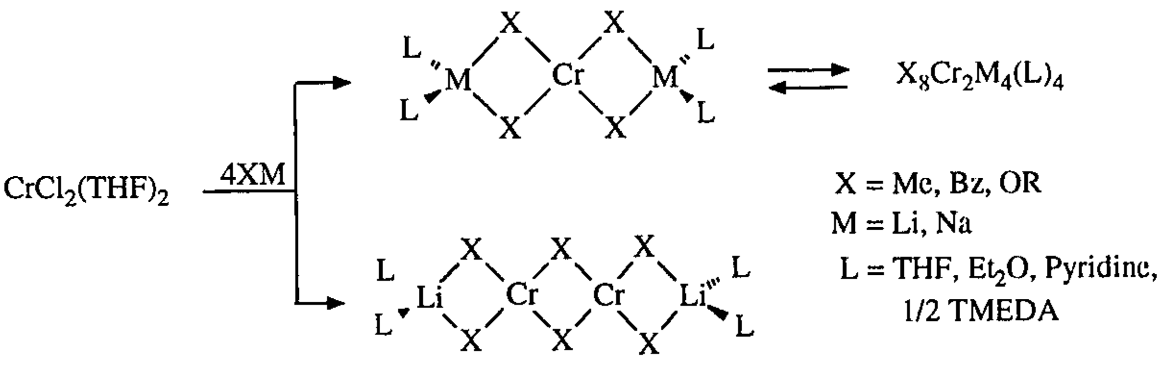
(Scheme 4-3). Unfortunately the crystal structure was not of sufficient quality to conclusively substantiate the positions of all the hydrogen atoms as determined from the difference Fourier maps. However, one peak, which was successfully refined as hydrogen, was located in the region intermediate between the benzylic carbon and chromium [Cr1-H26 = 1.31Å, C6-H26 = 1.14Å] and was rather close to the other aliphatic carbon of the benzylidene group [C13..H26 = 2.10Å].

Scheme 4-3



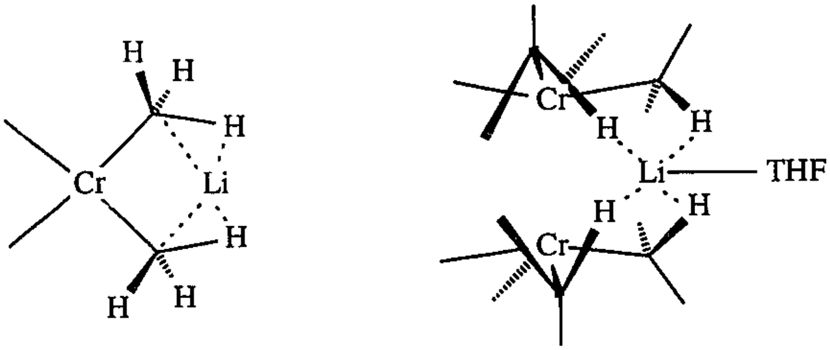
There is an interesting parallel between the chemical behavior and structural features of Cr(II) alkylchromates[63,67] with that observed in the chemistry of anionic Cr(II) alkoxides (Scheme 4-4),[54,55,59] thus reinforcing the idea that the Lewis acidity of the alkali cation is indeed a crucial factor for assembling the di- and polymetallic frames of these species.[54,67]

Scheme 4-4



However, while in the case of the dinuclear alkoxides it is rather straightforward to imagine how Cr-(OR)-M-(OR)-Cr bridges may hold together dimetallic structures of $(RO)_8Cr_2[M(L)]_4$ [R = Ph, i-Pr; M = Na; L = THF, Pyridine][54,59] in the absence of direct Cr-Cr bonds, it turns out to be more difficult to understand how extremely short Cr-Cr contacts might be enforced by Cr-Me-Li-Me-Cr bridges, such as in the case of complexes **4.1**, if no Cr-Cr bond is present in the complex.[67] The crystal structure of the monomeric $Me_4CrLi_2(TMEDA)_2$ has indicated that Li..H-CH_2-Cr interactions are folding $CrLiMe_2$ cores and that are responsible for the occurrence of rather short Cr-Li non-bonding distances (2.5 Å). It is thus possible that similar Li-CH_3 agostic interaction may be responsible also for holding together the dinuclear structures of $R_8Cr_2Li_4$ (**4.1**). In other words, the dissociation of TMEDA from $Me_4CrLi_2(TMEDA)_2$ during the formation of $Me_8Cr_2Li_4(THF)_4$ is making available an empty coordination site on the lithium atom which is then available to form another agostic interaction, thus assembling the dimer. The very short Cr-Cr contact may be nothing more than the optimization of C-H-Li bond distances and angles (Scheme 4-5). Unfortunately, the crystal

Scheme 4-5



structure reported by Krausse more than 20 years ago,[7] was not sufficiently accurate to allow the location and refinement of the hydrogen atom positions. Therefore, in order to clarify the important issue of the Cr-Cr bonding in $Me_8Cr_2Li_4$, we felt that it was worthwhile to attempt to improve upon this feature. A correct assignment of the space group combined with the employment of low temperature data collection gave better agreement factors and allowed us to locate and successfully refine the hydrogen atom positions. The crystal structure which has confirmed the overall chemical connectivity as described by Krausse (Fig. 4-8), also shown

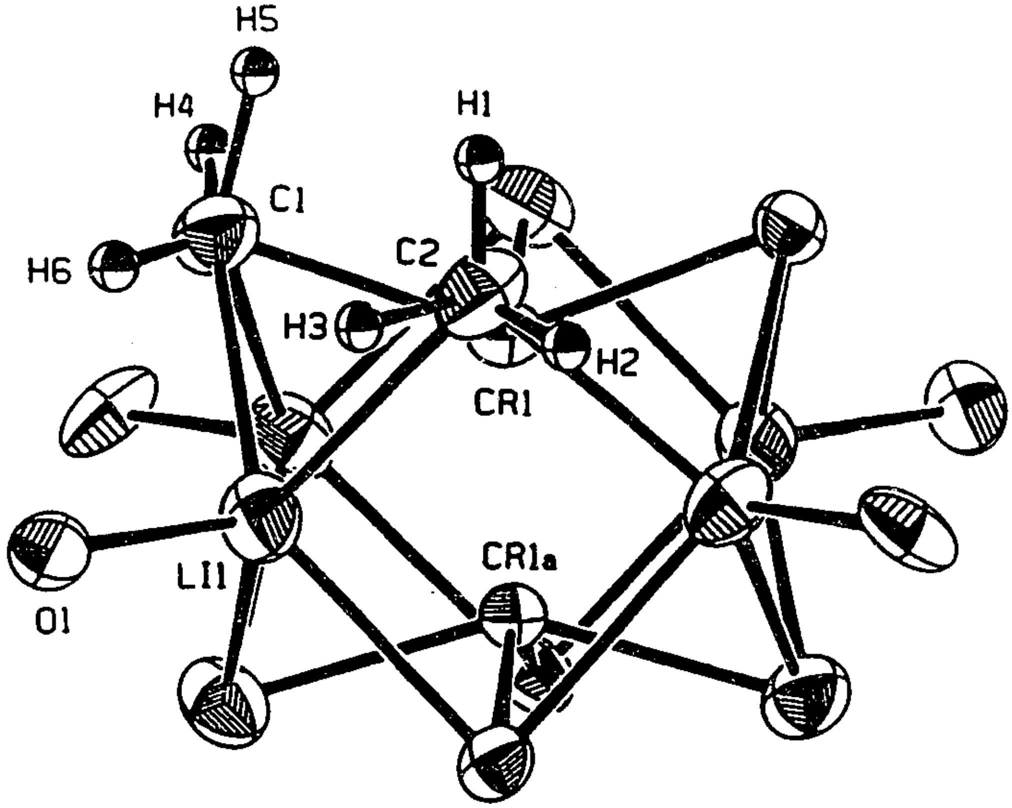


Figure 4-8. ORTEP plot of **4.1a**

that indeed the same Li-H agostic-like interactions present in the monomeric Me_4CrLi_2-$(TMEDA)_2$ are present in **4.1a**. The Li-H distances [Li-H4 = 2.03 Å, Li-H6 = 2.05 Å] and, even more strikingly, the Li-H-C angles [Li-H2-C2 = 85.12°], are very comparable to those of $Me_4CrLi_2(TMEDA)_2$ thus suggesting that the Cr-Cr very short contact of $Me_8Cr_2Li_4(THF)_4$ [Cr-Cr = 1.968(2) Å] is just the result of favorable geometrical features. This idea is further corroborated by the fact that the same Li..H agostic interactions are also present in the neopentyl derivative **4.4** and, as in the case of **4.2**, they are capable of folding $CrLiR_2$ cores. The fact that these interactions have been determined so far in three different Cr(II) alkyls suggests that they are significant and that may be a characteristic of the chemistry of Cr(II) alkyls. In line with these observations, the aromatic analogues $Ph_4CrLi_2L_n$ [Ph = phenyl n=2, mesityl n=1; L = THF, pyridine][63] are monomeric and isostructural with **4.2**. The failure of these species to dimerize can likely be ascribed to both the absence of α-hydrogen atoms and consequent inability to form agostic interactions with the alkali cation, and to the interaction of the alkali cation with the π orbitals of the aromatic rings which probably quenches the Lewis acidity of the alkali cation.

In conclusion, the synthesis, characterization and stability properties of a novel series of Cr(II) alkylchromates have been described. While the structures were strongly dependent on the reagent stoichiometric ratio used during the preparation, the employment of a chelating diamine as ancillary ligand gave a surprising series of transformations enabling the preparation and characterization of highly reactive functionalities such a alkylidene and chromacyclobutane.

4.3 X-ray crystallography

Refer to Section **2.3**. Details on data collection and structure refinement for **4.4, 4.5, 4.6, 4.7, 4.9, 4.10,** and **4.1a** are reported in Table 4-1, 4-2, 4-3 and 4-4. Selected bond distances and angles are given in Table 4-5, 4-6, 4-7, and 4-8.

Table 4-1 Crystal Data and Structural Analysis Results

complex	**4.4**	**4.5**
formula	$C_{27}H_{64}Li_2CrN_4$	$C_{38}H_{72}CrLiN_6$
formula weight	510.71	671.96
crystal system	monoclinic	monoclinic
Space Group	C2/c	$P2_1/n$
a (Å)	14.743(3)	11.629(2)
b (Å)	14.090(4)	23.259(5)
c (Å))	16.919(4)	15.726(3)
α (deg)		
β (deg)	106.58(1)	107.89(1)
γ (deg)		
V (Å^3)	3368(2)	4048(1)
Z	4	4
Radiation (MoKα Å)	0.71069	0.71069
T (°C)	-160	-160
D_{calcd}(g cm^{-3})	1.007	1.102
μ_{calcd} (cm^{-1})	3.48	3.05
R_F, R_w	0.061, 0.047	0.059, 0.069
G.o.F.	3.20	1.79

Table 4-2 Crystal Data and Structural Analysis Results

complex	**4.6**	**4.7**
formula	$C_{25}H_{55}Cl_3CrN_6Li_2$	$C_{20}H_{30}CrN_2$
formula weight	611.99	350.47
crystal system	triclinic	monoclinic
Space Group	P-1	$P2_1/n$
a (Å)	11.976(5)	9.596(1)
b (Å)	17.251(5)	18.128(2)
c (Å))	8.828(3)	11.803(1)
α (deg)	92.43(3)	
β (deg)	101.79(3)	110.692(9)
γ (deg)	84.05(3)	
V ($Å^3$)	1775(1)	1920.8(4)
Z	2	4
Radiation (MoKα Å)	0.71069	0.71069
T (°C)	-160	-157
D_{calcd}($g\ cm^{-3}$)	1.145	1.212
μ_{calcd} (cm^{-1})	5.63	5.82
R_F, R_w	0.066, 0.071	0.029, 0.041
G.o.F.	3.62	1.81

Table 4-3 Crystal Data and Structural Analysis Results

complex	**4.9**	**4.10**
formula	$C_{26}H_{42}CrN_2$	$C_{20}H_{29}CrN_2$
formula weight	434.63	349.46
crystal system	orthorhombic	orthorhombic
Space Group	Pbcn	Pbca
a (Å)	15.808(8)	23.085(5)
b (Å)	9.562(4)	14.455(6)
c (Å))	16.036(5)	11.243(3)
α (deg)		
β (deg)		
γ (deg)		
V ($Å^3$)	2424(3)	3751(3)
Z	4	8
Radiation (MoKα Å)	0.71069	0.71069
T (°C)	-160	-158
D_{calcd}(g cm^{-3})	1.191	1.237
μ_{calcd} (cm^{-1})	4.73	5.96
R_F, R_w	0.041, 0.057	0.064, 0.072
G.o.F.	2.34	6.29

Table 4-4 Crystal Data and Structural Analysis Results

complex	**4.1a**
formula	$C_{24}H_{56}Cr_2Li_4O_4$
formula weight	540.46
crystal system	tetragonal
Space Group	I4
a (Å)	11.476(3)
b (Å)	
c (Å))	11.856(4)
α (deg)	
β (deg)	
γ (deg)	
V (Å^3)	1562.5(8)
Z	2
Radiation (MoKα Å)	0.71069
T (°C)	-160
R_F, R_w	0.030, 0.039

Table 4-5 Selected Bond Distances (Å) and Angles (deg)

4.4	**4.5**
Cr1-C1 = 2.267(6)Å	Cr1-N1 = 2.335(4)
Cr1-C6 = 2.198(7)	Cr1-N2 = 2.328(4)
Cr1..Li1 = 2.70(1)	Cr1-C1 = 2.083(5)
Li1-N1 = 2.15(1)	Cr1-C23 = 2.172(5)
Li1-C1 = 2.29(1)	Cr1-C7 = 2.162(5)
Li1-C6 = 2.12(1)	Cr1-C8 = 2.093(5)
Li1-H32 = 1.93	C8-Cr1-N2 = 165.4(2)
Li1-H33 = 2.24	C1-Cr1-C23 = 80.0(2)
Li1-H34 = 2.39	C1-Cr1-N1 = 166.0(2)
Cr1-C6-C7 = 91.6(4)	C7-Cr1-C23 = 175.4(2)
Cr1-C6-Li1 = 77.4(4)	C7-Cr1-C8 = 79.8(2)
C6-C7-C6a = 108.2(7)	N1-Cr1-N2 = 79.3(1)
Cr1-C1-Li1 = 72.5(3)	Cr1-C7-C14 = 113.0(3)
C1-Cr1-C6 = 164.2(3)	Cr1-C23-C24 = 112.6(3)
C1-Li1-C6 = 102.3(5)	C1-C6-C24-C23 = 17.2(6)
Li1-Cr1-Li1a = 167.9(5)	
Cr1-C1-C2 = 113.9(4)	
C6-Cr1-C6a = 68.5(4)	
C1-Cr1-C1a = 92.1(3)	

Table 4-6 Selected Bond Distances (Å) and Angles (deg)

4.6

Cr1-N1 = 2.209(6)

Cr1-N2 = 2.184(6)

Cr1-C1 = 2.141(7)

Cr1-Cl1 = 2.425(2)

Cl1-Li1 = 2.34(1)

Cr1..Cl2 = 2.671(2)

Cl2-Li1 = 2.34(1)

Li1-N3 = 2.07(1)

Li1-N4 = 2.06(1)

C1-Cr1-Cl2 = 97.6(2)

N1-Cr1-N2 = 81.8(2)

C1-Cr1-N2 = 95.8(2)

C1-Cr1-Cl1 = 92.1(2)

C1-Cr1-N1 = 170.9(3)

Cl1-Cr1-N2 = 165.1(2)

Cr1-C1-C2 = 116.5(4)

Cr1-Cl1-Li1 = 85.3(3)

Cl1-Cr1-Cl2 = 91.40(7)

Cl2-Cr1-N2 = 100.0(2)

4.7

Cr1-N1 = 2.227(2)

Cr1-N2 = 2.225(2)

Cr1-C1 = 2.185(2)

Cr1-C8 = 2.177(2)

C1-C2 = 1.477(3)

C8-C9 = 1.474(3)

N1-Cr1-N2 = 80.15(6)

N1-Cr1-C1 = 95.58(7)

C1-Cr1-C8 = 165.10(8)

N2-Cr1-C8 = 91.02(7)

N1-Cr1-C8 = 165.10(8)

Cr1-C8-C9 = 111.9(1)

Cr1-C1-C2 = 120.5(1)

Table 4-7 Selected Bond Distances (Å) and Angles (deg)

4.9	**4.10**
Cr1-N1 = 2.249(3)	Cr1-C6 = 2.170(7)
Cr1-C1 = 2.146(3)	Cr1-C13 = 2.169(7)
C1-C2 = 1.553(4)	Cr1-H26 = 1.31Å
N1-Cr1-C1 = 92.8(1)	C6-H26 = 1.14
N1-Cr1-C1a = 158.0(1)	C13-H26 = 2.10
N1-Cr1-N1a = 79.6(1)	Cr1-N1 = 2.228(5)
Cr1-C1-C2 = 118.2(2)	Cr1-N2 =2.209(5)
	Cr1-C6-C7 = 115.5(4)
	Cr1-C13-C14 = 120.9(5)
	N1-Cr1-N2 = 79.9(2)
	N1-Cr1-C6 = 94.0(2)
	N1-Cr1-C13 = 174.6(2)
	N2-Cr1-C6 = 173.9(2)
	N2-Cr1-C13 = 94.7(2

Table 4-8 Selected Bond Distances (Å) and Angles (deg)

4.1a

Cr1-Cr1a = 1.968(2)

Cr1-C1 = 2.22(1)

Cr1-C2 = 2.15(2)

C1-Li1 = 2.41(2)

C2-Li1 = 2.40(2)

Li1-O1 = 1.967(7)

Li...H4 = 2.03

Li...H6 = 2.05

Li-H2-C2 = 85.1

C1-Cr1-C2 = 83.0(6)

Li1-C1-Cr1 = 67.4(4)

4.4 Experimental Section

All operations were performed under an inert atmosphere in a nitrogen-filled dry-box (Vacuum Atmosphere) or by using standard Schlenk techniques. **(WARNING: all the complexes prepared in this work were extremely air-sensitive and pyrophoric. Appropriate precautions should be taken for their safe manipulation.)** $CrCl_2(THF)_2$,[176] $PhCH_2Li$[177] and $PhCH_2Li(TMEDA)$[178] [TMEDA = N,N,N',N'-tetramethylethylenediamine] were prepared following published procedures. $(CH_3)_3CCH_2Li$ and $Ph(CH_3)_2CCH_2Li$ were prepared from metallic lithium and the appropriate organic halide (Aldrich) in hexane by following standard procedures. $(CH_3)_8Cr_2[Li(THF)]_4$ **(4.1a)** was prepared with minor modification of a published procedure.[7] TMEDA was chromatographed over Al_2O_3 and distilled over molten potassium after refluxing; pyridine was refluxed over CaH_2 and distilled under nitrogen using a Vigreux column. Infrared spectra were recorded on a Perkin-Elmer 283 instrument from Nujol mulls prepared in a dry-box. Samples for magnetic susceptibility measurements were weighed inside a dry-box equipped with an analytical balance, and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature. The magnetic moment was calculated following standard methods[111] and corrections for underlying diamagnetism were applied to data.[112] Elemental analysis of C, H, and N was carried out with combustion techniques. The thermal instability of **4.1b**, **4.1c**, **4.1d** and **4.3** prevented any analytical determination.

Preparation of $CrCl_2(TMEDA)$

A suspension of $CrCl_2(THF)$ (1.67 g, 6.2 mmol) in THF (100 mL) was treated with neat TMEDA (3 mL, 20.7 mmol). The initially light-green solid became bright light-blue during one hour of stirring. The solid was isolated by filtration and stored in ampoules under nitrogen without further purification (1.5 g, 6.2 mmol, 98%). I.R. [nujol, KBr, cm^{-1}] ν: 1460(s), 1385(s), 1290(m), 1250(w), 1200(w), 1170(w), 1130(w), 1050(sh), 1030(s), 1010(m), 960(s), 890(m), 880(m), 810(s), 780(m), 730(br), 590(w), 500(br). [$\mu_{eff} = 4.80\ \mu_B$]. Anal. (calcd. for $C_6H_{16}N_2CrCl_2$) found: C (30.14) 29.77, H (6.75) 6.66, N (11.72) 11.28, Cr (21.75) 21.19.

Preparation of $(CH_3)_8Cr_2[Li(THF)]_4$ (4.1a)

Solid $CrCl_2(THF)_2$ (4.4 g, 16.5 mmol) was added to a stirred solution of CH_3Li (47 ml, 1.4 M, 65.8 mmol) in Et_2O (200 mL) at -30°C. The light blue starting material slowly disappeared forming a deep-yellow solution. The insoluble residue was filtered out and the resulting solution concentrated to small volume. Bright-yellow pyrophoric crystals of **4.1a** (3.1 g, 5.7 mmol, 69%) were obtained upon standing overnight at -30°C. I.R. [nujol, KBr, cm^{-1}] ν: 1340(m), 1250(w), 1220(w), 1180(m), 1045(w), 1040(vs), 920(vs), 890(vs), 670(m), 610(s), 420(vs). ^{1}H-NMR [C_6D_6, 200 MHz, 25^{0}C] δ: 3.95(m, 2H, THF) 1.32(m, 2H, THF) -0.35(s, 3H, CH_3). Anal. (calcd for $C_{24}H_{56}Cr_2Li_4O_4$) found: C (53.34) 52.99, H (10.44) 10.25, Cr (19.24) 19.07.

Preparation of $(CH_3)_8Cr_2[Li(pyridine)]_4$ (4.1a')

Neat pyridine (0.25 g, 3.2 mmol) was added to a bright yellow solution of **4.1a** (0.43 g, 0.80 mmol) in toluene (80 mL) at room temperature. Pyrophoric, yellow microcrystals of **4.1a'** separated almost immediately (0.4 g, 0.70 mmol, 88%). I.R. [nujol, KBr, cm^{-1}] ν: 2780(sh), 1596(m), 1460(s), 1220(w), 1150(w), 1070(m), 1036(m), 1005(m), 750(s), 700(s), 620(m), 420(sh). ^{1}H-NMR [C_6D_6, 200 MHz, 25^{0}C] δ: 8.81(m, 2H, Py) 6.80 (m, 1H, Py) 6.59(m, 2H, Py) 0.01(s, 6H, CH_3). Anal. (calcd. for $C_{28}H_{44}N_4Cr_2Li_4$) found: C (59.16) 58.98, H (7.80) 7.77, N (9.86) 9.57, Cr (18.29) 18.01.

Attempted isolation of $[PhCH_2]_8Cr_2[Li(THF)]_4$ (4.1b)

Solid $CrCl_2(THF)_2$ (1.6 g, 6.0 mmol) was added at -60°C to a stirred solution of $PhCH_2Li$ in ether (24.1 mL, 1.0 M, 24.1 mmol). A deep red-brown color started to develop immediately while the insoluble starting material disappeared. Stirring was continued for 1 h. at -30°C. The solution was filtered while cold, rapidly concentrated to small volume and allowed to stand overnight at the same temperature. Pyrophoric deep-orange well-formed crystals separated upon cooling at -50°C. The product rapidly decomposed at room temperature forming a black paramagnetic oil thus preventing further characterization

Preparation of $[(CH_3)_3CCH_2]_8Cr_2[Li(Et_2O)]_4$ (4.1c)

Solid $CrCl_2(THF)_2$ (1.6 g, 6.0 mmol) was added at -50°C to a stirred solution of $(CH_3)_3CCH_2Li$ (1.84 g, 23.6 mmol) in Et_2O (50 mL). The color turned red upon mixing and stirring was continued for 1 h at low T. The orange microcrystalline **4.1c** which separated during the stirring was collected on a filtration column cooled at -40°C and then dried at room temperature (0.4 g, 0.39 mmol, 15%). Dry solid samples were stable at room temperature for a few hours. I.R. [nujol, KBr, cm^{-1}] ν: 1360(s), 1235(m), 1205(m), 1110(w), 1085(w), 1045(s), 990(w), 925(w), 890(s), 740(m), 660(w), 605(w), 535(w), 450(sh). [$\mu_{eff} = 1.72\ \mu_B$]

Preparation of $[Ph(CH_3)_2CCH_2]_8Cr_2[Li(Et_2O)]_4$ (4.1d)

Solid $CrCl_2(THF)_2$ (1.2 g, 4.5 mmol) was added to a solution of $Ph(CH_3)_2CCH_2Li$ (2.6 g, 18.6 mmol) in Et_2O (80 mL) cooled at -40°C. Stirring was continued for two hours at low temperature until the starting $CrCl_2(THF)_2$ disappeared completely from the reaction mixture. The initial green color of the suspension slowly turned red and finally deep-yellow. The gray insoluble material was eliminated by filtration and the resulting solution was allowed to stand overnight at -30°C upon which yellow microcrystalline **4.1d** separated (0.5 g, 1.4 mmol, 15%). The solid slowly decomposed at room temperature under nitrogen. I.R. [nujol, KBr, cm^{-1}] ν: 3040(sh), 1565(m), 1420(sh), 1360(sh), 1265(w), 1235(w), 1220(w) 1190(w), 1170(m), 1120(w), 1090(w), 1070(w), 1045(s), 920(sh), 890(s), 770(s), 720(s), 700(w), 560(w), 450(sh). [$\mu_{eff} = 0.55\ \mu_B$].

Preparation of $(CH_3)_4Cr[Li(TMEDA)]_2$ (4.2)

Method A: A light-yellow solution of **4.1a'** (0.8 g, 1.5 mmol) in Et_2O (200 mL) was treated with neat TMEDA (20 mL). The resulting orange solution was concentrated to small volume and a small amount of insoluble material was eliminated by filtration. Extremely air-sensitive orange-yellow crystals of **4.2** (0.6 g, 1.7 mmol, 57% yield) were obtained upon standing overnight at -30°C. Satisfactory analytical results were obtained. I.R. [nujol mull, cm^{-1}, KBr] ν: 1360(s), 1295(s), 1260(m), 1180(m), 1160(s), 1135(s), 1100(m), 1070(s), 1040(s), 1020(s), 950(s), 840(w), 790(s), 770(s), 720(w), 615(s), 590 (sh). [$\mu_{eff} = 4.98\ \mu_B$]. Anal. (calcd. for $C_{16}H_{44}N_4CrLi_2$) found: C (53.62)53.44, H (12.37)12.28, N (15.63)15.44, Cr (14.51)14.35.

Method B: A suspension of $CrCl_2(THF)_2$ (12.4 g, 46 mmol) in neat TMEDA (400 mL) was refluxed overnight forming a blue insoluble solid. The resulting mixture was cooled to -50°C and a solution of MeLi in Et_2O (130 mL, 1.4 M) was added dropwise by syringe. The green solid initially formed, disappeared upon stirring at room temperature forming an orange suspension. The solid was isolated by filtration and recrystallized from neat TMEDA (80°C), yielding bright-orange octahedral crystals (10 g, 28mmol, 61% yield).

Preparation of $[(PhCH_2)_6Cr_2][Li(TMEDA)]_2$ (4.3)

A suspension of $CrCl_2(THF)_2$ (1.46 g, 5.5 mmol) in ether (200 mL) was cooled at -50°C. Solid $PhCH_2Li(TMEDA)$ (4.61 g, 21.5 mmol) was added to the mixture and the resulting suspension was vigorously stirred while slowly warming up to room temperature. The diamagnetic, brick-red and poorly soluble **3** (1.3 g, 1.44 mmol, 53%) was collected on a filtration column and washed with two portions of toluene. I.R. [nujol, KBr, cm^{-1}] ν: 3050(m), 1580(s), 1460(s), 1370(m), 129-0(m), 1240(w), 1220(m), 1180(m), 1160(w), 1130(w), 1030(w), 1010(sh), 980(w), 950(m), 890(m), 820(w), 790(s), 740(s), 690(s), 600(w), 510(w). ^{1}H-NMR [C_6D_6, 200 MHz, 25^{0}C] δ: 7.10-6.70(m, 15H, phenyl), 2.20(s, 4H, CH_2 TMEDA), 2.05(s, 12H, CH_3 TMEDA) 1.36(s, 6H, benzyl).

Preparation of $[(CH_3)_3CCH_2]_2[CH_2C(CH_3)_2CH_2]Cr[Li(TMEDA)]_2$ (4.4)

A suspension of $CrCl_2(THF)_2$ (1.7 g, 6.4 mmol) in hexane (80 mL) was stirred at -50°C in the presence of $(CH_3)_3CCH_2Li$ (2.13 g, 27.3 mmol). The light-green solid slowly dissolved forming a yellow solution which became red after one hour. When all the starting material had disappeared, the addition of TMEDA (4 mL) to the cold solution turned the color deep-green. The temperature was allowed to rise up to ambient values and the insolubles were eliminated by filtration. Deep-red crystals of **4.4** (0.29g, 0.58 mmol, 9 %) separated from the resulting solution after concentration to small volume and upon standing overnight at -30°C. [$\mu_{eff} = 4.66\ \mu_B$]. Anal. (calcd. for $C_{27}H_{64}N_4CrLi_2$) found: C (63.50)63.11, H (12.63)12.38, N (10.97)10.88, Cr (10.18)9.91.

Preparation of $[o\text{-}C_6H_4(CH_3)_2CCH_2]_2Cr(TMEDA)][Li(TMEDA)_2]$ (4.5)

An ether solution (100 mL) of $Ph(CH_3)_2CCH_2Li$ (2.72 g, 19.4 mmol) cooled at -50°C was treated with $CrCl_2(THF)_2$ (1.32 g, 4.9 mmol). The mixture was stirred at low temperature until the starting $CrCl_2(THF)_2$ disappeared, forming a deep-green solution with a bright-yellow suspension. The addition of neat TMEDA (3 mL) to the cold mixture formed a green solid which, when isolated, melted into a green oil at room temperature. The red mother liquor, which became green at room temperature, was decanted, concentrated and cooled to -30°C. A small amount of gray solid (c.a 0.3 g) which separated upon standing overnight at -30°C, was eliminated by filtration. The resulting dark-red solution was concentrated and allowed to stand two days at -30°C upon which deep-red crystals of **4.5** separated (1.4 g, 2.0 mmol, 41%). I.R. [nujol, KBr, cm^{-1}] ν: 3030 (sh), 2780(sh), 1560(w), 1360(sh), 1340(sh), 1290(s), 1270(w), 1250(m), 1230(w), 1210(w), 1190(w), 1160(m), 1130(m), 1100(w), 1090(w), 1075(m), 1035(s), 1015(s), 990(w), 960(sh), 950(s), 935(sh), 800(s), 790(sh), 770(s), 730(s), 600(m), 570(m), 510(m), 490(m), 465(m). [$\mu_{eff} = 3.52\ \mu_B$]. Anal. (calcd. for $C_{38}H_{72}N_6CrLi$) found: C (67.92)67.78, H (10.80)10.66, N (12.51)12.43, Cr (7.74)7.17.

$(TMEDA)Cr(CH_2Ph)Cl(\mu\text{-}Cl)[Li(TMEDA)].1/2[LiCl(TMEDA)]_2$ (4.6)

A suspension of $CrCl_2(THF)_2$ (2.36 g, 8.8 mmol) in THF (100 mL) was cooled to -40°C and treated with $PhCH_2Li(TMEDA)$ (2.01 g, 9.4 mmol). The stirring of the resulting slurry for 1 h at -40°C formed a dark greenish-blue solution. The suspension was evaporated to dryness and the residual oil redissolved in Et_2O (120 mL). The solution was filtered, concentrated and allowed to stand overnight at -30°C upon which deep-blue crystals of **4.6** separated (1.4 g, 2.3 mmol, 26%). I.R. [nujol, KBr, cm^{-1}] ν: 3060(sh), 1585(s), 1295(sh), 1285(m), 1265(w), 1250(w), 1205(s), 1180(m), 1155(w), 1125(w), 1105(w), 1065(w), 1050(w), 1020(s), 1000(m), 955(sh), 940(s), 880(m), 840(w), 800(s), 790(s), 785(w), 740(s), 695(s), 595(m), 500(w), 430(m). [μ_{eff} = 5.10 μ_B]. Anal. (calcd. for $C_{25}H_{55}N_6CrLi_2Cl_3$) found: C (49.07)48.81, H (9.06)9.00, N (13.73)13.65, Cr (8.50)8.13.

Preparation of (TMEDA)Cr$(CH_2Ph)_2$ (4.7)

A suspension of $CrCl_2(THF)_2$ (1.8 g, 6.7 mmol) in THF (100 mL) was stirred at -40°C for 1 h with $PhCH_2Li$(TMEDA) (2.7 g, 12.8 mmol). The resulting dark greenish-blue solution was evaporated to dryness and the residual oil redissolved in Et_2O (120 mL). The solution was filtered, concentrated and allowed to stand overnight at -30°C upon which deep-purple crystals of **4.7** separated (0.7 g, 2.0 mmol, 30%). I.R. [nujol, KBr, cm^{-1}] ν: 3060(sh), 1585(s), 1410(w), 1350(w), 1295(m), 1285(m), 1240(w), 1210(s), 1190(w), 1180(m), 1165(m), 1120(m), 1070(m), 1050(w), 1025(s), 1000(sh), 940(s), 920(sh), 870(s), 795(s), 770(w), 740(s), 700(s), 620(w), 600(m), 570(w), 540(w), 520(m), 485(w), 470(w), 450(w), 400(sh). [μ_{eff} = 4.68 μ_B]. Anal. (calcd. for $C_{20}H_{30}N_2Cr$) found: C (68.54)68.35, H (8.63)8.44, N (7.99)7.71, Cr (14.84)14.67.

Preparation of (TMEDA)Cr$[CH_2C(CH_3)_3]_2$ (4.8)

A suspension of $CrCl_2(THF)_2$ (1.96 g, 7.3 mmol) in THF (100 mL) was stirred for one hour at room temperature in the presence of TMEDA (2 mL). After cooling to -30°C, the addition of $(CH_3)_3CCH_2Li$ (1.07 g, 13.7 mmol) to the resulting bright-blue suspension turned the color red. After stirring for another hour at room temperature, the solvent was removed in vacuo and the residual oil redissolved in hexane (140 mL). The solution was filtered, concentrated and allowed to stand overnight at -50°C upon which deep-red crystals of **4.8** separated (1.4 g, 4.5 mmol, 62%). I.R. [nujol, KBr, cm^{-1}] ν: 2760 (sh), 1405(w), 1345(s), 1280(s), 1260(w), 1245(w), 1225(s), 1200(s), 1160(w), 1120(m), 1095(m), 1090(sh), 1060(s), 1040(w), 1025(s), 1010(s), 995(sh), 955(s), 900(w), 795(vs), 770(m), 740(m), 620(sh), 595(m), 530(m), 480(w), 440(m), 380(sh). [μ_{eff} = 4.99 μ_B]. Anal. (calcd. found: C (62.71)62.61, H (11.18)11.00, N (9.14)9.01, Cr (16.97)16.71.

Preparation of (TMEDA)Cr[$CH_2C(CH_3)_2Ph$]$_2$ (4.9)

A suspension of $CrCl_2(THF)_2$ (2.6 g, 9.7 mmol) in toluene (100 mL) was stirred in the presence of TMEDA (2 mL). After stirring one hour at room temperature, the resulting bright-blue suspension was cooled to -30°C. After addition of $Ph(CH_3)_2CCH_2Li$ (2.76 g, 19.7 mmol), the resulting red mixture was allowed to warm up to room temperature. The suspension was filtered, concentrated and cooled to -30°C, upon which deep-red crystals of **4.9** (1.1 g, 2.5 mmol, 26%) separated. I.R. [nujol, KBr, cm^{-1}] ν: 3060(sh), 3040(sh), 1595(m), 1575(w), 1490(sh), 1410(w), 1365(sh), 1350(m), 1280(s), 1240(w), 1170(w), 1160(w), 1120(w), 1110(m), 1080(w), 1055(w), 1020(s), 1005(s), 950(s), 905(w), 795(s), 765(s), 730(w), 700(s), 610(w), 590(m), 490(w), 430(w). [μ_{eff} = 4.97 μ_B]. Anal. (calcd. for $C_{26}H_{42}N_2Cr$) found: C (71.85)71.66, H (9.74)9.51, N (6.45)6.29, Cr (11.96)11.71.

Preparation of (TMEDA)Cr(=CHPh)(CH_2Ph) (4.10)

A suspension of $CrCl_2(THF)_2$ (5.5 g, 20 mmol) in THF (100 mL) was treated at -40°C with $PhCH_2Li(TMEDA)$ (12.8 g, 60.0 mmol). After stirring one hour at -40°C, the resulting slurry formed a dark greenish-blue solution. The suspension was evaporated to dryness and the residual oil redissolved in Et_2O (150 mL). The solution was filtered, concentrated and allowed to stand overnight at -30°C upon which orange crystals of **4.10** separated (4.2 g, 12.0 mmol, 60%). I.R. [nujol, KBr, cm^{-1}] ν: 3060(w), 1590(s), 1470(sh), 1405(w), 1360(sh), 1300(w), 1285(m), 1210(s), 1180(w), 1125(w), 1020(m), 1000(w), 950(s), 880(m), 795(s), 770(w), 740(s), 695(s), 595(w), 570(w), 550(w), 525(w), 450(w). [$\mu_{eff} = 3.96\ \mu_B$]. Anal. (calcd. for $C_{20}H_{29}N_2Cr$) found: C (68.74)68.59, H (8.36)8.18, N (8.02)7.88, Cr (14.88)14.69.

Cyclic Voltammetry

Cyclic voltammograms were recorded in THF solutions using tetrabutylammonium tetrafluoborate ($TBABF_4$) (Aldrich) as a supporting electrolyte. All the solutions and the electrochemical cell were prepared in a dry box. The experiments were performed under nitrogen in an air-tightened cell equipped with a 0.5 mm diameter Pt wire as a working electrode. A silver wire in contact with a THF solution of $TBABF_4$ (0.2 M) and saturated with AgCl was used as a reference electrode. The contact with the cell was realized through a porous vycor frit. THF solutions were 0.01 M of each complex and 0.2 M of $TBABF_4$. Potentials were referenced to the ferrocenium/ferrocene potential obtained under identical conditions. A PAR 273 potentiostat/signal generator in combination with Headstart software was employed for the measurements.

Chapter 5

Ligand steric bulk: a neglected factor in the formation of Cr-Cr supershort contacts.

5.1 Introduction

Historically, the chemistry of Cr-Cr multiple bond began with the preparation, reported in the early 1960s by Hein and Tille, of an almost diamagnetic divalent dichromium species supported by a three-center chelating ligand.[182] The correct formulation and the presence of a Cr-Cr metal bond was correctly postulated on the basis of analytical and magnetic data. Subsequent X-ray work[183] on a closely related complex demonstrated the existence of the shortest Cr-Cr contact ever found, thus giving strong credit to the initial proposal of the existence of a direct Cr-Cr bond of high multiplicity and also giving the legitimate expectation that these bonds might be strong. Since then, the discovery of Cr-Cr supershort quadruple bonds has marked a milestone in coordination chemistry and boosted interest in the preparation, characterization and chemical reactivity of this unique functionality.[2,100,184] As a result of considerable research activity in this field, M-M multiple bonds are today widely documented across the periodic table,[61] and a rich and diversified chemical reactivity has been discovered.[5,185-194]

While very short M-M quadruple bonds are commonly encountered in the chemistry of divalent Mo and W with[195-199] and without bridging ligands,[200-206] the dozens of examples of quadruply bonded dichromium systems reported in the literature to date,[1] are invariably stabilized by bridging ligands, as a rule with only one exception.[12] In addition, apart from a very few cases,[7,8,113,174] the bridging ligands employed for the stabilization of quadruply-bonded dichromium units always possess, the unique three-center chelating geometry characteristic of the carboxylates and of the allylic systems in general. Since it has been proven that these ligands are able to work as a binucleating ligands[33,41,93,207-214] and to enforce very short metal-metal contacts even in the absence of M-M bond,[28,38,40] the possibility that short and even supershort Cr-Cr contacts might be artifacts of the unique bridging ability of three-center chelating ligands cannot be ruled out *a priori*.[104] This idea, which at first glance seems to contradict with the experimental evidence, is however corroborated by theoretical work[22,116-118] which has determined that Cr-Cr quadruple bonds are so extremely weak that they are likely unable to hold together a dimetallic frame in the absence of bridging interactions: a Cr-Cr quadruple bond is expected to be as weak as a Cr-Cr single bond.[25] Although theoretical work on this topic[21,114,115,215] has been rather controversial the striking weakness of Cr-Cr quadruple bonds has been further confirmed by experimental studies on the reversible cleavage of the Cr(II) carboxylates in solution.[18,101-103,216,217] Such a chemical paradox has been interpreted in terms of a small singlet/triplet gap, where low-lying antibonding orbitals are thermally populated by electrons from high-energy metal-metal bond orbitals.[26] Unfortunately, this elegant theoretical argument clashes with the idea of a chemical bond commonly regarded as an electronic mechanism able to generate both stabilization energy and a significant attraction force between two atoms. A tantalizing question thus arises about how a paradoxically weak bond could yet be so extremely short. In other words, *if a Cr-Cr quadruple bond is so extremely weak, how can the intermetallic distance possibly be so extremely short?*

We believe that the definition of chemical bond is not appropriate for very short

Cr-Cr contacts, an efficient magnetic coupling, either through space (antiferromagnetic) or ligand (superexchange) or a combination of both, is likely a more adequate description of the intermetallic interaction. This proposal is supported by the recently described reversible cleavage of $Me_8Cr_2Li_4$[67] long regarded as a rare example of a supershort Cr-Cr quadruple bond without bridging ligands. Since the cleavage proceeds without modification of the coordination sphere of the chromium atom, this result has demonstrated that no significant Cr-Cr bond exists in $Me_8Cr_2Li_4$ despite the exceedingly short Cr-Cr distance. By way of contrast, successful characterization of the first dichromium unit supported by a macrocyclic ligand $[(TAA)Cr]_2$ [TAA = tetraazaannulene][12] and without bridging ligands, has shown that formation of a significant Cr-Cr multiple bond is indeed possible, provided that transition metal can be "pyramidalized" with a ligand of suitable geometry.[218] Although these two results appear to contradict each other, the reversible cleavage of $[(TAA)Cr]_2$ obtained via coordination of pyridine[66] has confirmed that the very short Cr-Cr quadruple bond is a weak interaction even in this unbridged dimer.

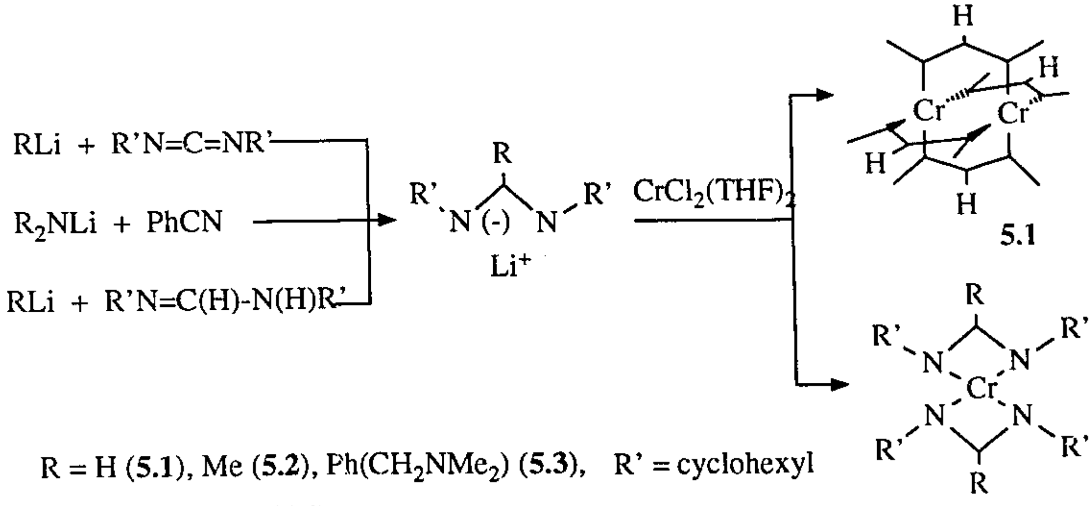
While the intriguing weakness of Cr-Cr multiple bonds has so far been clearly demonstrated only in the two above-mentioned systems and carboxylates,[18,101-103,216,217] it remains more difficult to verify if the large family of lantern-type systems with supershort Cr-Cr contacts is also subject to the same type of behavior. Although the idea that no Cr-Cr bonds exist in the lantern-type systems has been recently dismissed as "obviously inadmissible",[26] yet three-center chelating ligands undoubtedly possess a unique ability to assemble dimetallic units with and without M-M bonds all across the periodic table.[28,33,38,40,41, 93,207,220] Moreover, these ligands are capable of performing efficient magnetic couplings even when the Cr-Cr distances are elongated up to 2.6 Å.[59] Therefore, with the aim of understanding the nature of the Cr-Cr interaction in lantern- type compounds, we have undertaken a study of selected lantern-type systems where the bite of the three-center chelating ligand,[64] its electronic configuration,[76] the nature of the donor atom, its steric hindrance, and the magnetic properties of the final complex are evaluated in a consistent series of compounds and correlated to the nuclearity (monomeric versus dimeric).

The purpose of the present study is to verify the possibility that the ability of three-center chelating ligands both to assemble dinuclear structures and to promote formation of short M-M contacts, resides in a very favorable "bite", regarded not as the distance between the two donor atoms, but instead as the normal orientation of the ligand orbitals used for ligating the two transition metals. Since the ligand steric hindrance is the factor which more effectively may affect the "bite", we have examined how the steric hindrance of three-center chelating ligands determines the nuclearity of chromium complexes. For this purpose, we have prepared and characterized a novel series of monomeric and dimeric cyclohexylamidinate derivatives CyN=C(R)-NCy [R = H, Me, Ph, CH_2Ph]. The choice of this particular ligand was suggested by: *i*) the well established ability of the aromatic congeners to favor the formation of very short M-M contacts with many different metals,[70-74] and *ii*) the possibility of making available an ample series of ligands, where the large steric hindrance introduced by the two cyclohexyl groups may be increased or released via replacement of the R group located on the amidinate carbon atom.

5.2 Results and Discussion

The lithium amidinate ligands used in this work were prepared by using three different synthetic procedures (Scheme 5-1). Addition reaction of several RLi [R = Me, Bz, Ph, Ph(o-CH_2NMe_2)] reagents to N,N'-dicyclohexylcarbodiimide, or of lithium amide to benzonitrile gave the corresponding series of alkyl cyclohexylamidinate lithium derivatives [R'N-C(R)-NR']Li [R = Me, Ph, Bz,[223] Ph(o-Me_2NCH_2); R' = cyclohexyl, $SiMe_3$]. The cyclohexylformamidinate lithium salt was obtained from treatment of the N,N'-cyclohexylformamidine with n-BuLi in hexane. Preparation of the chromium complexes was rather straightforward and was carried out at room temperature via reaction of the appropriate lithium amidinate with $CrCl_2THF_2$ starting material in either toluene or THF.

Scheme 5-1



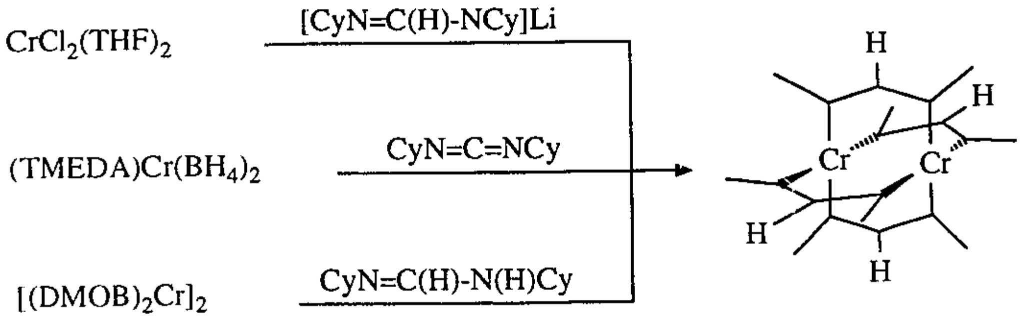
5.1

5.2, 5.3, 5.4

R = H (**5.1**), Me (**5.2**), Ph(CH_2NMe_2) (**5.3**), R' = cyclohexyl
R = Ph, R' = $SiMe_3$ (**5.4**)

The nuclearity of **5.1** and **5.2** was not affected by that of the starting material. In fact, dimeric **5.1** was also obtained via an insertion reaction of the monomeric (TMEDA)$Cr(BH_4)_2$[35] with N,N'-cyclohexylcarbodiimide (Scheme 5-2). The product was obtained in good yield although co-crystallization of $(BH_3)_2$TMEDA byproduct made the

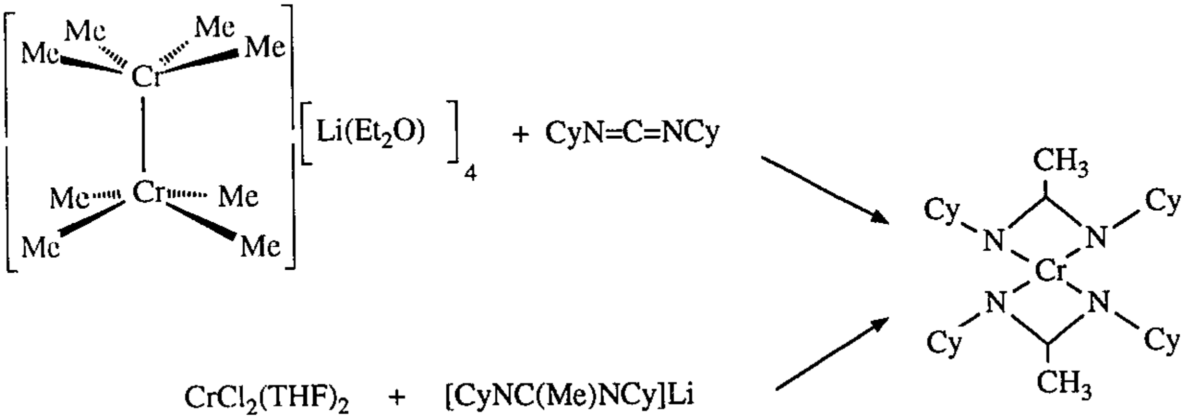
Scheme 5-2



5.1

purification of **5.1** via fractional crystallization difficult. Complex **5.1** was conveniently identified in this case on the basis of I.R. and NMR spectra. The same result was obtained using a dimeric starting material with a supershort Cr-Cr distance. By way of contrast, attempts to prepare a dimeric cyclohexyl acetamidinate complex by using a dinuclear starting material with a very short Cr-Cr contact yielded the same monomeric and paramagnetic **5.2** as obtained from the reaction of $CrCl_2(THF)_2$ and lithium acetamidinate (Scheme 5-3).

Scheme 5-3



5.2

As expected, the cyclohexylformamidinate complex **5.1** possesses the characteristic lantern-type geometry (Figure 5-1) of complexes formed by three-center chelating ligands, and

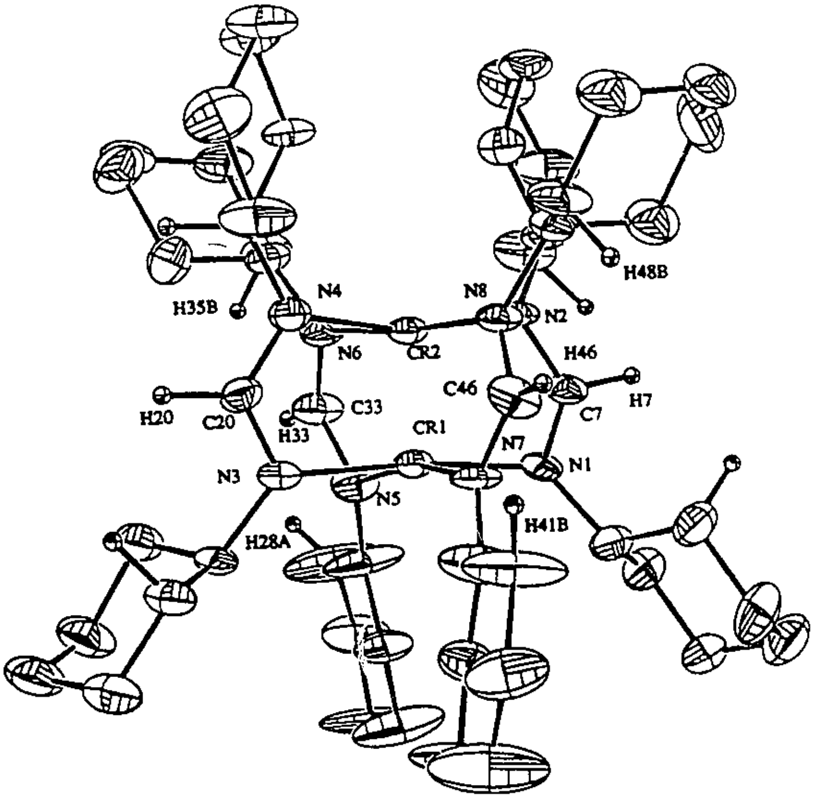


Figure 5-1. ORTEP plot of **5.1**

a very short Cr-Cr contact [Cr1-Cr1a = 1.913Å] which assigns this species to the family of the quadruply-bonded systems. Furthermore, complex **5.1** is diamagnetic as indicated by both the well-resolved sharp ^{1}H-NMR spectrum (Figure 5-2) and the complete absence of line broadening and shifting as a function of the temperature in the range 5-80°C. The perfect diamagnetism indicates that the singlet-triplet gap[27] is in this case not particularly small and that all the features which indicate the existence of a real Cr-Cr quadruple bond (short Cr-Cr contact and efficient electronic coupling) are present in complex **5.1**. However, we have recently observed that $Me_8Cr_2Li_4(THF)_4$, which has a Cr-Cr distance [Cr-Cr = 1.968(2)Å] only

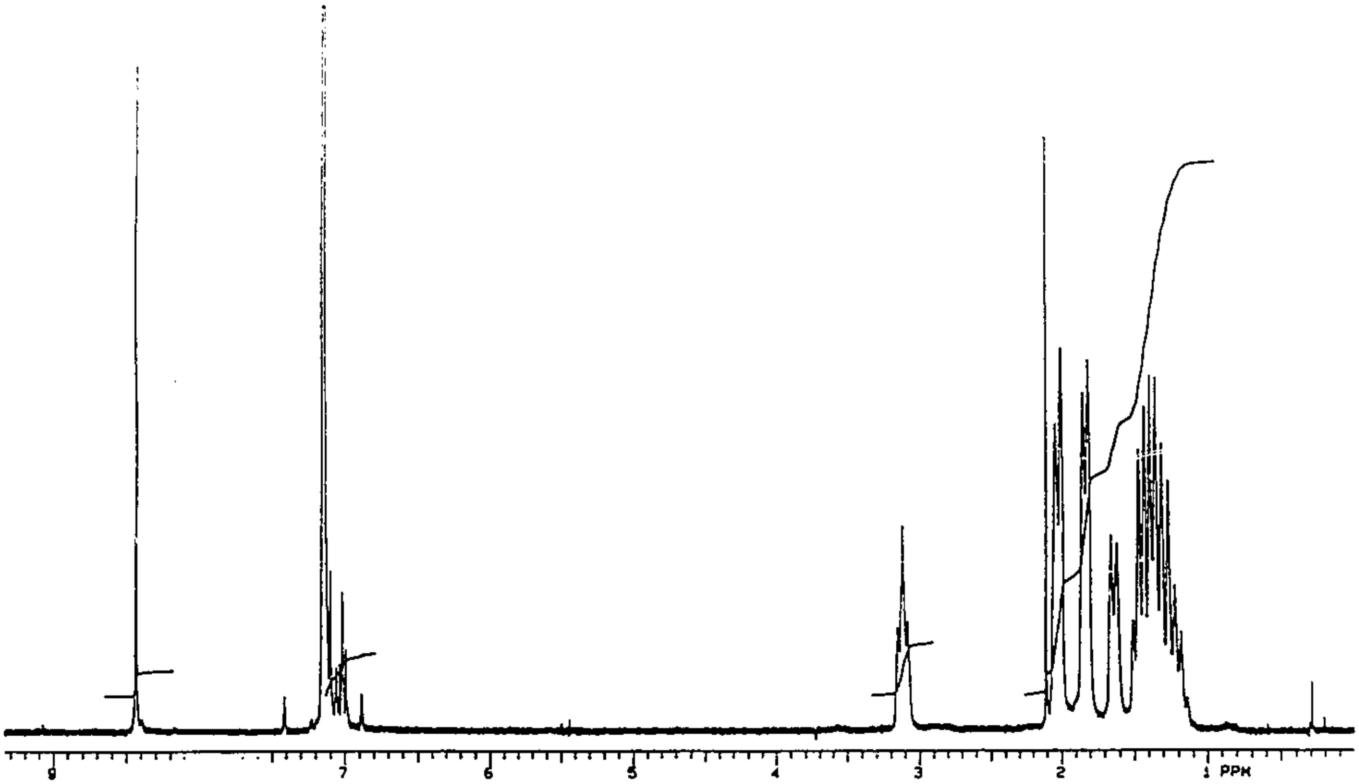


Figure 5-2. ^{1}H-NMR spectrum of **5.1** in C_6D_6

0.038Å longer than in the diamagnetic $[(p\text{-tolyl})formamidinateCr]_2$[224] and 0.055Å than in complex **5.1**, displays the characteristic small residual paramagnetism which is diagnosed by line broadening and significant chemical shift variation as a function of the temperature.[27] This indicates that the nature of the bridging ligand (and probably its electronic configuration) is the factor which, rather than the Cr-Cr distance alone, is capable of determining the extent of electronic coupling.

An interesting observation can be made by comparing the structure of **5.1** with that of the recently reported p-tolylformamidinate dichromium isostructural complex.[223] In spite of the fact that the steric hindrance introduced by the eight cyclohexyl groups of **5.1** is considerably larger than in the case of the aromatic homologue, the Cr-Cr distance of **5.1** is slightly but significantly shorter, not longer, as it would first be expected on the basis of the behavior of the multiple bonds between main group elements, where larger steric hindrance usually results in longer bonds. Furthermore, an increased steric interaction among the alkyl groups at the periphery of the complex should pull the chromium atoms out of the coordination polyhedron in order to transform the square- pyramidal coordination geometry of the two metals into a more roomy square-planar. Therefore, should this trend be confirmed, it will imply that a larger encumbrance of the amidinic ligand, with resulting increased repulsion between the central group and the two lateral ones, will determine shorter intermetallic distances.

Closer analysis of the structural features of **5.1** has revealed that one hydrogen of each of the two cyclohexyl rings forms a short contact with the formamidinic hydrogen (H..H = 1.8-2.0 Å). Comparable H..H non-bonding distances (H..H = 2.1 Å) between the cyclopentadienyl rings of the two Cp_2Zr moieties of the $[Cp_2ZrX]_2$ [X = I, PR_2] dimers are responsible for introducing a destabilization energy estimated in the range of 6 kcal mol^{-1} but which rapidly increases up to 38 kcal mol^{-1} when the H..H distances become slightly shorter. These H..H repulsions are thought to be responsible for the considerable stretching of the Zr-Zr bonds (up to 3.67Å from a distance otherwise expected to be in the range of 3.05Å).[224,225] The crystal structure of the monomeric **5.2** (Figure 5-3) has shown that short H..H non bonding contacts [H..H = 1.99-2.14 Å] are also formed by the methyne H atoms of the two cyclohexyl rings with the methyl hydrogen atoms of the acetamidinate group. Replacement of the methyl group by a phenyl ring did not significantly modify the steric hindrance with respect to complex **5.2**. The complex (Figure 5-4) is still monomeric and the shorter contact between the

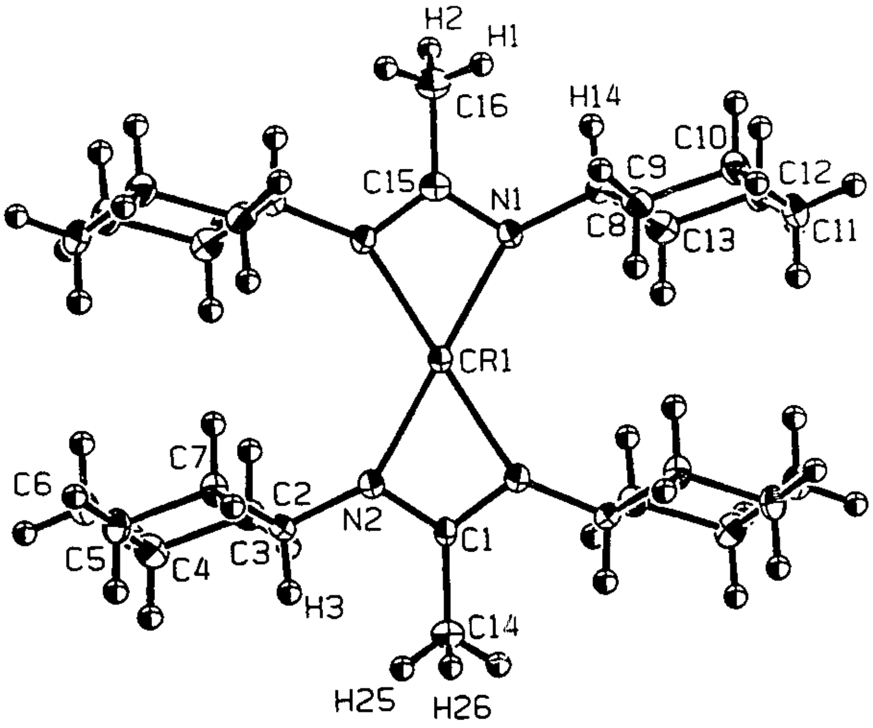


Figure 5-3. ORTEP plot of **5.2**.

phenyl and cyclohexyl groups is realized between the hydrogen atoms of the cyclohexyl ring and three carbon atoms of the central phenyl ring [C..H = 2.44-2.48Å]. Finally, the large increase in steric bulk introduced by the trimethylsilyl groups of complex **5.4** not only determines the monomeric structure[234] but also results in a significant deviation of the core from the planarity, now forced to adopt a rather unusual flattened tetrahedral coordination geometry.

The monomeric structures of **5.2**, **5.3** and **5.4** indicate that replacement of the formamidine hydrogen atom with alkyl groups (methyl, phenyl), and consequent increase of steric repulsion between the central amidinate group and the peripheral cyclohexyls, suppresses the ligand's ability to accommodate a dimetallic unit (Scheme 5-4). In the case of

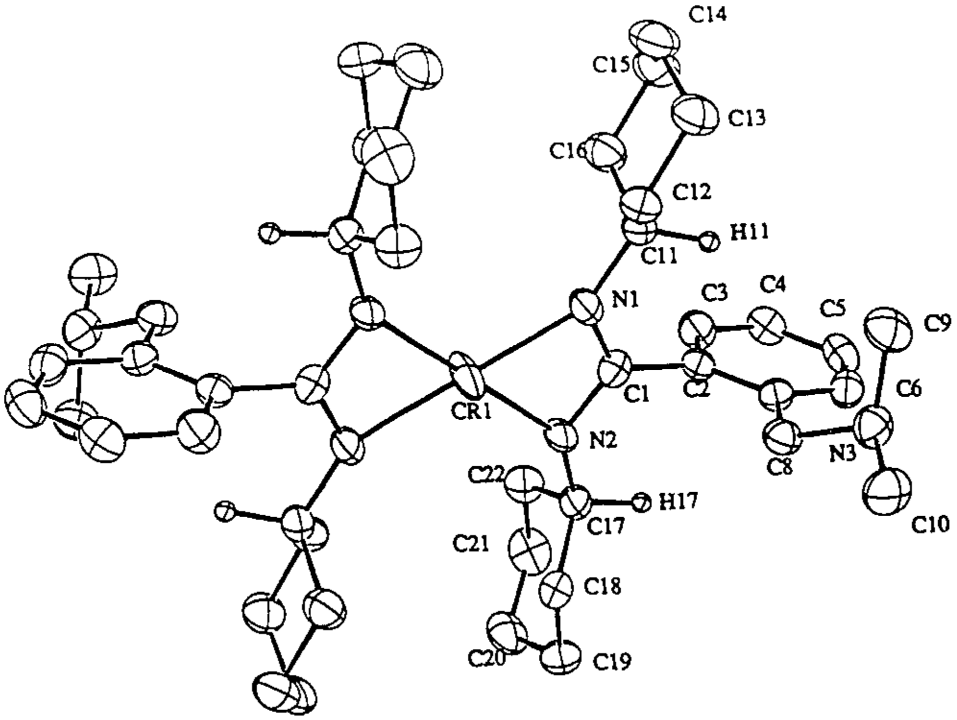
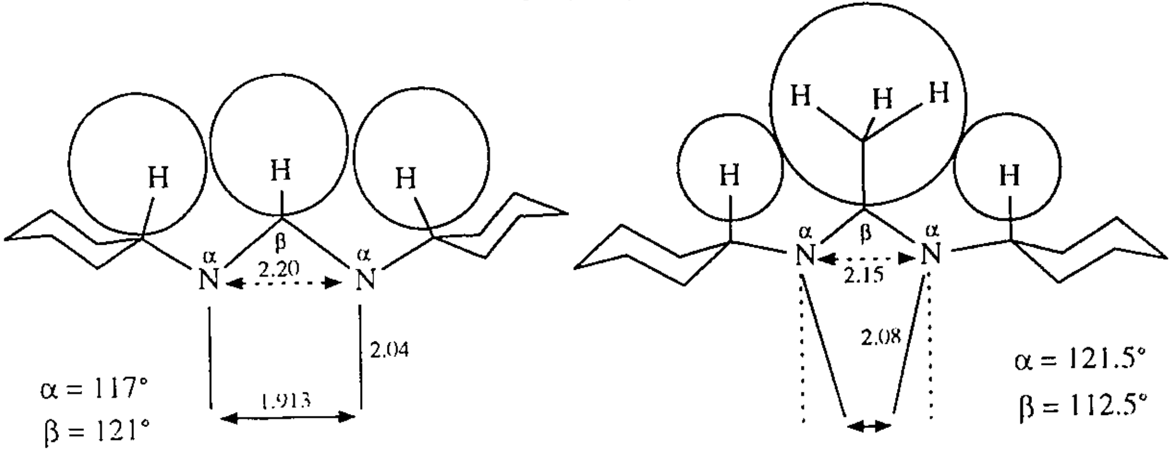


Figure 5-4. ORTEP plot of **5.3**.

Scheme 5-4



5.2, **5.3** and **5.4**, the ligands are obviously unable to overlap with the orbitals of the dimetallic unit and thus behave as normal mononucleating chelating ligands.

While the differences in bond distances in **5.1**, **5.2** and **5.3** are rather small (including the Cr-N and N..N distances) considering the completely different structures (monomeric versus dimeric), small but probably significant variations can be observed in the angles formed by the N atom with the ring and the amidinic group (α), and by the central amidinic carbon atom with the two donor atoms (β) (Scheme 5-4). Unfortunately, only a few structures of amidinate complexes are available to enable a significant comparative structural analysis. However, the data reported in Table 5-1 indicate that the intermetallic separation and the nuclearity are related to the variation of steric interaction within the ligand as probed by the two α and β angles. In particular, the α angle, which in the series of complexes reported in Scheme 5-4 is directly determined by the intramolecular contacts between the ligand "wings" and the central amidinic group, displays a trend which is rather consistent with the increase of steric crowd and the shortening of Cr-Cr distance. Conversely, the β angle shows a significant variation only in the monomeric complexes and it is therefore difficult to evaluate whether the narrowing of β is the cause or rather an effect of the monomeric structure.

Table 5-1

complex	a	**5.1**	b	c	**5.2**	**5.3**
N..N (Å)	2.29	2.19	2.27	2.27	2.15	2.25
Cr-Cr (Å)	1.93	1.91	1.84	1.84	monomer	monome
α (°)	116	117	118	118	121.5	121.5
β (°)	119	121	121	121	112.5	113

a = (p-tolyl)formamidinate[223]
b = (i-Pr)formamidinate[80]
c = (methyl)benzamidinate[96]

It is obviously impossible to draw from these empirical observations a definitive conclusion on how the steric hindrance of the ligand does determine so spectacularly the existence of Cr-Cr supershort contacts. However, what has been demonstrated is that the steric interactions within the ligand, which have never before been regarded as a factor capable of determining the nuclearity and of promoting the formation of very short Cr-Cr contacts, does indeed determine the existence of the dichromium unit, since simple replacement of the hydrogen by a methyl group formed only monomeric species.

Although these arguments are only qualitative, however, we believe that they deserve some attention. Should theoretical calculations confirm that the steric repulsions within the ligand are capable to determine not only the existence of the dimetallic unit but also the extent of the intermetallic separation (as these results seem to suggest), a significant progress will be achieved towards the understanding of the nature of the intermetallic interaction of Cr-Cr supershort contacts.

5.3 X-ray crystallography

Refer to Section **2.3**. Details on data collection and structure refinement for **5.1, 5.2, 5.3,** and **5.4** are reported in Table 5-2 and 5-3. Selected bond distances and angles are given in Table 5-4 and 5-5.

Table 5-2 Crystal Data and Structural Analysis Results

complex	**5.1**	**5.2**
formula	$C_{59}H_{92}N_8Cr_2$	$C_{28}H_{50}N_4Cr$
formula weight	1017.41	494.73
crystal system	monoclinic	orthorhombic
Space Group	P21/c	Pnma
a (Å)	13.682(5)	8.104(1)
b (Å)	17.446(3)	26.572(4)
c (Å))	24.521(3)	12.533(2)
β (deg)	90.02(5)	
V ($Å^3$)	5853(3)	2699(1)
Z	4	4
Radiation (MoKα Å)	0.71069	0.71069
T (°C)	-30	-157
D_{calcd}($g\ cm^{-3}$)	1.155	1.217
μ_{calcd} (cm^{-1})	4.0	4.34
R, R_w	0.104, 0.077	0.054, 0.069
G.o.F.	5.72	3.34
Parameters	588	158
Observations	4030	1580

Table 5-3 Crystal Data and Structural Analysis Results

complex	**5.3**	**5.4**
formula	$C_{52}H_{84}N_6O_2Cr$	$C_{26}H_{45}Si_4N_4Cr$
formula weight	853.16	578.01
crystal system	triclinic	triclinic
Space Group	P-1	P-1
a (Å)	12.293(5)	12.019(3)
b (Å)	20.437(5)	13.499(2)
c (Å))	11.071(4)	11.292(1)
α (deg)	94.55(3)	108.29(1)
β (deg)	111.72(3)	91.25(2)
γ (deg)	73.86(3)	106.82(2)
V ($Å^3$)	2481(1)	1652.4(6)
Z	2	4
Radiation (MoKα Å)	0.71069	0.71069
T (°C)	-157	-160
D_{calcd}(g cm^{-3})	1.142	1.162
R, R_w	0.093, 0.081	0.039, 0.068
G.o.F.	5.08	2.58
Parameters	572	316
Observations	6492	3838

Table 5-4 Selected Bond Distances (Å) and Angles (deg)

5.1	5.2
Cr1-Cr2 = 1.913(3)	Cr1-N1 = 2.088(4)
Cr1-N1 = 2.061(14)	Cr1-N2 = 2.078(4)
Cr1-N1 = 2.060(14)	C1-N1 = 1.326(5)
Cr1-N5 = 2.059(13)	N1-C15 = 1.331(5)
Cr1-N7 = 2.031(14)	N1-C8 = 1.462(6)
N1-C7 = 1.321(20)	N2-C2 = 1.475(6)
N2-C7 = 1.332(20)	C1-C14 = 1.51(1)
N7-C46 = 1.314(20)	C15-C16 = 1.52(1)
N8-C46 = 1.310(21)	C8-N1-C15 = 122.1(4)
N1-C7-N2 = 121.8(16)	N1-C15-N1a = 121.8(6)
N3-C20-N4 = 119.4(14)	C2-N2-C1 = 121.0(4)
N5-C33-N6 = 124.5(16)	N2-C1-N2a = 112.2(6)
N7-C46-N8 = 117.8(14)	N1-Cr1-N2 = 115.9(1)
C7-N2-C8 = 117.0(14)	N1-Cr1-N1a = 64.2(2)
C14-N3-C20 = 117.6(13)	Cr1-N1-C15-N1a = -7.2(6)
C20-N4-C21 = 115.3(13)	Cr1-N2-C1-N2a = 6.4(6)
H33..H28a = 1.89	H1..H14 = 2.14
H46-H48b = 1.93	H3..H25 = 1.99
H41b-H46 = 2.01	

Table 5-5 Selected Bond Distances (Å) and Angles (deg)

5.3	5.4
Cr1-N1 = 2.122(4)	Cr1-N1 = 2.105(4)
Cr1-N2 = 2.091(4)	Cr1-N2 = 2.093(4)
N1-C1 = 1.325(6)	Cr1-N3 = 2.102(4)
N2-C1 = 1.336(6)	Cr1-N4 = 2.098(4)
N1-C11 = 1.451(6)	N1-C1 = 1.328(6)
N2-C17 = 1.468(6)	N2-C1 = 1.344(6)
N1-Cr1-N1a = 179.9	N3-C14 = 1.333(6)
N2-Cr1-N1 = 116.4(2)	N4-C14 = 1.333(6)
N1-C1-N2 = 113.0(4)	N1-Si1 = 1.741(4)
C1-N1-C11 = 120.4(4)	N1-Si2 = 1.746(4)
C1-N2-C17 = 122.6(4)	N1-Cr1-N2 = 65.5(1)
H11..C2 = 2.44	N1-Cr1-N3 = 116.4(1)
H17..C2 = 2.48	N1-Cr1-N4 = 168.2(1)
	Cr1-N1-C1 = 89.0(3)
	N1-C1-N2 = 116.4(4)
	Si1-N1-C1 = 128.7(3)
	Si2-N2-C1 = 127.7(3)
	Cr1-N1-C1-N2 = -0.6(4)
	N1-C1-N2-Si2 = -167.0(3)

5.4 Description of the crystal structures.

Complex 5.1. The structure of the complex shows the typical dimeric arrangement (lantern-type) of the well-known quadruply bonded complexes of dichromium (Figure 5-1). The molecule is formed by a Cr_2 unit bridged by four formamidinate groups. Each formamidinate ligand adopts the classical three-center chelating geometry where each of the two donor atoms of one ligand molecule binds one of the two metal centers, forming a five-membered ring with the Cr_2 unit. In common with the other complexes reported in this work, the coordination geometry of the chromium atom is square planar [N1-Cr1-N3 = 173.8(5)°, N3-Cr1-N7 = 90.3(6)°, N1-Cr1-N7 = 89.4(6)°] with the chromium atom slightly elevated above the plane defined by the four nitrogen atoms [Cr2-Cr1-N angles ranging from 93.1(3)° and 97.6(4)°]. The Cr-Cr distance [Cr1-Cr2 = 1.913(3)Å] places complex **5.1** in the family of the quadruply bonded dichromium complexes with a supershort intermetallic contact. The Cr-N bonding distance are normal [Cr1-N1 = 2.06(1)Å, Cr1-N3 = 2.06(1)Å, Cr1-N5 = 2.06(1)Å, Cr1-N7 = 2.03(1)Å] and compare well with those of other monomeric and dimeric Cr(II) complexes. The five-membered metallacycles formed by the four ligands with the two chromium atoms are planar. The angles formed by the formamidinic carbon with the nitrogen donor atoms [N7-C46-N8 = 118(1)°, N3-C20-N4 = 119(1)°, N5-C33-N6 = 124(1)°, N1-C7-N2 = 122(2)°] are on average [av. angle = 121°] larger of those of the monomeric species. The angles formed by the nitrogen donor atoms with the cyclohexyl rings and formamidinic carbon atoms [ranging from 115(1)° to 120(1)°] are on average [av. angle = 117°] smaller than in the case of the monomeric species as a result of a smaller steric hindrance. Short H..H contacts are observed between the formamidinic hydrogen atoms and some of the hydrogens of the cyclohexyl rings [H33..H28a = 1.89Å, H46..H48b = 1.93Å, H46..H41b = 2.01Å]

Complex 5.2. The molecule is monomeric with the chromium atom in the center of the rectangular plane [N1-Cr1-N2 = 179.9(2)°, N1-Cr1-N1a = 64.2(2)°, N1-Cr1-N2a = 115.9(1)°] defined by the four nitrogen donor atoms of the two acetamidinate ligands (Figure 5-3). The Cr-N distances [Cr1-N1 = 2.088(4)Å, Cr1-N2 = 2.078(4)Å] are very comparable with those of the other two monomeric complexes reported in this work. The two metallacycles formed by the two chelating ligands slightly deviate from the planarity [Cr1-N1-C15-N1a = -7.2(6)°, Cr1-N2- C1-N2a = -6.4(6)°]. The angle formed by the amidinic carbon atom [N1-C15-N1a = 112.8(6)°, N2-C1-N2a = 112.2(6)°] with the two nitrogens and by the nitrogen atoms with the rings and the amidinic carbon [C8-N1-C15 = 122.1(4)Å, C1-N2-C2 = 121.0(4)Å] compares very well with those of the other monomeric complexes. The four cyclohexyl rings are perpendicular with respect to the plane of the metallocycle and parallel to each other. The distorted trigonal planar geometry of the nitrogen atoms [Cr1-N1-C8 = 145.3(3)°, Cr1-N2-C2 = 145.0(3)°] is also very similar to those of the other monomeric complexes, thus indicating that the steric interaction between the bulky cyclohexyl groups is comparable. As in the previous case, short non bonding contacts are present between the hydrogen atoms of the methyl groups with the methyne hydrogen atoms of the cyclohexyl rings [H1..H14 = 2.14Å, H3..H25 = 1.99Å].

Complex 5.3. Two crystallographically independent, but chemically identical, molecules were found in the unit cell together with two disordered molecules of THF. The complex is monomeric (Figure 5-4) and is formed by a square planar chromium atom placed in the center of the square plane defined by the four nitrogen atoms of the two benzamidinate ligands [N1-Cr1-N2 = 116.4(1), N1-Cr1-N2a = 63.6(2), N1-Cr1-N1a = 179.9]. The Cr-N distances [Cr1-N1 = 2.122(4), Cr1-N2 = 2.091(4)] compare well with those of the above complex. The two metallacycles formed by the two chelating ligands are also planar [Cr1-N1-C1-N2 = 0.5(3)] with similar C-N distances [C1-N1 = 1.325(6), C1-N2 = 1.336(6)] and angles [Cr1-N1-C1 = 91.1(3), N1-C1-N2 = 113.0(4)]. The planes bound by the phenyl and cyclohexyl rings are perpendicular to the metallacycle plane and to each other. The dimethylaminomethyl group placed in the *ortho* position of the two phenyl rings has the nitrogen atom pointing away from the chromium atom and does not cause any significant distortion or bending. The considerable steric interaction between the four cyclohexyl rings is shown by the wide angles formed by the distorted trigonal planar nitrogen atoms with the first carbon atom of the cyclohexyl ring and chromium [Cr1-N1-C11 = 148.3(3), Cr1-N2-C17 = 144.4(3)]. The angles formed by the nitrogen donor atoms with the cyclohexyl rings and the benzamidine carbon atoms [C1-N1-C11 = 120.4(4), C1-N2-C17 = 122.6(4)] are very comparable to those of the other monomeric derivatives. Once again, a short intramolecular non-bonding contact can be observed between the hydrogen of the cyclohexyl rings and the carbon atoms of the phenyl ring [C2..H11 = 2.48Å, C2..H17 = 2.44Å].

5.5 Experimental Section

All operations were performed under an inert atmosphere in a nitrogen-filled dry-box (Vacuum Atmosphere) or by using standard Schlenk techniques. $CrCl_2(THF)_2$,[176]

$\{[(Me_3Si)N]_2C(Ph)\}Li$,[219] $(o\text{-}Me_2NCH_2)PhLi$[220] and CyN(H)-C=NCy,[221] were prepared according to published procedures. MeLi, PhLi, $(Me_3Si)_2NLi$ were prepared following standard procedures. CyNCNCy, (i-Pr)NCN(i-Pr) and $(Me_3Si)_2NH$ (Aldrich) were used as received. NMR spectra were recorded on a Varian Gemini 200 at room temperature and on a 400 Varian spectrometer at variable temperatures, by using samples sealed in vacuum in NMR tubes prepared in a dry-box. Solvents for NMR spectroscopy were dried over the appropriate drying agent, vacuum transferred into appropriate ampoules and stored inside a dry-box. Infrared spectra were recorded on a Perkin- Elmer 283 instrument from Nujol mulls prepared in a dry-box. Samples for magnetic susceptibility measurements were weighed inside a dry-box equipped with an analytical balance, and sealed into calibrated tubes. Magnetic measurements were carried out with a Guy balance (Johnson Mattey) at room temperature. The magnetic moment was calculated following standard methods,[111] and corrections for underlying diamagnetism were applied to data.[112]

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

A solution of CyN-C(H)-N(H)Cy (13.3 g, 64 mmol) in hexane (160 mL) was treated with a solution of n-BuLi in hexane (26 mL, 2.5M, 64 mmol) at room temperature. The resulting light-yellow solution was allowed to stand at room temperature overnight upon which colorless crystals of [CyN-C(H)-NCy]Li precipitated (11.0 g, 51 mmol, 80%). I.R. [nujol mull, KBr, cm^{-1}] ν: 1565(s), 1330(s), 1295(s), 1260(m), 1230(m), 1150(w), 1100(m), 1060(m), 1030(w), 990(w), 890(m), 840(m), 805(m), 785(w), 720(m), 600(w), 580(m) ^{1}H-NMR [C_6D_6, 200 MHz, 25C^0] δ: 8.38(s, 1H, C-H formamidinic), 2.81(pseudoquintet, 2H, cyclohexyl), 1.89(m, 4H, cyclohexyl), 1.71-1.24(series of lines, 16H, cyclohexyl).

[CyN-C(CH_3)-NCy]Li(THF)

A solution of CyNCNCy (2.1 g, 10.2 mmol) in THF (30 mL) was cooled to -30C° and then treated with a solution of MeLi in ether (7.3 mL, 1.4M, 10.2 mmol). After standing at room temperature overnight, the resulting yellowish solution was concentrated to a small volume (20 mL) by evaporation of the solvent in vacuo, filtered and allowed to stand at -30C° overnight, upon which colorless crystals of [CyN-C(CH_3)-NCy]Li(THF) precipitated (2.4 g, 8.0 mmol, 78%). I.R. [nujol mull, KBr, cm^{-1}] ν: 1510(vs), 1410(s), 1350(s), 1305(w), 1250(m), 1160(m), 1130(w), 1070(sh), 1050(s), 1020(w), 990m), 1030(w), 990(w), 950(w), 920(m), 890(m), 840(w), 820(w), 795(m), 720(w), 650(m), 600(m), 570(m), 495(br), 460(w), 410(m). ^{1}H-NMR [C_6D_6, 200 MHz, 25C°] δ: 3.57(m, 4H, THF) 3.20(broad s, 2H, cyclohexyl), 1.99(m, 4H, cyclohexyl), 1.88(m, 3H, CH_3), 1.80-1.45 (series of multiplets, cyclohexyl), 1.38(m, 4H, THF).

{CyN-C[Ph(o-CH_2NMe_2)-NCy]Li(Et_2O)

A solution of CyNCNCy (9.2 g, 44.7 mmol) in ether (200 mL) was treated at room temperature with freshly prepared (o-Me_2NCH_2)PhLi (6.3 g, 44.7 mmol). The resulting yellowish solution was allowed to stand at room temperature overnight. The solution was concentrated to a small volume by evaporation of the solvent in vacuo at room temperature. The resulting solution was filtered and cooled to -30C°, upon which colorless crystals of {CyN-C[Ph(o-CH_2NMe_2) -NCy]Li(Et_2O) precipitated (17 g, 40.4 mmol, 90%). I.R. [nujol mull, KBr, cm^{-1}] ν: 1470(s), 1410(sh), 1380(w), 1355(m), 1310(m), 1235(s), 1170(s), 1150(m), 1110(s), 1060(s), 1030(s), 980(s), 945(w), 920(w), 885(m), 860(m), 840(m), 820(w), 800(m), 770(s), 750(m), 730(s), 660(m), 560(br), 500(m), 380(br). ^{1}H-NMR [C_6D_6, 200 MHz, 25C°] δ: 7.81, 7.55, 7.41, 7.23(m, 4H, phenyl), 3.63(s, 2H, benzyl), 3.29(q, 4H, Et_2O), 2.80(m, 2H, cyclohexyl), 2.30(s, 6H, Me), 2.10, 1.80, 1.55, 1.20(m, cyclohexyl), 1.18(t, 6H, Et_2O).

{[CyN-C(H)-NCy]$_2$Cr}$_2$.toluene (5.1)

A suspension of $CrCl_2(THF)_2$ (1.96 g, 7.3 mmol) in toluene (50 mL) was stirred for two hours at room temperature in the presence of [CyN-C(H)-NCy]Li (3.24 g, 15.1 mmol). The resulting deep-yellow suspension was filtered at 80°C to eliminate a gray solid and then allowed to cool slowly to room temperature. Orange air-sensitive crystals of **5.1** were obtained upon standing two days at room temperature (2.5 g, 2.7 mmol, 74%). I.R. [nujol mull, KBr, cm^{-1}] ν: 1590(vs), 1360 (s), 1340(s), 1320(s), 1290(vs), 1250(s), 1230(sh), 1185(m), 1150(s), 1100(s), 1080(s), 1070(s), 1020(w), 990(w), 950(m), 880(s), 840(m), 780(w), 725(vs), 690(s), 510(s), 460(m), 425(s). ^{1}H-NMR [C_6D_6, 200 MHz, 25C°] δ: 8.43 (s, 4H, formamidine), 7.08(pseudo quartet, 4H, toluene), 3.11(pseudo quintet, 8H, cyclohexyl), 2.10(s, 3H, toluene), 2.07(pseudo d, 16H, cyclohexyl), 1.81(pseudo d, 16H, cyclohexyl), 1.63(pseudo d, 8H, cyclohexyl), 1.30(m, 40H, cyclohexyl).

[CyN-C(CH$_3$)-NCy]$_2$Cr (5.2)

A suspension of $CrCl_2(THF)_2$ (1.82 g, 6.8 mmol) in THF (50 mL) was stirred for two hours at room temperature in the presence of [CyN-C(CH_3)-NCy]Li(Et_2O) (3.22 g, 14.1

mmol). The resulting purple-red solution was filtered and concentrated to a small volume. Deep-red air-sensitive crystals of **5.2** were obtained upon standing two days at room temperature (0.9 g, 1.8 mmol, 26%). I.R. [nujol mull, KBr, cm^{-1}] ν: 1510(s), 1370(sh), 1360(sh), 1345(sh), 1270(w), 1255(w), 1245(w), 1200(s), 1190(s), 1140(w), 1100(sh), 1090(s), 1075(sh), 1000(s), 960(w), 920(w), 900(m), 890(s), 870(w), 850(w), 830(m), 805(m), 785(w), 725(w), 660(s), 610(m), 575(m), 505(w), 480(w), 450(w), 410(s), 370(sh). $\mu_{eff} = 4.75\ \mu_B$.

{CyN-C[Ph(o-CH_2NMe_2)]-NCy}Cr.2THF (5.3)

A suspension of $CrCl_2(THF)_2$ (0.97 g, 3.6 mmol) in THF (60 mL) was boiled for two minutes and stirred for two hours at room temperature in the presence of {CyN-C[Ph(o-CH_2NMe_2)]-NCy}Li(THF) (3.53 g, 8.4 mmol). The resulting deep-blue solution was filtered and concentrated to a small volume (20 mL). The mixture was boiled, filtered while hot, and allowed to cool slowly to room temperature. Deep-blue air-sensitive crystals of **5.3** were obtained upon standing two days at room temperature (1.2 g, 1.6 mmol, 45%). I.R. [nujol mull, KBr, cm^{-1}] ν: 2770(w), 1360(s), 1345(m), 1260(s), 1215(m), 1175(w), 1150(w), 1115(w), 1080(s), 1030(s), 990(m), 940(w), 900(w), 890(w), 870(w), 850(w), 800(w), 775(s), 735(m), 720(w), 660(w), 550(w), 490(w). $\mu_{eff} = 4.83\ \mu_B$.

{[(Me_3Si)N]$_2$C(Ph)}$_2$Cr (5.4)

A solution of $(Me_3Si)_2NLi$ (2.01 g, 12.0 mmol) in toluene (100 mL) was treated with PhCN (1.25 g, 12.0 mmol) at room temperature. After standing overnight at room temperature, the addition of $CrCl_2(THF)_2$ (1.6 g, 6.0 mmol) to the mixture changed the color to purple-red.

The mixture was boiled for a few minutes, stirred for two hours at room temperature then subsequently filtered and concentrated to a small volume until crystalline material started to separate. The mixture was heated until the crystalline material redissolved, then filtered hot and allowed to cool slowly to room temperature. Subsequent standing at -30°C for two days yielded dark pinkish-purple crystals of **5.4** (1.5 g, 2.7 mmol, 45%). I.R. [nujol mull, KBr, cm^{-1}] ν: 1435(s), 1265(sh), 1245(s), 1175(w), 1080(w), 1005(m), 990(s), 925(w), 850(vs), 790(w), 765(s), 705(s), 605(w), 530(s), 450(w). $\mu_{eff} = 4.66\ \mu_B$.

Chapter 6

Diphenylphosphinomethanide Complexes of Cr(II) and Sm(III): Preparation and Characterization

6.1 Introduction

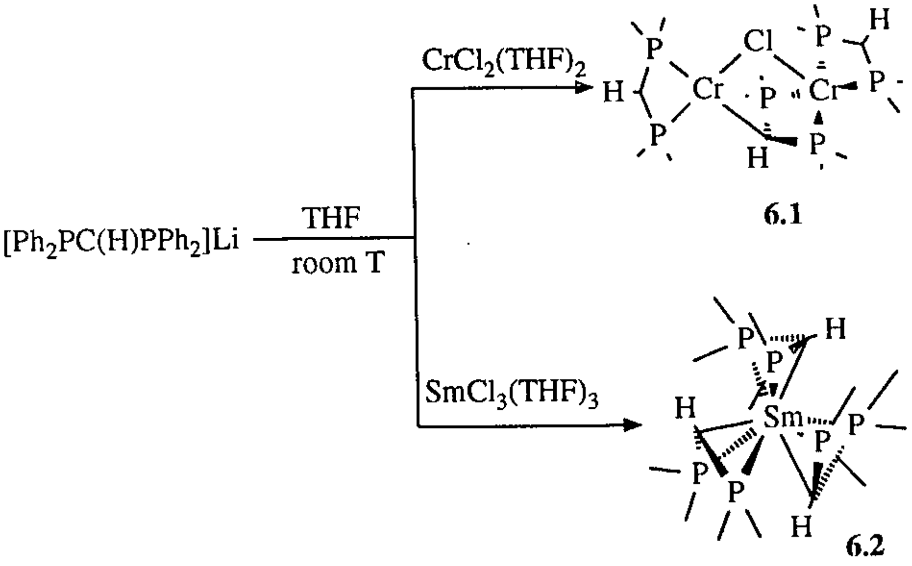
Three-center allylic-like chelating ligands (monoanionic, with three-atom bite, two donor atoms, four π-electrons) undoubtedly play a pivotal role[69,104,227] in the formation of supershort metal-metal contacts.[2,61] Chelating phosphines with three-atom bite such as dppm or dmpm [dppm = diphenylphosphinomethane, dmpm = dimethylphosphinomethane] have also been shown to stabilize dimetallic units with short M-M contacts.[75,228,229] Since these ligands work as four electron donors and given their characteristic geometry, they may be associated with the large family of the three center chelating ligands. The only significant variation with respect to the anionic three-center congeners is that the electronic conjugation between the two terminal donor atoms is interrupted by the central CH_2 group. Although the electronic communication between the two P atoms might be restored via deprotonation of the CH_2 group, the resulting diphosphino methanide anion $[Ph_2PC(H)PPh_2]Li$ possesses up to 6 electrons which may be delocalized over the three atoms, only in the event that the two phosphorus atoms adopt an sp^2 hybridization. A literature survey shows that whereas this ligand works as a binucleating three-center chelating ligand in only a few cases,[230] in the majority of cases it functions as a normal mononucleating ligand with both late[231-244] and early transition metals.[245] Moreover, in all these complexes the bonding is achieved via the P atoms since the M-C distances usually are significantly beyond the bonding range.

In this chapter we describe the unusual structural features of the complexes formed by the reaction of $[Ph_2PC(H)PPh_2]Li$ with both $CrCl_2(THF)_2$ and $SmCl_3(THF)_3$.

6.2 Results and Discussion

Both reactions proceed rapidly at room temperature in THF to afford clear solutions from which large blue crystals of the dinuclear $[Cr(Ph_2PC(H)PPh_2)](\mu\text{-}Cl)(\mu\text{-}\eta^3\text{-}C\text{:}P,P\text{-}C(H)(PPh_2)_2)[Cr(Ph_2PC(H)PPh_2)]$ (**6.1**) and orange crystals of the monomeric $Sm(\eta^3\text{-}Ph_2PC(H)PPh_2)_3$ (**6.2**) were obtained after solvent evaporation and recrystallization of the residual solid at room temperature from toluene/hexane mixtures (Scheme 6-1).

Scheme 6-1



The structure of **6.1**, as determined by an X-ray diffraction analysis, consists of one penta- and one tetra-coordinated chromium atom (Figure 6-1). The distorted square-pyramidal geometry of Cr1 is determined by the four phosphorus atoms of two $[Ph_2PC(H)PPh_2]$ ligands which bind the basal plane [P1-Cr1-P5 = 163.72(7)°, P2-Cr1-P6 = 173.21(7)°]. The Cr1-P

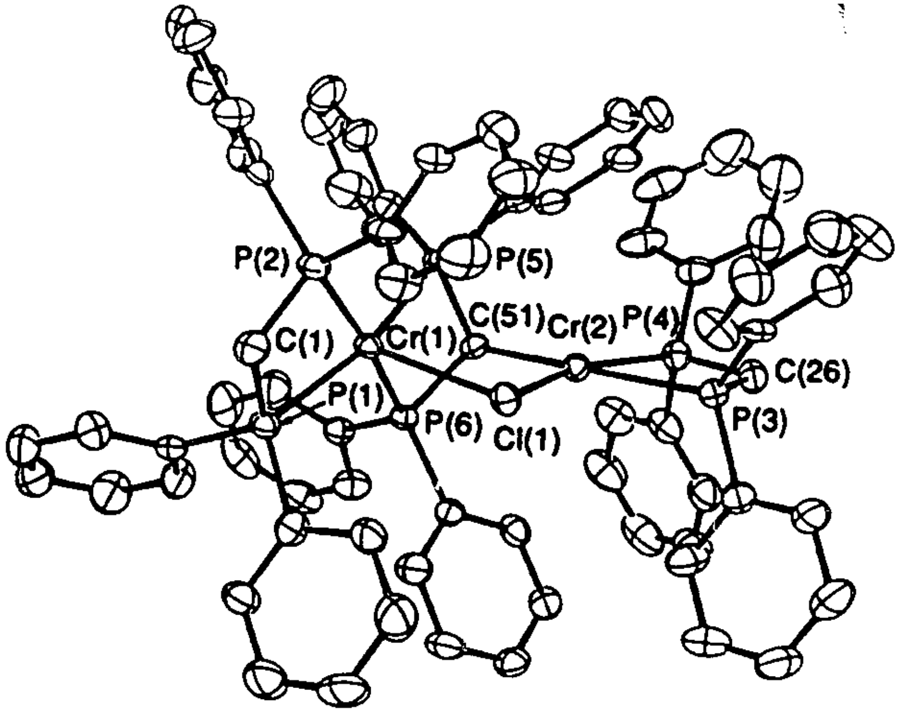


Figure 6-1. ORTEP drawing of **6.1**, showing the labeling scheme.

bond distances [Cr1-P1 = 2.467(2)Å, Cr1-P2 = 2.468(2)Å, Cr1-P5 = 2.526(2)Å, Cr1-P6 = 2.484(2)Å] compare well with those of other Cr(II) phosphine complexes.[75] One chlorine atom is placed on the apical position [Cr1-Cl1 = 2.535(2)Å, P1-Cr1-Cl1 = 105.32(7)°; P6-Cr1-Cl1 = 84.24(6)°] of the ideal square-pyramid based on chromium and is shared with the second square-planar chromium atom [Cr2-Cl1 = 2.375(2)Å]. The other three coordination sites of the second chromium atom are occupied by the two phosphorus of one $Ph_2PC(H)PPh_2$ moiety [Cr2-P3 = 2.462(2)Å, Cr2-P4 = 2.488(2)Å], and by the carbon atom of one of the two phosphines which chelates the first chromium atom [Cr2-C51 = 2.220(6)Å]. Except for this Cr-C bonding contact, all the other Cr-C distances are rather long and out of the bonding range [Cr1..C1 = 3.068(2)Å, Cr1..C51 = 3.065(2)Å, Cr2..C26 = 3.101(2)Å]. The large steric bulk of the complex is apparent in the distortion of the square-planar coordination geometry of the second Cr atom [P3-Cr2-P4 = 67.14(6)°, Cl1-Cr2- P3 = 96.64(7)°, P4-Cr2-C51 = 99.13(17)°, Cl1-Cr2-C51 = 9.86(17)°]. One and half molecule of toluene and a disordered half molecule of THF were also found in the lattice.

The Cr-Cr distance [Cr-Cr = 3.714(1)Å] is rather long and rules out any direct bonding interaction. However, the magnetic moment [μ_{eff} = 6.07μ_B per dinuclear unit] is slightly lower than that expected for a combination of high-spin square-planar Cr(II) and low-spin square-pyramidal Cr(II). Surprisingly, the complex is ESR silent in both solid state and frozen toluene solution (-200°C).

The visible spectrum of **6.1** shows one very broad absorption between 530 and 800 nm centered at 620 nm due to superimposed $^5B_{1g}$to $^5B_{2g}$ and ^5E_g transitions of high-spin Cr(II).[246-247] Cyclic voltammogram of **6.1** showed two successive reversible one-electron reductions at around -1.66 (Epa-Epc = 76 mV) and -1.86 V (Epa- Epc = 74 mV) vs ferrocene/ferrocenium (scan rate: 200mV/s^{-1}) in THF-TBABF$_4$ (TBABF$_4$ = tetra-n-ammonium tetrafluoroborate) solution at room temperature which we tentatively assign to the two reduction waves of each of the two Cr(II) metal centers.

The crystal structure of complex **6.2** revealed a monomeric complex with the central samarium atom nine-coordinated to three identical diphosphinomethanide ligands (Figure 6-2). The samarium atom is placed side-on with respect to each plane bound by the two phosphorus and bridging carbon atoms of each diphosphinomethanide molecule [Sm1-C1 = 2.787(9)Å, Sm1-C2 = 2.756(9)Å, Sm1-C3 = 2.720(9)Å, Sm1-P1 = 2.857(2)Å, Sm1-P2 = 2.845(3)Å, Sm1-P3 = 2.818(3)Å, Sm1-P4 = 2.903(3)Å] thus resulting in a curious allylic-like

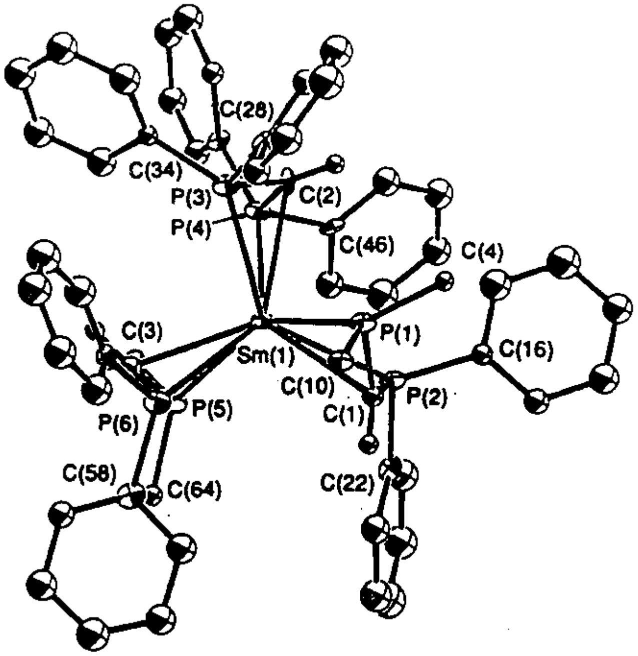


Figure 6-2. ORTEP drawing of **6.2**, showing the labeling scheme; some of the phenyl rings have been omitted for clarity

bonding mode.[248] All the other bond distances and angles are comparable.

In spite of the rather symmetric side-on bonding mode, closely reminiscent of the allylic systems, the orientation for the phenyl rings defines a tetrahedral coordination geometry of the two phosphorus atoms thus indicating an sp^3 hybridization of the phosphorus atoms which rules out the presence of a π system. Although complex **6.2** is paramagnetic with a magnetic moment [$\mu_{eff} = 1.77\ \mu_B$] which is rather high for an f^5 Sm(III) atom, it shows a well resolved ^{1}H-NMR spectrum with the expected δ values for the resonances of the aromatic and methanide protons.[246,247]

6.3 X-ray crystallography

Refer to Section **2.3**. Details on data collection and structure refinement for **6.1** and **6.2** are reported in Table 6-1. Selected bond distances and angles are given in Table 6-2.

Table 6-1 Crystal Data and Structural Analysis Results

complex	**6.1**	**6.2**
formula	$C_{87.5}H_{82}ClP_6Cr_2O_{0.5}$	$C_{75}H_{63}P_6Sm$
formula weight	1466.90	1300.56
crystal system	monoclinic	triclinic
Space Group	C2/c	P-1
a (Å)	29.968(12)	13.331(4)
b (Å)	22.445(12)	21.860(8)
c (Å))	22.832(4)	12.524(3)
α (deg)		97.58(3)
β (deg)	94.20(3)	94.20(2)
γ (deg)		75.69(3)
V ($Å^3$)	15317(11)	3159(4)
Z	8	2
Radiation (MoKα Å)	0.71069	0.71069
T (°C)	-153	-160
R, R_w	0.065, 0.064	0.048, 0.067
GoF	4.05	3.82
Parameters	754	404
Observations	8032	3833

Table 6-2 Selected Bond Distances (Å) and Angles (deg)

6.1	**6.2**
Cr1-Cl1 = 2.535(2)	Sm1-P1 = 2.857(2)
Cr2-Cl1 = 2.375(2)	Sm1-P2 = 2.845(3)
Cr1-P1 = 2.467(2)	Sm1-C1 = 2.787(9)
Cr1-P2 = 2.468(2)	Sm1-P3 = 2.818(3)
Cr1-P5 = 2.526(2)	Sm1-P4 = 2.903(3)
Cr1-P6 = 2.484(2)	Sm1-C2 = 2.756(9)
Cr2-P3 = 2.462(2)	Sm1-P5 = 2.852(3)
Cr2-P4 = 2.488(2)	Sm1-P6 = 2.876(3)
Cr2-C51 = 2.220(6)	Sm1-C3 = 2.720(9)
P1-C1 = 1.735(7)	P1-C1-P2 = 117.7(5)
P2-C1 = 1.708(7)	P3-C2-P4 = 114.7(5)
P3-C26 = 1.717(7)	P5-C3-P6 = 114.1(5)
P4-C26 = 1.714(7)	P1-Sm1-P2 = 63.91(7)
P5-C51 = 1.793(6)	P1-Sm1-C1 = 36.4(2)
P6-C51 = 1.809(6)	P2-Sm1-C1 = 36.5(2)
P1-Cr1-P5 = 163.72(7)	P1-Sm1-P3 = 87.31(8)
P2-Cr1-P6 = 173.21(7)	P1-Sm1-P4 = 122.50(7)
Cl1-Cr1-P1 = 105.32(7)	
Cl1-Cr2-P4 = 163.33(7)	

6.4 Experimental Section

All operations were performed under inert atmosphere in a dry-box (Vacuum Atmosphere) or using standard Schlenk techniques. $CrCl_2THF_2$,[176] $SmCl_3THF_3$ and $(Ph_2PCHPPh_2)Li$ were prepared according to published procedures. NMR spectra were obtained on a Varian Gemini 200 by using vacuum-sealed samples prepared in a dry-box. Solvents for NMR spectroscopy were appropriately dried and vacuum-transferred into ampoules for storage inside a dry-box. Infrared spectra were recorded on a Mattson 9000 FT-IR instrument from Nujol mulls prepared in a dry-box. Samples for magnetic susceptibility measurements were weighed inside a dry-box equipped with an analytical balance, and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature. The magnetic moment was calculated according to standard methods,[111] and corrections for underlying diamagnetism were applied to data.[112] Combustion analysis data were obtained which satisfactorily verified the composition of all the complexes.

Cyclic voltammetry was performed in a N_2-filled dry-box with a EG&G cell equipped with a 0.1 mm cross-section Pt-wire as working electrode, with a 5 mm long identical Pt wire as a counter-electrode, and with a PAR 272 potentiostat-galvanostat (scan rate of 200 mV/s^{-1}). A Pt wire electrode was used as a pseudo-reference in this experiment and potentials were referred to the ferrocene/ferrocenium potential obtained under identical conditions. Solutions were 0.01 M of parent compound in 0.3M $TBABF_4$/THF solutions.

The preparation of Complex 6.1.

Solid $Li-(Ph_2PC(H)PPh_2)$ (3.576g, 9.1 mmol) was added to a suspension of

$CrCl_2(THF)_2$ (1.18g, 4.4 mmol) in THF (60 mL) under a nitrogen atmosphere at room temperature. After stirring for 30 minutes, the solvent was evaporated *in vacuo*. The residual solid was redisolved in toluene (90 mL) and the insoluble material filtered out from the hot solution. Large deep-blue crystals of **6.1** (2.0 g, 1.5 mmol, 68%) were obtained upon standing the solution 5 days at room temperature. I.R. (KBr, Nujol, cm^{-1}) ν: 1583w, 1432s, 1301w, 1114m, 1094m, 1024m, 887s, 827w, 772m, 738s, 694s, 558s, 5079s0, 481w. Elem. Anal. Calcd (Found) for $C_{75}H_{66}P_6Cr_2Cl$. 1.5toluene . 0.5THF: C 71.92 (72.30), H 5.69 (5.81). μ_{eff} = 6.07 μ_B.

The preparation of Complex 6.2.

A colorless solution of $SmCl_3(THF)_3$ (2.6 g, 5.5 mmol) in THF (100 mL) turned light orange upon treatment with solid $(Ph_2P)_2C(H)Li$ (4.4 g, 11.3 mmol) at room temperature. The solvent was removed in vacuo and the residual solid redissolved in toluene. After removal of the insoluble material by filtration, the solution was concentrated to small volume and layered with hexane. Red-brownish crystals of **6.2** (3.0 g, 2.3 mmol, 42%) were obtained upon standing at room temperature for two days. I.R. (KBr, Nujol, cm^{-1}) ν: 1583(w), 1570(w), 1477(m), 1432(s), 1324(w), 1301(w), 1260(w), 1180(w), 1154(w), 1092(m), 1066(w), 1025(m), 999(w), 911(w), 865(s), 775(w)), 736(s), 694(s), 648(w), 616(w), 603(w), 513(m), 485(m), 470(m). Elem. Anal. Calcd (Found) for $C_{75}H_{63}P_6Sm$: C 69.27 (70.10), H 4.88 (5.00). ^{1}H-NMR (200 MHz, C_6D_6, 25°C) δ: 9.00(C-H methanide), 7.18, 6.70 (m, phenyl). μ_{eff} = 1.77 μ_B.

Chapter 7

Preparation and Characterization of a New Series of Cr(II) Hydroborates

7.1 Introduction

Tetrahydroborate complexes of transition metals are widely used not only as versatile precursors for the preparation of transition metal polyhydrides[249-255] and alkyls,[256] but also as important and efficient catalysts for hydrogenation and polymerization reactions.[257-263] For example, tetrahydroborate complexes of group 4, 5, and 6 metals are commonly used in the catalytic hydrorefinement of petroleum sludges and residues to light hydrocarbons and to other useful commodity chemicals freed from asphaltenes, metal impurities, and sulfur.[264] In view of these useful applications transition metal, lanthanide and actinide tetrahydroborate complexes have been widely investigated[265-268] and, as a result of the considerable amount of research in this field, only a few transition metal tetrahydroborate complexes remain unexplored. Unfortunately, a large variety of catalytic transformations promoted by these systems has been reported only in the patent literature and therefore knowledge about the chemical behavior of these species remains scarce.

Aside from their importance in industrial processes, tetrahydroborate complexes of transition metals are also popular because of their close relation with transition metal hydrides. As a matter of fact, a common method of preparing polyhydride complexes typically consists of the reaction of transition metal tetrahydroborates with a Lewis base or water.[265-267,269-274] In addition, although the mechanisms of reactions catalyzed by transition metal hydroborates have not been completely elucidated, there is evidence that *in situ* generated polyhydride complexes are likely to be the most important intermediates of the catalytic cycles.[275]

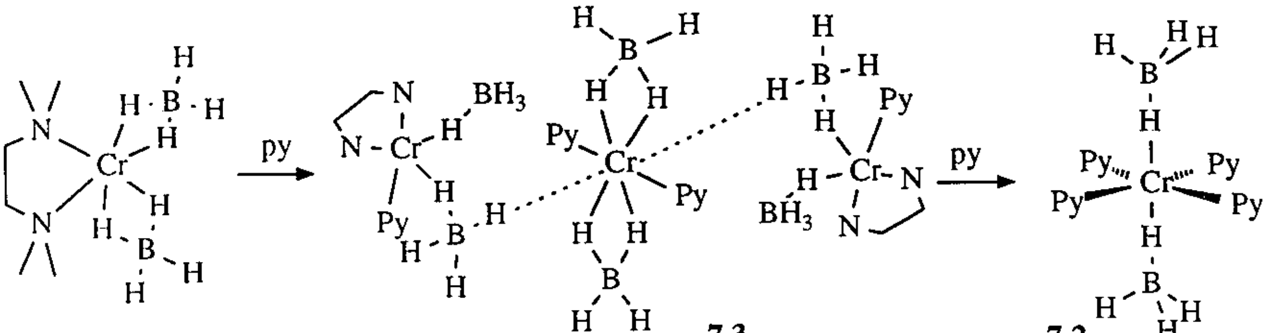
Given this background, it is surprising that chromium tetrahydroborates are poorly known, and that only a few very stable species such as $CpCr(BH_4)$,[276] $Cr(BH_4)_2THF_2$[277] and $Cr(BH_4)H(dmpe)_2$[268] have been reported and formulated on the exclusive basis of their spectroscopic and microanalytical data. This is also in striking contrast with the great potential offered by these compounds for the preparation of rare chromium hydrides.[48,278,279]

In this chapter we describe the preparation and characterization of a novel series of chromium(II) tetrahydroborates together with a preliminary study of their chemical reactivity. One of the *stimuli* to undertake this study was provided by the variety of possible bonding modes displayed by the BH_4^- anion.[265] Since Cr(II) complexes generally display a marked preference for square-planar structures with high-spin electronic configurations,[104] we were interested in testing the ability of the tetrahydroborate anion to facilitate the assembly of dimers with a lantern-type structure, where the BH_4^- anion would adopt a three-center chelating bridging bonding mode. In order to achieve this goal we have decided to use a chelating amine such as TMEDA [TMEDA = N,N,N',N'-tetramethylethylenediamine] as supporting ligand. This ligand offers sufficient stabilization for the complex, while at the same time may dissociate to enable dimerization reactions. Chelating amines are also desirable because of their ability to remove BH_3 from the BH_4^- anion, which in the present case should lead to the formation of new Cr(II) hydrides.

7.2 Results and Discussion

The reaction of $CrCl_2(THF)_2$ with $NaBH_4$ in THF at room T and in the presence of an excess TMEDA [TMEDA = N,N,N',N'-tetramethylethylenediamine] gave the divalent chromium tetrahydroborate complex $Cr(BH_4)_2(TMEDA)$ (**7.1**) in good yield (Scheme 7-1).

Scheme 7-1



7.1 **7.3** **7.2**

Although the reaction was rather straightforward, the purification was somewhat problematic due to the thermal instability of **7.1**, which prevented normal extraction techniques from being used for its separation from the excess of $NaBH_4$ and NaCl. Complete decomposition of the complex with formation of black tarry material was observed after refluxing for one hour in THF. The magnetic moment of **7.1** [μ_{eff} = 4.87 μ_B at room T] was as expected for the d^4 electronic configuration of a Cr(II) ion, according to the formulation indicated by analytical data. The infrared spectrum showed the characteristic absorptions of BH_4^- as two very intense and broad resonances at 2380 and 2120 cm^{-1} (terminal boron-hydrogen stretching) and a medium resonance at 2230 cm^{-1} (B-H stretching). These resonances, together with an intense band at 1120 cm^{-1} (BH_2 deformation), diagnose a bidentate bonding mode of the BH_4 group.[265] This conclusion is substantiated by the X-ray crystal structure.

Complex **7.1** is monomeric (Fig. 7-1) with the chromium atom adopting a distorted pseudo square-planar geometry. The molecular plane centered on chromium is defined by the two nitrogen atoms of TMEDA and the two boron atoms. The coordinated TMEDA shows

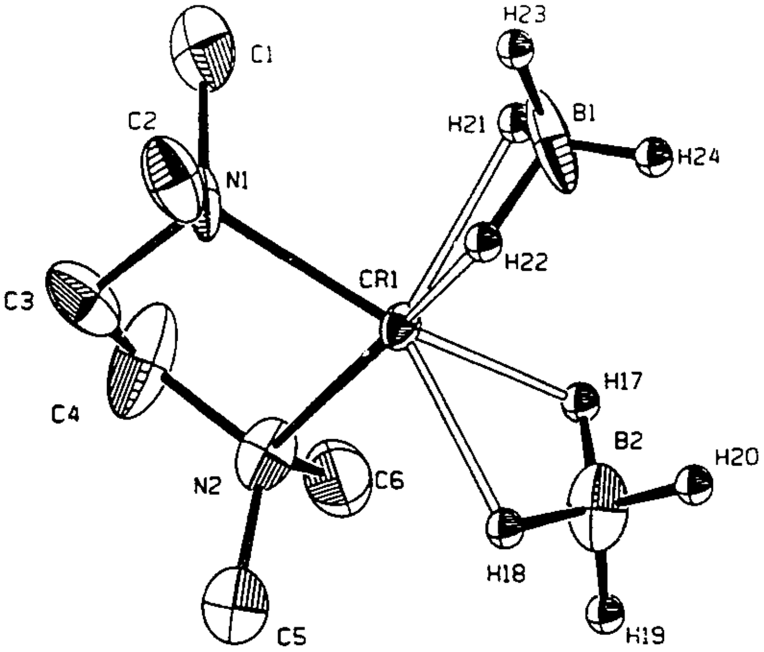


Figure 7-1. ORTEP plot of **7.1**.

rather normal bond distances and angles [Cr1-N1 = 2.128(7)Å, Cr-N2 = 2.171(7)Å]. As a possible result of the bidentate bonding mode of the BH_4^- groups, the Cr-B distances [Cr1-B1 = 2.44(1)Å, Cr1-B2 = 2.42(1)Å] are rather short compared to those of other Ti and V borohydride complexes.[253,254,266,267] The difference Fourier maps revealed the positions of all the hydrogen atoms. Each of the two BH_4^- tetrahedra points two of the four hydrogen atoms, located above and below the molecular plane, towards the Cr atom [Cr1-H22 = 1.87Å, Cr1-H17 = 1.93Å, Cr1-H21 = 2.08Å, Cr1-H18 = 2.09Å]. The coordination geometry of the boron atom is that of a regular tetrahedron with normal B-H distances [from 0.995 to 1.198Å] and H-B-H angles. No significant differences were observed between the B-H bond distances of bridging and terminal hydrogens.

Following a trend commonly observed in the chemistry of low-valent early transition metals, the coordinated TMEDA of complex **7.1** was easily replaced by pyridine, forming different products, depending on the amount of pyridine added. For example, the addition of 2 equiv. of pyridine to an intense blue solution of **7.1** afforded a light-green solution from which thermally robust brown-red crystals of $Cr(Py)_4(BH_4)_2$ (**7.2**) were obtained in good yield. While the formula was suggested by analytical results, the I.R. spectrum showed the resonances characteristic of a BH_4 group bonded in a monodentate fashion. The magnetic moment [μ_{ef} = 2.83 μ_B] was also as expected for a d^4 low spin electronic configuration of Cr(II), possibly indicating an octahedral structure. Although complex **7.2** can be conveniently recrystallized from THF, the structure in solution is probably very different since the red crystals dissolved to yield deep-green paramagnetic solutions. Unfortunately, attempts to investigate the structure in solution by both NMR and EPR technique were unsuccesful because the spectra were uninformative.

Complex **7.2** is monomeric with the chromium atom placed in the center of a regular octahedron defined by the four nitrogen atoms of the four pyridine molecules [Cr1-N1 = 2.104(9)Å, Cr1-N2 = 2.128(9)Å, Cr1-N3 = 2.12(1)Å, Cr1-N4 = 2.156(9)Å, N1-Cr1-N2 = 89.5(4)°, N1-Cr1-N4 = 180.00°] and two BH_4^- groups placed in *trans* positions with respect to each other (Figure 7-2). The positions of the hydrogen atoms were revealed by the difference Fourier maps. Although the data file was not of sufficient quality to refine the hydrogen atom positions, the H atoms were found at their expected positions forming normal bond distances and angles. The bonding between chromium and the two hydroborate groups is realized through only one bridging hydrogen per each η^1-BH_4 group. The bridging hydrogen atom was found at a rather long distance from the chromium atom [Cr1-H37 = 2.33Å, Cr1-H41 = 1.94Å]

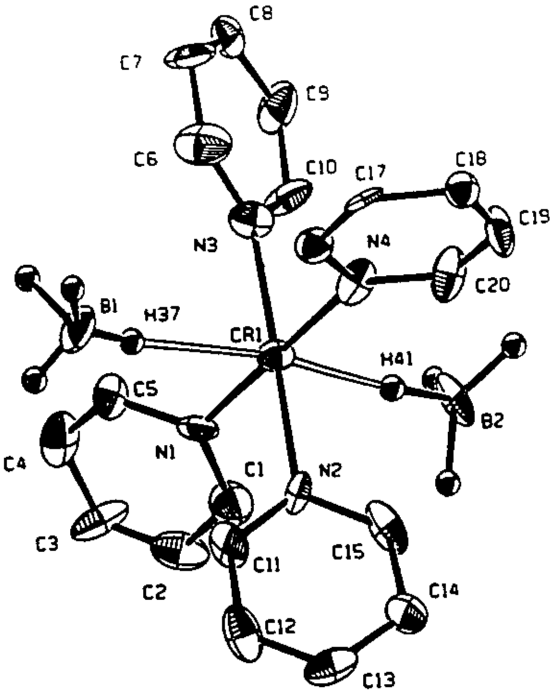


Figure 7-2. ORTEP plot of **7.2**.

but close to the boron atom [B1-H37 = 0.98Å. B2-H41 = 1.16Å] forming an almost linear Cr-H-B array [H37-Cr1-H41 = 171.7°]. Therefore, the bonding of the BH_4^- groups may be considered somewhere between the ionic and the η^1- covalent. The two H atoms of the two BH_4^- groups used for bridging the metal atom, are also aligned with the chromium atom forming an axis perpendicular to the $Cr(Py)_4$ plane [Cr1-H37-B1 = 173.9°]. The η^1-bonding mode of the BH_4^- groups is also substantiated by the much longer Cr-B distances [Cr1-B1 = 3.309(9)Å, Cr1-B2 = 3.253(9)Å] comparing to complex **7.1**.

When the reaction of **7.1** was carried out with a smaller amount of pyridine, the red crystalline mass of **7.2** was found to be contaminated by a variable amount of bright green crystals of a new compound, **7.3**. Repeated attempts to make the reaction selective by modifying the amount of pyridine failed and therefore it was not possible to obtain **7.3** in analytically pure form. Nevertheless, addition of pyridine to the heterogeneous crystalline mass dissolved the green crystals and improved the yield of the red **7.2**, which could be then isolated in analytically pure form. This indicated that the green **7.3** might be just an intermediate during the formation of **7.2**. The green crystals of **7.3** were sufficiently large and of adequate quality to undertake an X-ray crystal structure determination.

The most interesting feature of the structure is that the unit cell contains two different types of fragments: two $Cr(BH_4)_2(Py)TMEDA$ units and a central $Cr(BH_4)_2Py_2$ unit which, differently from **7.2**, contains only two coordinated pyridine moieties rather than four (Figure 7-3). The three fragments are loosely connected by bridging hydrogen interactions. The central $Cr(BH_4)_2Py_2$ unit can be regarded as *trans* square-planar with the molecular plane bound by the nitrogen of the two pyridine and the two boron atoms [N1-Cr1-N1a = 180.00°, N1-Cr1-B2 = 90.2(1)°, N1-Cr1-B2a = 89.8(1)°, B2-Cr1-B2a = 180.00°]. Even in this case it was possible to locate all the H atom positions thus revealing the bonding of the BH_4^- groups. As indicated

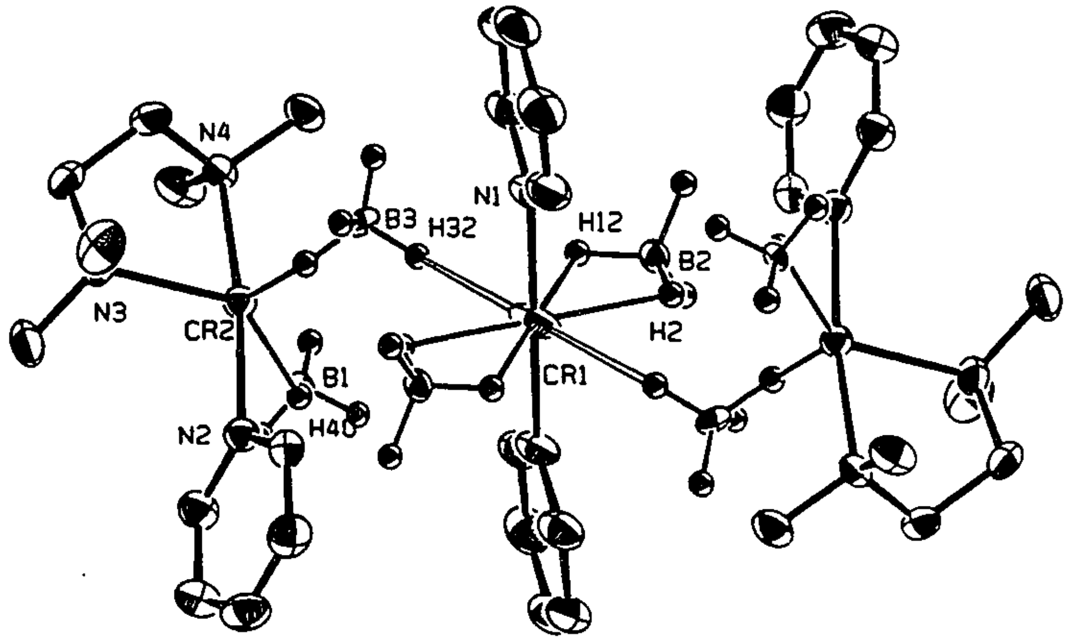
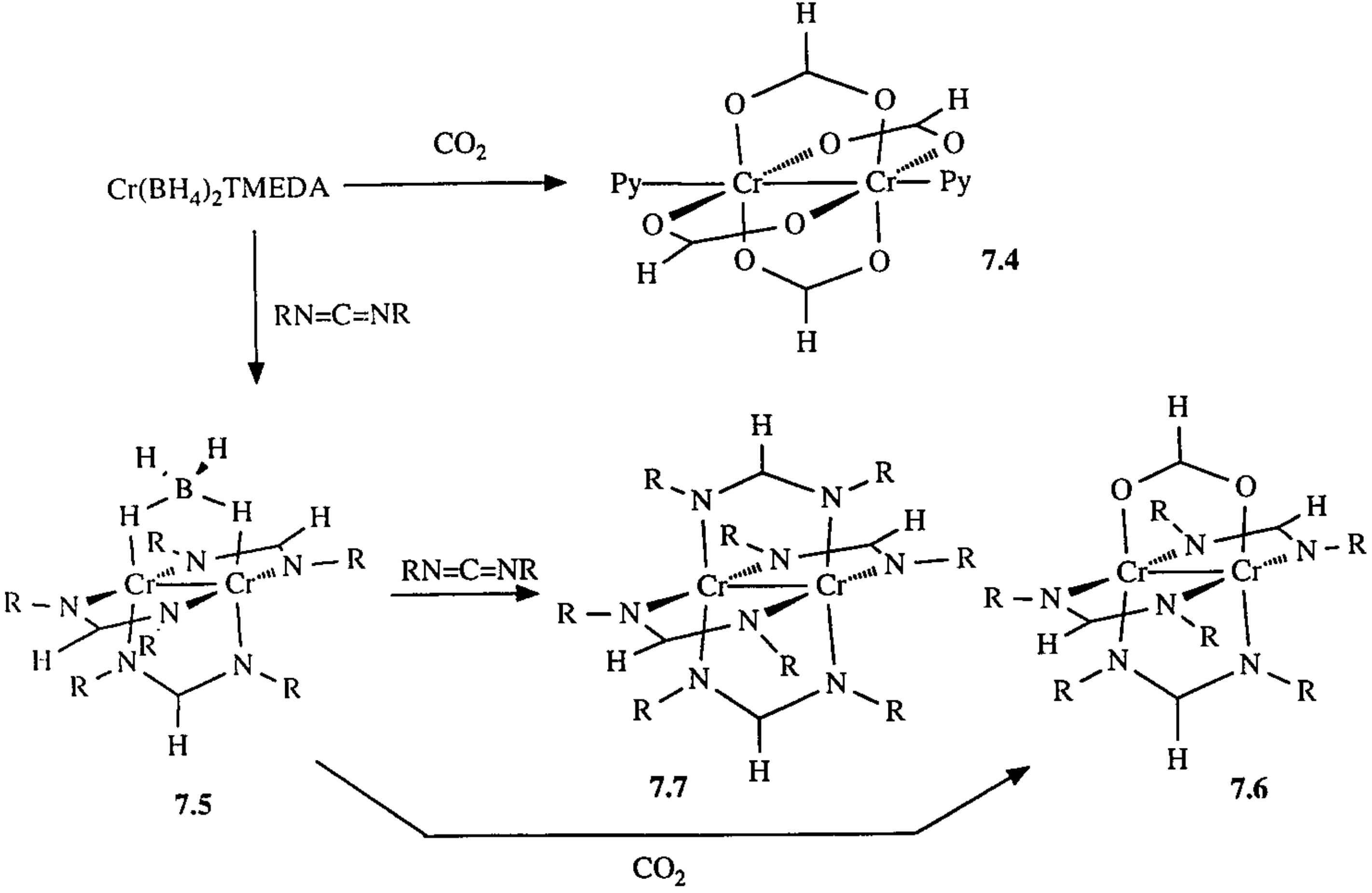


Figure 7-3. ORTEP plot of **7.3**

by the short Cr-B distances [Cr1-B2 = 2.426(5)Å], the two BH_4^- groups adopt the η^2-bonding mode. The coordination geometry of the Cr atom in the two identical lateral units is that of a distorted trigonal bipyramid with one nitrogen atom of pyridine and one nitrogen atom of TMEDA placed in the axial positions [N2-Cr2-N4 = 172.8(1)°, N2-Cr2-B1 = 87.4(1)°, N2-Cr2-N3 = 92.0(1)°, N3-Cr2- N4 = 82.6(1)°], and two BH_4^- groups and the second nitrogen atom of TMEDA defining the equatorial plane [N4-Cr2-B1 = 93.2(1)°, N4-Cr2-B3 = 92.8(1)°, N3-Cr2-B1 = 136.7(1)°, N3-Cr2-B3 = 106.6(1)°, B1-Cr-B3 = 116.7(1)°]. The two BH_4^- groups are placed at remarkably different distances from the chromium atom [Cr2-B1 = 2.488(4)Å, Cr2-B3 = 2.716(4)Å] in spite of the fact that both are placed in two equivalent equatorial positions, as a result of two different monodentate bonding modes. While the first BH_4^- forms a significantly bent Cr-H-B vector [Cr2-H4-B1 = 110.3°], the second BH_4 forms an almost linear array [Cr2-H34-B3 = 178.1°]. In addition, one of the hydrogens of the second BH_4^- group points toward the chromium atom of $Py_2Cr(BH_4)_2$ forming a short non-bonding contact [Cr1-H32 = 3.20Å]. Obviously, it is impossible to decide whether these contacts are artifacts of the crystal packing or are weak hydrogen bonds. In any case, unlikely these contacts are able to preserve the trimeric aggregation in solution. The Cr-N distances [Cr-N1 = 2.098(3)Å, Cr2-N2 = 2.119(3)Å, Cr-N3 = 2.227(3)Å, Cr-N4 = 2.137(3)Å] are comparable to those of the other two complexes reported in this work.

The ability of nitrogen donor ligands such as TMEDA and pyridine to stabilize a monomeric "$Cr(BH_4)_2$" moiety is rather remarkable in the view of the fact that "$Cr(BH_4)_2THF_2$" exists only below - 20 °C and rapidly decomposes at room T.[11] Complexes **7.1** and **7.2** in addition of possessing significantly different geometries from those of the phosphine derivative $Cr(BH_4)H(dmpe)_2$,[280] are chemically rather inert and do not react with a number of substrates such as CO (1 atm, room T), $H_2C=CH_2$(1 atm, room T), ^tBuCCH or $Me_3SiN=C=NSiMe_3$. However, complex **7.1** readily reacted with CO_2 in the presence of pyridine at room T to form the paramagnetic $Cr_2(CO_2H)_4Py_2$ (**7.4**). It also reacted with other cumulenes such as RN=C=NR [R = Cy, i-Pr] forming a series of diamagnetic chromium dimers $[RNC(H)NR]_3Cr_2(\mu\text{-}BH_4)$ (**7.5**) and $[RNC(H)NR]_4Cr_2$ (**7.7**), depending on the stoichiometry employed (Scheme 7-2). Reaction of **7.1** with three equivalents of 1,3-di-

Scheme 7-2



cyclohexylcarbodiimide in THF at room T yielded a mixture of $[CyNC(H)NCy]_3Cr_2(\mu\text{-}BH)_4$

(7.5a) and $(BH_3)_2$TMEDA. The separation of the two components was somewhat problematic due to their rather similar solubility properties. However, it was possible to obtain analytically pure samples, albeit in very poor yield, after several recrystallizations from THF. A very similar behavior was observed with 1,3-diisopropylcarbodiimide. However, in this case not only the purification of the corresponding $Cr_2[(i\text{-}Pr)NC(H)N(i\text{-}Pr)]_3(BH_4)$ (**7.5b**) was more easily achieved through standard extraction techniques, but also the crystallinity was sufficient to allow an X-ray crystal structure determination.

The structure of the complex showed the typical dimeric arrangement (lantern-type) observed in many other formamidine complexes of several transition metals[69] (Figure 7-4).

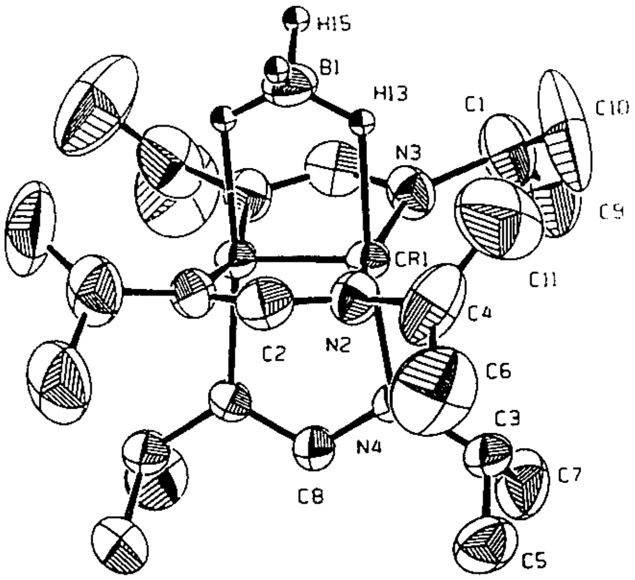


Figure 7-4. ORTEP plot of **7.5b**

The molecule consists of a Cr_2 unit bridged by three formamidinate groups and one borohydride group, with one pair of *trans*- positioned ligands defining a plane perpendicular to the plane bound by the third formamidine, the Cr_2 unit and the BH_4^- moiety. Each formamidinate ligand adopts the characteristic three-center chelating geometry where each of the two donor atoms of one ligand molecule binds one of the two metal centers, forming a five-membered ring with the Cr_2 unit. The borohydride also adopts the three-center chelating geometry where boron is connected to each of the two chromium atoms via bridging hydrogens. The coordination geometry of the two chromium atoms is distorted square planar [N2-Cr1-N3 = 163.5(2)°, N2-Cr1-N4 = 94.5(2)°, N3-Cr1-N4 = 95.1(2)°] with the chromium atoms slightly elevated above the plane defined by the three nitrogen atoms and a hydrogen atom of the μ-BH_4^- group [Cr1-Cr1-N angles ranging from 95.7(2)° to 96.5(2)°]. The Cr-Cr distance [Cr1-Cr1 = 1.844(2)Å] is among the shortest formed in this type of complexes and places **5b** in the family of the supershort quadruply bonded dichromium species.[61] The Cr-N bonding distances are normal [Cr1-N2 = 2.018(5)Å, Cr1-N3 = 2.021(5)Å, Cr1-N4 = 2.012(5)Å] and compare well with those of other monomeric and dimeric Cr(II) complexes reported in this work. The angles subtended at the formamidinic carbon by the nitrogen donor atoms [N4-C8-N4 = 121.3(8)°, N2-C2-N3 = 121.1(6)°] are similar to those of the dimeric compound $Cr_2(CyNCHNCy)_4$.

Both **7.5a** and **7.5b** are diamagnetic at room T and showed well resolved ^1H-NMR spectra. The two resonances expected for the two inequivalent formamidine groups (*cis* and *trans* with respect to the BH_4^- group) were observed at the expected positions. The resonance of the BH_4^- group appeared as a broad multiplet centered at 1.32 ppm in the case of **7.5b**, while in the case of **7.5a** the resonance was hidden by the resonances of the cyclohexyl groups. Magnetic measurements carried out with a Gouy balance at room T were also consistent with the diamagnetism inferred by the NMR data. In fact, no significant variation of chemical shift was observed when NMR spectra in d^8-toluene were recorded at -80°C, thus indicating that these compounds do not posses a significant magnetic anisotropy. This is in contrast to the case of $[(tol)NC(H)N(tol)]_4Cr_2$[223] which has a comparable Cr-Cr distance. Nevertheless, spectra carried out at variable temperatures above 25°C showed that the two C-H formamidinic signals coalesce, while a very significant signal broadening was observed for all the resonances. Since the coalescence can be reversed by lowering the temperature, so far we are unsure as to whether this phenomenon is generated by conformational motions or by dissociation equilibria to yield monomeric and paramagnetic units. On the other hand, supershort quadruple bonds are well known to be paradoxically weak in dichromium species,[69] unlikely to be able to maintain a dinuclear structure in the absence of bridging interactions and to spontaneously dissociate.[66] Therefore, we believe that dissociation equilibria are more likely to be responsible for this behavior in solution. The by-product $(BH_3)_2$TMEDA was often isolated in variable amounts and characterized by an X-ray crystal structure.[61] Its formation suggests that more than one process occurred simultaneously during the insertion reactions.

Further reaction of **7.5** with CO_2, carried out in deuterated benzene solution, showed during an NMR-tube experiment, that the intensities of the original peaks were slowly diminished to yield a new spectrum which accounts very well for a $[(i\text{-}Pr)NC(H)N(i\text{-}Pr)]_3Cr_2(O_2CH)$ (**7.6**) formulation. The reaction was rather slow at 25°C and it was 48 h. before the resonances of the unreacted starting material disappeared from the NMR spectrum. Similarly, reaction of **7.5** with excess carbodiimide gave the corresponding diamagnetic $[RNC(H)NR]_4Cr_2$ (**7.7**) dimers.

7.3 X-ray crystallography

Refer to Section **2.3**. Details on data collection and structure refinement for **7.1, 7.2, 7.3**, and **7.5b** are reported in Table 7-1 and 7-2. Selected bond distances and angles are given in Table 7-3 and 7-4.

Table 7-1 Crystal Data and Structural Analysis Results

complex	**7.1**	**7.2**
formula	$C_6H_{24}B_2N_2Cr$	$C_{28}H_{44}B_2N_4O_2Cr$
formula weight	197.88	534.23
crystal system	monoclinic	monoclinic
Space Group	Cc	$P2_1/n$
a (Å)	8.517(2)	12.021(1)
b (Å)	15.921(5)	15.555(1)
c (Å))	9.624	15.723(1)
α (deg)		
β (deg)	115.59(1)	90.13(2)
γ (deg)		
V ($Å^3$)	1177.0(5)	2940.1(6)
Z	4	4
Radiation (MoKα Å)	0.71069	0.71069
T (°C)	-160	-143
D_{calcd}(g cm^{-3})	1.117	1.207
μ_{calcd} (cm^{-1})	9.02	4.07
R, R_w	0.022, 0.029	0.074, 0.086
G.o.F.	1.92	3.10

Table 7-2 Crystal Data and Structural Analysis Results

complex	**7.3**	**7.5b**
formula	$C_{32}H_{76}N_8B_6Cr_3$	$C_{21}H_{49}N_6BCr_2$
formula weight	793.85	500.46
crystal system	monoclinic	monoclinic
Space Group	$P2_1/n$	C2/c
a (Å)	8.515(1)	17.000(1)
b (Å)	14.525(1)	9.033(1)
c (Å))	18.286(2)	19.160(1)
α (deg)		
β (deg)	91.38(1)	105.579(9)
γ (deg)		
V (Å^3)	2261.1(7)	2834.0(9)
Z	2	4
Radiation (MoKα Å)	0.71069	0.71069
T (°C)	-150	-30
D_{calcd}(g cm^{-3})	1.166	1.173
μ_{calcd} (cm^{-1})	7.21	7.65
R, R_w	0.051, 0.060	0.069, 0.078
G.o.F.	2.97	3.82

Table 7-3 Selected Bond Distances (Å) and Angles (deg)

7.1	7.2
Cr1-N1 = 2.128(7)	Cr1-N1 = 2.104(9)
Cr1-N2 = 2.171(7)	Cr1-N2 = 2.128(9)
Cr1-B1 = 2.44(1)	Cr1-N3 = 2.12(1)
Cr1-B2 = 2.42(1)	Cr1-N4 = 2.156(9)
Cr1-H22 = 1.875	Cr1-H37 = 2.33
Cr1-H21 = 2.081	Cr1-H41 = 1.94
Cr1-H18 = 2.094	N1-Cr1-N2 = 89.5(4)
Cr1-H17 = 1.931	N1-Cr1-N4 = 178.8(4)
N1-Cr1-N2 = 84.30(9)	N1-Cr1-H37 = 85.4
N1-Cr1-B1 = 94.03	N1-Cr1-H41 = 90.9
N1-Cr1-B2 = 169.23	H37-Cr1-H41 = 171.7
H21-Cr1-H22 = 55.18	Cr1-H37-B1 = 173.9
H17-Cr1-H18 = 54.94	Cr1-H41-B2 = 159.1

Table 7-4 Selected Bond Distances (Å) and Angles (deg)

7.3	7.5b
Cr1-N1 = 2.089(3)	Cr1-Cr1a = 1.844(2)
Cr1-H2 = 2.049	Cr1-N2 = 2.018(5)
Cr1-H12 = 1.944	Cr1-N3 = 2.021(5)
Cr1-H32 = 3.20	Cr1-N4 = 2.012(5)
Cr2-N2 = 2.119(3)	Cr1-H13 = 1.95
Cr2-N3 = 2.227(3)	B1-H13 = 1.10
Cr2-N4 = 2.137(3)	N2-Cr1-N3 = 163.5(2)
Cr2-H40 = 1.970	N2-Cr1-N4 = 94.5(2)
Cr2-H34 = 2.173	N2-Cr1-H13 = 88.72
B3-H32 = 0.955	H13-B1-H13 = 125.5
B3-H34 = 1.051	N2-Cr1-Cra = 95.7(2)
N1-Cr1-N1a = 180.00	N2-C2-N3 = 121.1(6)
H2-Cr1-H12 = 52.12	C2-N2-C4 = 118.2(6)
N1-Cr1-H32 = 99.51	
H32-B3-H34 = 115.37	
N2-Cr2-N4 = 172.8(1)	
N2-Cr2-N3 = 92.0(1)	
H40-Cr2-N3 = 139.89	

7.4 Experimental Section

All operations were performed under inert atmosphere in a dry-box (Vacuum Atmosphere) or using standard Schlenk techniques. $CrCl_2THF_2$[176] was prepared according to published procedures. $NaBH_4$, CyN=C=NCy, (i-Pr)N=C=N(i-Pr), and $Me_3SiN=C=NMe_3$ (Aldrich) were purchased and used without further purification. NMR spectra were recorded on a Varian Gemini-200 and a Bruker AMX-500 spectrometer by using vacuum-sealed tubes. Solvents for NMR spectroscopy were dried over the appropriate desiccating agent, vacuum-transferred into ampoules and stored inside a dry-box. Infrared spectra were recorded on a Mattson 9000 FT-IR instrument from Nujol mulls. Samples for magnetic susceptibility measurements were weighted under inert atmosphere and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room T. The magnetic moments were calculated according to standard methods,[111] and corrections for underlying diamagnetism[112] were applied to data. Combustion analysis data were obtained with a PE 4000 analyzer.

$Cr(BH_4)_2$TMEDA (7.1)

A suspension of $CrCl_2THF_2$ (1.78 g, 6.7 mmol) in THF (100 ml) was stirred at room T in the presence of an excess TMEDA (5 ml, 34.5 mmol). The resulting bright-blue suspension was treated with excess $NaBH_4$ (1.06 g, 26.3 mmol). After stirring for 24 h at room T, NaCl and the excess $NaBH_4$ were removed by filtering the boiling solution. The deep-blue filtrate was allowed to cool slowly to room T upon which violet crystals of **7.1** were formed (0.7 g, 3.5 mmol, 52%). IR [nujol mull, cm^{-1}] ν: 2380(vs, br), 2230(m), 2120(vs, br), 1455(vs, br), 1405(w), 1375(vs, br), 1295(w), 1285(s), 1230(m), 1200(w), 1175(sh), 1155(s), 1120(vs, br), 1100(sh), 1060(m), 1040(), 1010(s), 1000(sh), 950(s), 800(s), 770(m), 720(w), 590(w), 5109w, br). Anal. Calcd. (found) for $C_6H_{24}N_2B_2Cr$: C 36.36(36.29), H 12.12(12.03), N 14.14(14.09). [$\mu_{eff} = 4.8\ \mu_B$].

$Cr(BH_4)_2Py_4$ (7.2)

A suspension of **7.1** (1.9 g, 9.6 mmol) in THF (30 ml) was treated with pyridine (3 ml, 38 mmol) at room T and boiled for a few minutes until a clear green solution was formed. The solution was allowed to cool slowly to room T upon which very air-sensitive red-orange crystals of **7.2** separated (1.8 g, 7.5 mmol, 78%). Occasionally-formed green prisms of $\{[(TMEDA)(Py)Cr(\eta^1\text{-}BH_4)]_2[(Py)_2Cr(\eta^2\text{-}BH_4)_2]\}(\mu,\eta^1\text{-}BH_4)_2$ **(7.3)** were eliminated by addition of one extra equivalent of pyridine. IR [nujol mull, cm^{-1}] ν: 2300(vs, br), 2180(s), 2120(s), 2080(s), 1650(w), 1610(s), 1490(s), 1464(sh), 1450(s, br), 1380(m), 1310(w), 1240(w), 1220(s), 1150(m), 1110(sh), 1080-1040(vs, br), 1015(s), 915(m), 770(s), 705(s), 640(s), 600(w), 510(w, br), 440(s). Anal. Calcd. (found) for $C_{20}H_{28}N_4B_2Cr.2THF$: C 62.01(61.95), H 8.18(8.16), N 10.33(10.26). [$\mu_{eff} = 2.83\ \mu_B$].

$Cr_2(CO_2H)_4Py_2$ (7.4)

A green solution, obtained by dissolving deep-red crystals of **7.2** (0.7 g, 2.9 mmol) in THF (100 ml), was saturated with CO_2 (room T, 1 atm.). The original green color turned red in about 20 min. The resulting solution was concentrated *in vacuo* and allowed to stand at -30°C overnight, upon which red crystals of **7.4** separated (0.2 g, 0.7 mmol, 48%). IR [nujol mull, cm^{-1}] v: 1620-1580(s, br), 1450(vs, br), 1380-1340(vs, br), 1220(m), 1155(w), 1065(w), 1036(m), 1006(w), 880(w), 770(s), 755(sh), 720(w), 700(s), 620(m), 435(s, br), 404(w). Anal. Calcd. (found) for $C_{14}H_{14}N_2O_8Cr_2$: C 38.02(37.99), H 3.19(3.22), N 6.33(6.26). [$\mu_{eff} = 0.6\ \mu_B$ per Cr_2 unit].

$Cr_2(CyNCHNCy)_3(BH_4)$ (7.5a)

Solid CyN=C=NCy (2.5 g, 12.1 mmol) was added to a blue suspension of **7.1** (1.2 g, 6.1 mmol) in THF (100 ml) at room T and the color turned dark yellow after a few minutes. The volume of the solution was reduced to c.a. 10mL and yellow crystals of **5a**, along with a small amount of white crystals of $TMEDA(BH_3)_2$, precipitated upon standing at -30 °C overnight. Analytically pure yellow crystals of **7.5a** were obtained in low yield after several recrystallizations from THF (0.6 g, 0.8 mmol, 26%). IR [nujol mull, cm^{-1}] v: 2410(s), 2360(s), 2220(w), 2062(m, br), 1930(m, br), 1840(w, br), 1578(vs), 1450(vs, br), 1375(s), 1362(s), 1342(s), 1326(s), 1300(m), 1285(s), 1252(m), 1185(m), 1160(sh), 1150(s), 1120(s), 1102(s), 1086(s), 1080(s), 1048(w), 1020(), 990(m), 962(w), 886(s), 846(m), 804(m), 782(m), 722(m), 508(s), 484(s), 436(s). ^{1}H-NMR [C_6D_6, 200 MHz, 25 °C, ppm] δ: 8.6 (s, 2H, C-H formamidine), 8.5 (s, 1H, C-H formamidine), 3.5 (m, 4H, C-H cyclohexyl), 2.65 (m, 2H, C-H cyclohexyl), 2.2-0.8 (series of lines, 34H, cyclohexyl and BH_4). Anal. Calcd. (found) for $C_{39}H_{73}N_6BCr_2$: C 63.23(63.17), H 9.93(9.86), N 11.34(11.19).

$Cr_2[(i\text{-}Pr)NC(H)N(i\text{-}Pr)]_3(BH_4)$ (7.5b)

The addition of neat (i-Pr)N=C=N(i-Pr) (2.9 ml, 18.5 mmol) to a blue suspension of

7.1 (1.83 g, 9.2 mmol) in THF (100 ml) at room T formed a dark yellow solution. The resulting solution was concentrated to small volume in vacuum and allowed to stand at -30°C overnight, upon which orange crystals of **7.5b**, contaminated by a small amount of colorless needles of $(BH_3)_2$TMEDA, precipitated. Analytically pure **7.5b** was obtained in low yield (less than 10%) after several recrystallizations from THF. IR [nujol mull, cm^{-1}] ν: 2401(s), 2365(s), 2236(w), 2102(m, br), 1966(w, br), 1583(s, br), 1456(s, br), 1409(m), 1375(s), 1360(s), 1301(s), 1175(s), 1122(s), 1101(s), 1056(w), 1025(m), 953(m), 932(w), 853(w), 816(w), 726(w), 668(w), 649(w), 570(w), 524(s), 486(s), 421(s). ^{1}H-NMR [C_6D_6, 400 MHz, 25°C, ppm] δ: 8.53 (s, 2H, C-H formamidine), 8.50 (s, 1H, C-H formamidine), 3.77 (hept, J = 6.5 Hz, 4H, C-H isopropyl), 2.97 (hept, J = 6.5 Hz, 2H, C-H isopropyl), 1.32 (m, 4H, BH_4), 1.21 (d, J = 6.5 Hz, 12H, CH_3 isopropyl), 1.03 (d, J = 6.5 Hz, 12H, CH_3 isopropyl), 0.82 (d, J = 6.5 Hz, 12H, CH_3 isopropyl). Anal. Calcd. (found) for $C_{21}H_{49}N_6BCr_2$: C 50.40(50.31), H 9.87(9.81), N 16.79(16.71).

Cr_2[(i-Pr)NC(H)N(i-Pr)]$_3$(O_2CH) (7.6)

A yellow solution of **7.5b** in d_6-benzene was saturated with CO_2 (1 atm, room T) inside an NMR tube. As the intensity of the signals of the starting material decreased, new peaks were observed. After two days the reaction was completed and the spectrum was consistent with the formulation Cr_2[(i-Pr)NC(H)N(i-Pr)]$_3$(O_2CH). ^{1}H-NMR [C_6D_6, 500 MHz, 25 °C, ppm] δ: 8.86 (s, 1H, CH formate), 8.65 (s, 2H, CH formamidine), 8.61 (s, 1H, CH formamidine), 3.71 (m, 4H, CH isopropyl), 3.15 (m, 2H, CH isopropyl), 1.31 (d, J = 6.2 Hz, 12H, CH_3 isopropyl), 1.05 (d, J = 6.2 Hz, 12H, CH_3 isopropyl), 0.87 (d, J = 6.2 Hz, CH_3 isopropyl).

$Cr_2(CyNCHNCy)_4$ (7.7a)

A suspension of $Cr_2Cl_2THF_2$ (2.23 g, 8.4 mmol) in THF (100 ml) was stirred at room T in the presence of an excess TMEDA (5 ml, 34.5 mmol). An excess $NaBH_4$ (1.85 g, 48.7 mmol) was added to the resulting bright-blue suspension. After stirring for 24 h at room T, a violet solid was formed. The addition of 1,3-dicyclohexylcarbodiimide (5.0 g, 24.3 mmol) at room T immediately produced a yellow suspension. After boiling the mixture for a few minutes, the solvent was evaporated *in vacuo*. The addition of toluene (40 ml) to the resulting residue produced a yellow solution and a white solid which was removed by filtration. The filtrate was allowed to stand at -30 °C overnight, upon which yellow crystals of **7.7a** (0.4 g, 0.86 mmol, 10%) separated. IR [nujol mull, cm^{-1}] ν: 1662(w), 1596(s, br), 1451(s, br), 1376(s), 1360(s), 1348(s), 1326(s), 1294(s), 1257(s), 1238(w), 1203(w), 1178(w), 1150(s), 1125(s), 1103(s), 1084(s), 1071(s), 1049(w), 1018(m), 986(w), 955(m), 917(w), 889(s), 845(m), 798(m), 729(m), 694(w), 600(w), 550(m), 512(s), 487(s), 465(s), 430(s). ^{1}H-NMR [C_6D_6, 200 MHz, 25C°] δ: 8.43 (s, 4H, formamidine), 7.08(pseudo quartet, 4H, toluene), 3.11(pseudo quintet, 8H, cyclohexyl), 2.10(s, 3H, toluene), 2.07(pseudo d, 16H, cyclohexyl), 1.81(pseudo d, 16H, cyclohexyl), 1.63(pseudo d, 8H, cyclohexyl), 1.30(m, 40H, cyclohexyl). Anal. Calcd. (found) for $C_{52}H_{92}N_8Cr_2$.toluene: C 69.10(68.99), H 9.83(9.77), N 10.93(10.85).

$Cr_2[(i\text{-}Pr)NC(H)N(i\text{-}Pr)]_4$ (7.7b)

A suspension of $CrCl_2THF_2$ (2.09 g, 7.8 mmol) in THF (100 ml) was stirred at room T in the presence of an excess of TMEDA (5 ml, 34.5 mmol). An excess of $NaBH_4$ (1.91 g, 50.3 mmol) was added to the resulting bright-blue suspension. After stirring for 24 h. at room T, a violet solid was formed. The addition of 1,3-diisopropylcarbodiimide (5.0 ml, 31.7 mmol) to the resulting suspension at room T formed a yellow suspension. The solvent was evaporated *in vacuo* after boiling for a few minutes. The addition of toluene (30 ml) to the resulting yellow solid produced a yellow solution and a white solid which was removed by filtration. The filtrate was allowed to stand at -30 °C overnight, upon which yellow crystals of **7.7b** (0.5 g, 1.8 mmol, 20%) separated. IR [nujol mull, cm^{-1}] ν: 1598(s, br), 1572(sh), 1458(s, br), 1408(m), 1373(s), 1357(s), 1348(s), 1297(, br), 1180(s), 1161(s), 1120(s), 1101(s), 1025(s), 952(s), 930(w), 911(w), 873(w), 861(w), 816(m), 800(m), 725(w), 649(w), 551(w), 525(m), 484(s), 446(w), 424(s). ^{1}H-NMR [C_6D_6, 200 MHz, 25 °C, ppm] δ: 8.42 (s, 4H, CH formamidine), 3.53 (hept, J = 6.6 Hz, 8H, CH isopropyl), 1.20 (d, J = 6.6 Hz, 48H, CH_3 isopropyl). Anal. Calcd. (found) for $C_{28}H_{60}N_8Cr_2$: C 54.88(54.81), H 9.87(9.85), N 18.28(18.21).

Chapter 8

The Role of the Ligand Steric Hindrance in Determining the Stability of Very Short V-V Contacts. Preparation and Characterization of a Series of V(II) and V(III) Amidinates.

8.1 Introduction

Multiple bonds between first row early transition metals are one of the most fascinating and intriguing functionalities of inorganic chemistry. The unusually short metal-metal distances determined in some dinuclear complexes of these metals (the shortest ever found)[1,2,61,100] might possibly indicate the existence of fairly strong intermetallic interactions. However, today it is generally recognized that these bonds are paradoxically weak,[22,25,116-118] and are unlikely to be able to hold together dinuclear frames in the absence of bridging ligands.[104] They are also easily cleaved to form monomeric species,[18,19,66,101-103,281] and therefore are very sensitive to ligand features such as electronic configuration, steric hindrance, nature of the donor atom, denticity, shape of the bite, etc.[69]

The employment of three-center chelating ligands (with two donor atoms, three atom bite, four π electrons and a negative charge) has enabled the preparation of divanadium complexes with short[245] and very short vanadium-vanadium bonds.[83-85,91,282] Theoretical work has predicted the existence of V-V triple bonds in these systems, although the single bond configuration was calculated to be considerably more stable than the triply bonded one.[91] However, these particular ligands have been proven able to promote the formation of very short metal-metal multiple bonds with a variety of metals[1,2,61] and metalloids,[283] and to possess a unique ability to assemble dimers and to form remarkably short M-M contacts even in the absence of a direct M-M bond.[28-41] Therefore, it is very difficult to assess the real strength of the V-V multiple bonds. For example, it is not unreasonable to expect that, by analogy with divalent chromium, efficient magnetic couplings (either antiferromagnetism, superexchange or a combination of them) may be the only significant interaction existing between the two vanadium atoms in spite of the remarkable shortness of the intermetallic distance. As for Cr(II), very short M-M distances could be nothing or little more than the result of ligand geometry optimization.[67,68]

The preferred coordination geometry of the transition metal, as imposed by the metal electronic configuration, is a factor able to prevail over the binucleating ability of the ligand.[64] In other words, whereas three center chelating ligands may easily interface two monomeric square-planar metal complexes, such as in the case of d^4 Cr(II), it is far more difficult to stabilize dimeric structures with divalent and octahedral d^3 vanadium atoms, unless severe distortions occur on the coordination geometry of the bridging donor atom. Such distortions have been observed in two of the three existing examples of divanadium complexes of three-center chelating ligands with short and very short V-V distances.[84,245] On the other hand, square-planar divalent vanadium, although rare, is documented in two examples of sterically encumbered complexes.[284,285] Therefore, the employment of sterically demanding three-center chelating ligands might be an interesting synthetic strategy to form divanadium species with very short V-V distances.

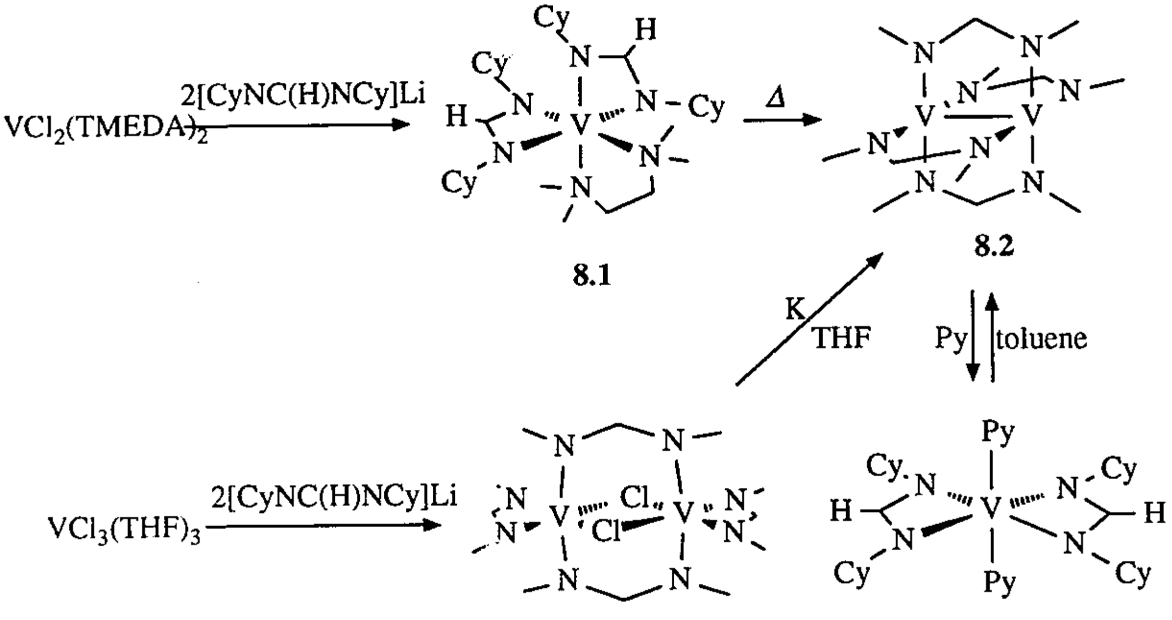
Amidinate anions[219,286,287] provide a wide choice of three-center chelating ligands where the variety of possible substituents makes possible the fine tuning of steric hindrance, thus allowing clarification of the factors which influence both the nuclearity and the extent of intermetallic separation. In this chapter we describe the synthesis, characterization and chemical behavior of a novel series of monomeric and dimeric V(II) and V(III) amidinate complexes.

8.2 Results

The lithium amidinates were prepared by either amidine deprotonation with bases or addition of alkyl lithium reagents to CyN=C=NCy. This second method is rather general and allows the preparation of a consistent series of amidinate lithium salts of formula [CyNC(R)NCy]Li [R = Me, Ph, Bz, 2-(Me_2NCH_2)Ph].

The room temperature reaction of $VCl_2(TMEDA)_2$ [TMEDA = N,N,N',N'-tetramethylethylenediamine] with two equivalents of [(Cy)NC(H)N(Cy)]Li formed a dark-red very air-sensitive solution from which dark-yellow air-sensitive crystals of the monomeric, paramagnetic $[(Cy)NC(H)N(Cy)]_2V(TMEDA)$ (**8.1**) were isolated in good yield (Scheme 8-1). Analytical data and magnetic moment were in accord with the formulation demonstrated by the X-ray diffraction analysis. Although complex **8.1** is indefinitely stable at room temperature in both solid state and solution, a fast reaction occurred in boiling toluene. The thermolysis gave a deep-brown solution from which light-green diamagnetic crystals of the dimeric lantern-type $\{[(Cy)NC(H)N(Cy)]_2V\}_2$ (**8.2**) were isolated in good yield. The diamagnetism of **8.2** was determined in both solid state and solution and a well-resolved NMR spectrum was obtained for this compound. In addition no significant change of the chemical shift was observed in the T range -80/+80 °C. The dinuclear frame of **8.2** was reversibly cleaved by treatment with pyridine, forming the thermally robust, blue, paramagnetic and monomeric

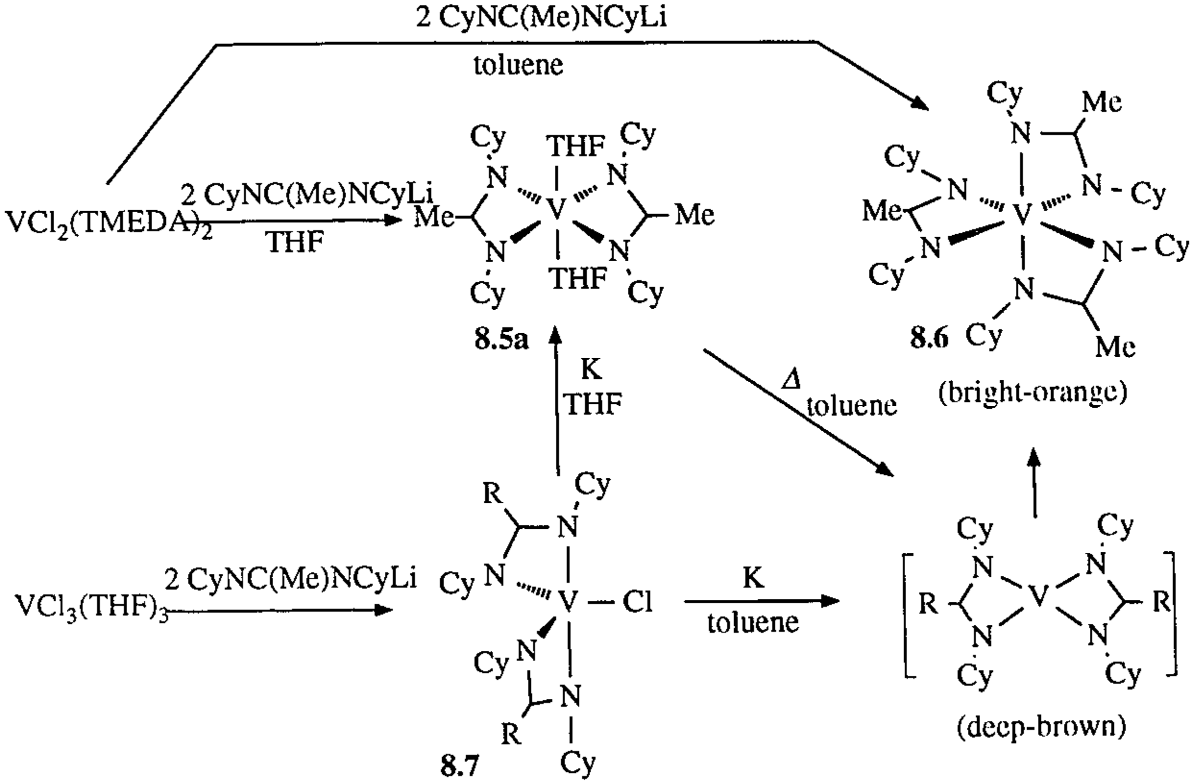
Scheme 8-1



$[(Cy)NC(H)N(Cy)]_2V$ $(pyridine)_2$ (**8.3**). Reflux of **8.3** in toluene reformed green crystals of **8.2**. Complex **8.2** may also be conveniently prepared using $VCl_3(THF)_3$ as the starting material. The reaction of $VCl_3(THF)_3$ in toluene with two equivalents of [(Cy)NC(H)N(Cy)Li led in this case to the dimeric and almost diamagnetic $\{[(Cy)NC(H)N(Cy)]_2VCl\}_2$ (**8.4**) which was isolated as orange, air-stable crystals. Reduction of **8.4** with metallic potassium in either THF or toluene/TMEDA gave the diamagnetic green **8.2**.

Simple replacement of the formamidinic hydrogen atom by a methyl group introduced a significant modification in the reactivity patterns of the two vanadium halides. As shown in Scheme 8-2, the reaction of $VCl_2(TMEDA)_2$ with two equivalents of the acetamidinate lithium salt $[(Cy)NC(Me)N(Cy)]Li.Et_2O$ formed the paramagnetic, monomeric and octahedral *trans*-$(THF)_2V[(Cy)NC(Me)N(Cy)]_2$ (**8.5a**) which was isolated in good yield as

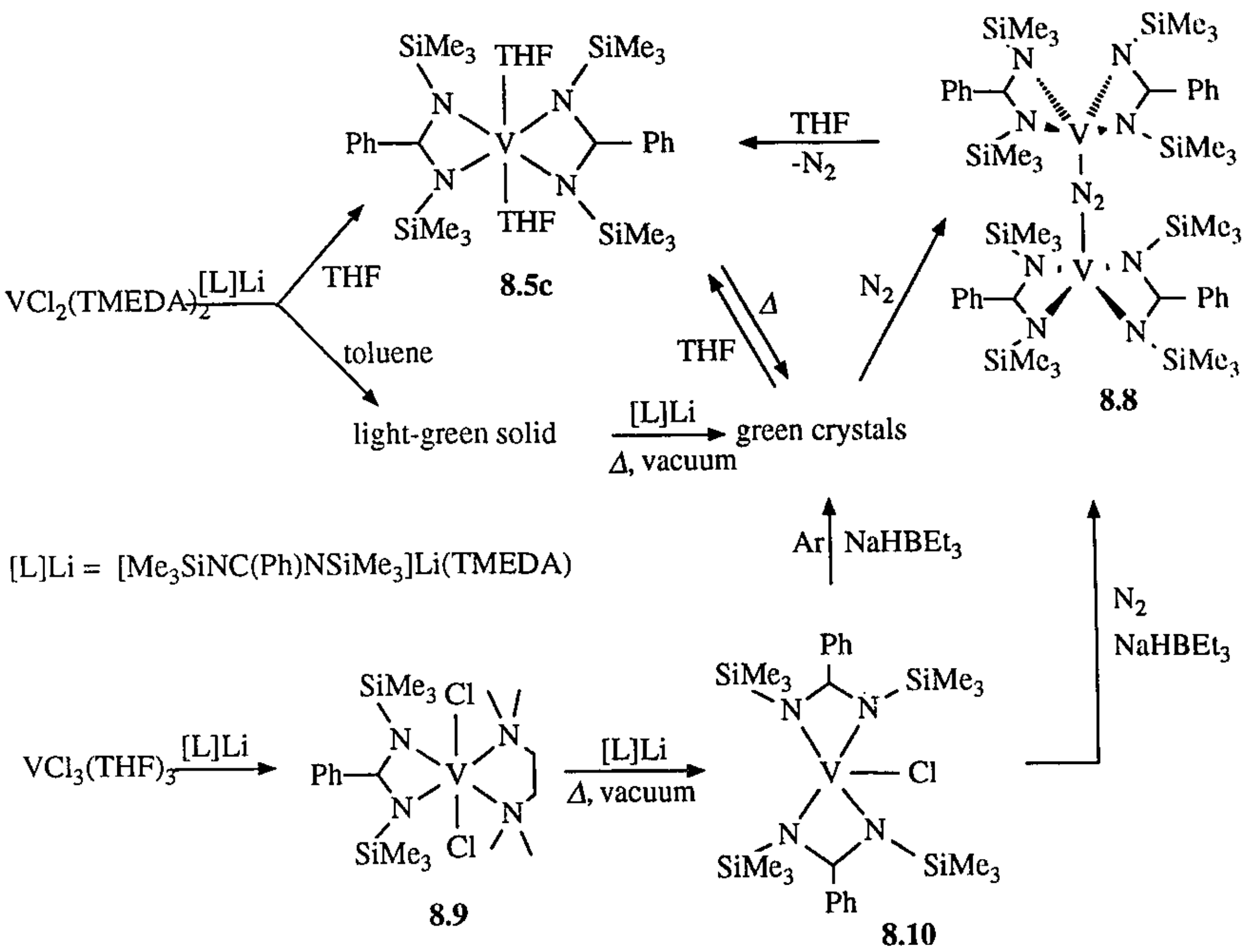
Scheme 8-2



light- green crystals. This reaction seems to be rather general since we have obtained isostructural compounds **8.5b** and **8.5c** in the case of CyNC(Ph)NCy and $Me_3SiNC(Ph)NCy$ ligands. However, attempts to obtain other dinuclear lantern-type compounds via thermal dissociation of one or two molecules of coordinated THF from **5a** yielded only the monomeric V(III) complex $[CyNC(Me)NCy]_3V$ (**8.6**). The same compound was obtained when the reaction of $VCl_2(TMEDA)_2$ with two equivalents of lithium acetamidinate salt was carried out in toluene. Consistent results were obtained by using $VCl_3(THF)_3$ as starting material. In contrast to the case of formamidine which gave a dinuclear compound **8.4**, the reaction yielded the monomeric and paramagnetic $[(Cy)NC(Me)N(Cy)]_2VCl$ (**8.7**). Once again, reduction of **8.7** with finely dispersed potassium in toluene gave **8.6**, while reduction in THF yielded **8.5a**. The presence of an intermediate during the formation of **8.6**, probably a tetracoordinated square-planar complex, is suggested by the initial deep-brown color which rapidly turned bright-orange upon heating at 40°C. Attempts to isolate the intermediate species at low T were unsuccessful.

Although the series of results obtained from the reactions of vanadium halides with the sterically demanding $[Me_3SiNC(Ph)NSiMe_3][Li(TMEDA)]$ were consistent with those found in the case of the acetamidinate, it is possible to remark a few significant differences (Scheme 8-3). Reaction of $VCl_2(TMEDA)_2$ with $[Me_3SiNC(Ph)NSiMe_3][Li(TMEDA)]$ yielded the monomeric and paramagnetic V(II) derivative $[Me_3SiNC(Ph)NSiMe_3]_2V(THF)_2$ (**8.5c**) isostructural with **8.5a** and **8.5b**. Even in this case, dissociation of THF was achieved by heating in vacuum. However, we found no evidence that in this case the reaction might lead to oxidation and formation of $[Me_3SiNC(Ph)NSiMe_3]_3V$ analogue of **8.6**. The reaction rather produced a green crystalline material which was indefinitely stable while kept under Ar, but which rapidly turned brown upon exposure to N_2 even in solid state. Recrystallization from toluene under N_2 allowed the isolation and characterization of the new V(II) dinitrogen complex $\{[Me_3SiNC(Ph)NSiMe_3]_2V\}_2(\mu\text{-}N_2)$ (**8.8**). A similar result was obtained by carrying out the reaction of $VCl_2(TMEDA)_2$ with $[Me_3SiNC(Ph)NSiMe_3]Li(TMEDA)$ in toluene rather than in THF. The formation of the same green complex which upon exposure to N_2 formed the dinitrogen complex **8.8**, was observed even in this case. However, in order to obtain the chlorine-free green crystalline material the reaction mixture had to undergo a prolonged heating at 120°C in vacuum in solid state after removal of the solvent in vacuo. This unusual

Scheme 8-3



procedure is probably necessary to assure the complete removal of TMEDA. Employment of $VCl_3(THF)_3$ as a starting material gave a thermally robust [$Me_3SiNC(Ph)NSiMe_3$]-VCl_2(TMEDA) (**8.9**) complex which yielded the monomeric and paramagnetic [$Me_3SiNC(Ph)NSiMe_3$]$_2$VCl (**8.10**) only after reaction with a second equivalent of [$Me_3SiNC(Ph)NSiMe_3$]Li(TMEDA), evaporation of the solvent in vacuo, heating for 3 h at 120°C in vacuo, and recrystallization of the residue from toluene. The reduction of **8.10**, carried out under Ar with a solution of $NaHBEt_3$ in toluene, originated the same green crystalline precursor of the dinitrogen complex. Even in this case, recrystallization of the green solid under N_2 gave good yield of the N_2 complex. Complex **8.8** could be conveniently prepared in good yield and in one-pot synthesis by carrying out the reduction of **8.10** under N_2.

Complex **8.10** is one of the rare cases where coordination of dinitrogen on a V(II) metal center occurs with a non-organometallic complex.[288-291] The coordination of dinitrogen appears to be quite labile since simple treatment with THF released almost quantitatively N_2 during chemical degradation experiments carried out with a Toepler pump.

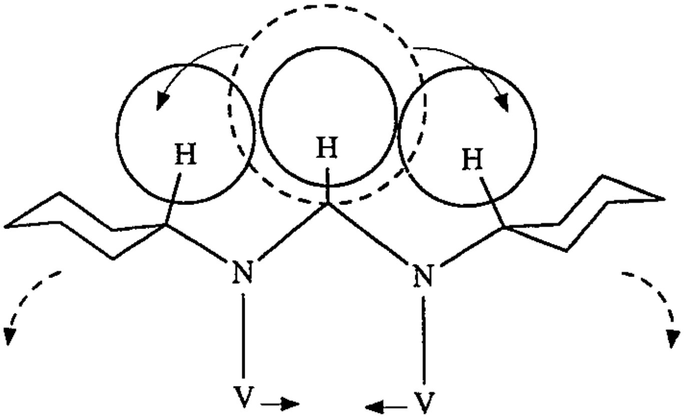
8.3 Discussion

The simple replacement of the formamidinic hydrogen atom with the methyl group of the acetamidine has a profound repercussion on the structure of the corresponding V(II) complex. The fact that one molecule of TMEDA is retained in the formamidine derivative **8.1**, while a complete replacement by two molecules of THF is observed in the amidinate **8.5**, can be ascribed only to the larger steric hindrance of the acetamidine and benzamidine ligands since the reaction conditions employed in the three reactions are identical. The most remarkable difference between **8.1** and **8.5** in terms of chemical behavior, is provided by the fact that while the dinuclear species **8.2** is easily formed from **8.1** through thermal dissociation of TMEDA or reduction of the corresponding V(III) complex **8.4**, no dimeric structures with a V-V bond were obtained in the case of the acetamidine and benzamidine derivatives. The two reactions rather gave an oxidation to the trivalent $[CyNC(Me)NCy]_3V$, probably via disproportionation. Conversely, in the case of the benzamidinate, where the very large steric hindrance prevents the formation of $[Me_3SiNC(Ph)NSiMe_3]_3V$, the reaction from both

$VCl_2(TMEDA)_2$ and $VCl_3(THF)_3$ yielded the precursor of the dinitrogen complex **8.8**. Although a full characterization of this complex could not be obtained, due to its enormous reactivity, given the result of the reaction with N_2, we tentatively propose a tetrahedrally distorted square-planar structure similar to that of the Cr(II) derivative $[Me_3SiNC(Ph)NSiMe_3]_2Cr$.[226]

The diamagnetism of **8.2** together with the very short V-V contact (the shortest ever found for a divanadium unit) might indicate the existence of a direct M-M bond with high degree of multiplicity (triple). Since the replacement of the formamidinic hydrogen with the methyl group of the acetamidine ligand cannot be reasonably expected to significantly modify the electronic configuration of the complex, it is evident that only the larger steric hindrance may be responsible for the failure of the acetamidinate ligand to stabilize a dimeric species. On the other hand, complex **8.2** has an intermetallic distance [V-V = 1.968(2)Å] which is even shorter than in the isostructural $[(p\text{-tolylformamidinate})_2V]_2$ [V-V = 1.978(2)Å]. This suggests that, similar to the case of the lantern-type compounds of divalent chromium, the increase of ligand steric hindrance results in shorter M-M bonds rather than longer,[6] as could be expected on the basis of the behavior of multiple bonds between main group elements (larger steric bulk within the molecule usually results in stretched bonds). The X-ray crystal structure of **2** has pointed out the presence of short H..H non-bonding contacts between the formamidinic hydrogen and other hydrogen atoms of the cyclohexyl groups [H..H ranging from 1.89Å to 2.01Å]. The same contacts have also been observed in the monomeric $[(Cy)NC(H)N(Cy)]_2V(TMEDA)$ [H..H ranging from 2.06 to 2.24]. In biscyclopentadienyl dinuclear species, these H..H non bonding contacts have shown energy profiles as a function of the distance which sharply rise up to 38 Kcal mol^{-1} when the distance becomes shorter.[232,233] Assuming that a comparable destabilization energy arises from the H..H non-bonding contacts of **8.2**, and given that the cyclohexyl-cyclohexyl hydrogen atom contacts are definitely longer [ranging from 2.5 to 3.15Å], it is obvious that the stability of the complex is determined primarily by the shortest H..H contacts, i.e. the contacts formed by the formamidinic hydrogen with the two cyclohexyl methyne hydrogens. The increase of steric hindrance introduced by the methyl group of the acetamidic ligand pushes apart the two cyclohexyl "wings" (Scheme 8-4) thus resulting in a considerable distortion of the N-C-N framework (confirmed by the X-ray analysis of the monomeric **8.5a, 8.6** and **8.7**). Therefore, in an hypothetical dimeric V(II) complex of CyN-C(Me)-NCy or of $Me_3SiNC(Ph)NSiMe_3$, where the V-V, V-N, C-N and N..N distances remained basically the same as in the dimeric **8.2**, the eight cyclohexyl rings should form extremely short H-H contacts thus introducing a large amount of destabilization energy with consequent destabilization of the dimeric species in favor of the monomeric one. The V-V multiple bond obviously does not provide enough stabilization energy to prevail over the

Scheme 8-4



destabilization introduced by the H..H interactions since simple treatment with pyridine *reversibly* cleaved the dinuclear structure of **8.2** forming **8.3**. This indicates that the energy of the V-V triple bond cannot exceed four times the energy of the V-py bond. In contrast, the dinuclear and almost diamagnetic **8.4** with far longer V-V distance [V-V = 2.871Å] could not be cleaved by similar treatment with pyridine under similar conditions.

In conclusion, the results described in this chapteer provide the first example where a relatively minor modification of ligand steric hindrance is shown to be capable of modifying the nuclearity and the chemistry of vanadium complexes. In the absence of a detailed theoretical analysis, it is obviously impossible to identify which factors, affected by the steric hindrance of the ligand (orientation of the orbitals used by the ligand donor atoms for bonding the metals, distortion of the normal hybridization angles, more or less efficient orbital overlaps, or a combination of them), determine the relative stabilization or destabilization of the monomeric structures with respect to the dimeric ones. Nevertheless, this work clearly shows that: *i*) the existence of the V-V multiple bonds is determined by the nature of the ligand and its steric bulk, and *ii*) V-V very short bonds possess an intrinsic weakness which is in contrast to the shortness of the intermetallic distance. The striking parallelism between this behavior and that of the quadruply bonded dichromium complexes, suggest that even in this case the very short intermetallic contacts might be just artifacts of the binucleating ability of the particular ligands employed for the stabilization of the dimetallic frame.

8.4 X-ray crystallography

Refer to Section **2.3**. Details on data collection and structure refinement for **8.1** and

8.2 are reported in Table 8-1. Selected bond distances and angles are given in Table 8-2.

Table 8-1 Crystal Data and Structural Analysis Results

complex	**8.1**	**8.2**
formula	$C_{32}H_{62}N_6V$	$C_{52}H_{92}V_2N_8$
formula weight	581.82	931.24
crystal system	monoclinic	monoclinic
Space Group	$P2_1/a$	$P2_1$
a (Å)	18.085(3)	11.671(3)
b (Å)	10.737(2)	10.371(2)
c (Å))	18.7212)	22.645(3)
α (deg)		
β (deg)	114.37(4)	100.65(1)
γ (deg)		
V ($Å^3$)	3311(2)	2694(1)
Z	4	2
Radiation (MoKα Å)	0.71069	0.71069
T (°C)	-160	-30
D_{calcd}($g\ cm^{-3}$)	1.167	1.148
μ_{calcd} (cm^{-1})	3.17	3.73
R, R_w	0.059, 0.065	0.075, 0.076

Table 8-2 Selected Bond Distances (Å) and Angles (deg)

8.1	**8.2**
V1-N1 = 2.164(3)	V1-V2 = 1.968(2)
V1-N2 = 2.137(3)	V1-N1 = 2.075(7)
V1-N3 = 2.282(3)	V1-N3 = 2.142(7)
V1-N4 = 2.296(3)	V1-N5 = 2.080(6)
V1-N5 = 2.260(3)	V1-N6 = 2.106(7)
V1-N6 = 2.256(3)	V2-N2 = 2.076(7)
N1-V1-N2 =94.5(1)	V2-N4 = 2.099(7)
N1-V1-N5 = 61.9(1)	V2-N7 = 2.115(6)
N3-V1-N4 = 80.3(1)	V2-N8 = 2.142(6)
N2-V1-N6 = 61.6(1)	V1-V2-N4 = 93.9(2)
N1-V1-N6 = 100.7(1)	V1-V2-N2 = 94.2(2)
N1-V1-N3 = 166.1(1)	V1-V2-N7 =92.8(2)
N1-C25-N5 =119.3(4)	V1-V2-N8 = 93.1(2)
N2-C26-N6 =117.3(4)	N3-C2-N4 = 122.7(8)
C1-N2-C26 =122.5(3)	N1-C1-N2 = 120.6(8)
C7-N1-C25 =118.9(3)	N5-C15-N7 = 121.5(7)
	N6-C52-N8 = 122.1(6)
	C1-N1-C3 = 112.6(7)
	V2-N2-C1 = 113.3(6)

8.5 Description of the crystal structures.

Complex 8.1. The structure of complex **8.1** consists of discrete monomeric units. The coordination geometry around the vanadium atom is distorted octahedral, with the two chelating formamidine ligands and the TMEDA molecule imposing an overall propeller shape configuration (Figure 8-1) [N1-V1-N2 = 94.5(1)°, N1-V1-N5 = 61.9(1)°, N3-V1-N6 = 93.0(1)°, N4-V1-N5 = 94.3(1)°, N1-V1-N6 = 100.7(1)°, N4-V1-N6 = 93.0(1)°, N1-V1-N4 = 93.0(1)°]. The two formamidine fragments are almost coplanar with vanadium forming four-membered rings [V1-N2-C26-N6 = 9.1(4)°, N1-V1-N5- C25 = 4.9(2)°]. In spite of the considerable differences between the electronic configurations of the formamidine and TMEDA nitrogen atoms, the V-N distances [V1-N1 = 2.164(3)Å, V1-N2 = 2.137(3)Å, V1-N4 = 2.296(3)Å,

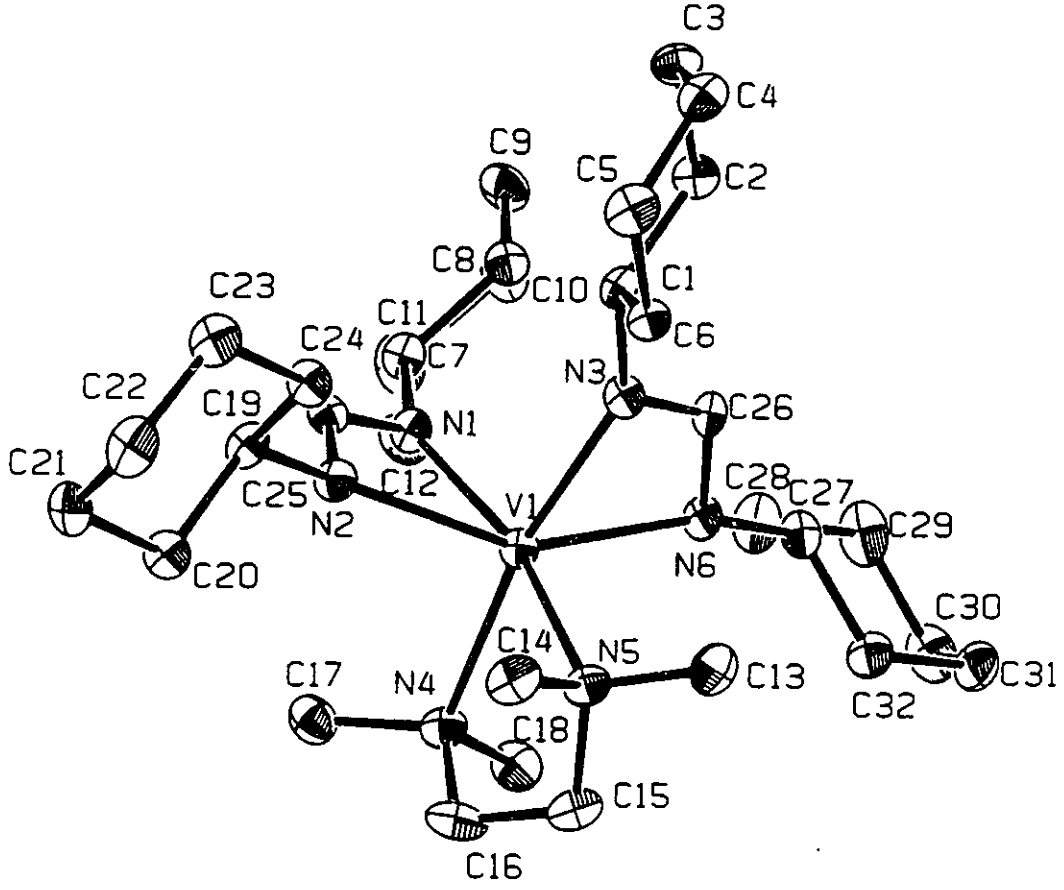


Figure 8-1. ORTEP plot of **8.1**.

V1-N5 = 2.260(3)Å] are rather similar. This is in striking contrast with the different hybridization of the two nitrogen atoms (sp^2 versus sp^3) in the two ligands, and perhaps suggests the absence of N→V π-bonding interaction with the formamidine moiety. Short H..H contacts are observed between the formamidinic hydrogen atoms and some of the hydrogens of the cyclohexyl rings [H50..H49 = 2.06Å, H50..H12 = 2.15Å, H51..H52 = 2.09Å, H52..H2 = 2.24].

Complex 8.2. The structure of the complex shows the typical dimeric arrangement (lantern-type) observed in all the complexes formed by formamidinate anions with several transition metals (Figure 8-2). Each formamidinate ligand adopts the classical three-center chelating geometry where each of the two donor atoms of one ligand molecule binds one of the two metal centers, forming a five-membered ring with the V_2 unit. The four vanadacycles rings are slightly puckered [V1-N5-C15-N7 = 8.0(1)°, V2-N7-C15-N5 = 7.0(1)°]. The coordination geometry of the two vanadium atoms is distorted square-planar [N1-V1-N3 = 173.0(3)°, N5-V1-N6 = 171.7(2)°, N1-V1-N5 = 91.2(3)°] with the vanadium atom slightly elevated above the plane defined by the four nitrogen atoms [V2-V1-N angles ranging from 93.1(3)° and 97.6(4)°]. The V-V distance [V1-V2 = 1.968(2)Å] is a rare cases of very short V-V distance and the shortest ever found so far. The V-N bonding distances are normal [V1-N1 = 2.057(7)Å, V1-N3 = 2.142(7)Å, V1-N5 = 2.080(6)Å, V1-N6 = 2.106(7)Å] and compare well with those of other monomeric V(II) complexes reported in this work. Short H..H contacts are observed between the formamidinic hydrogen atoms and some of the hydrogens of the cyclohexyl rings [H2..H81 = 1.89 Å, H1..H3 = 1.93 Å, H1..H48 = 2.01 Å].

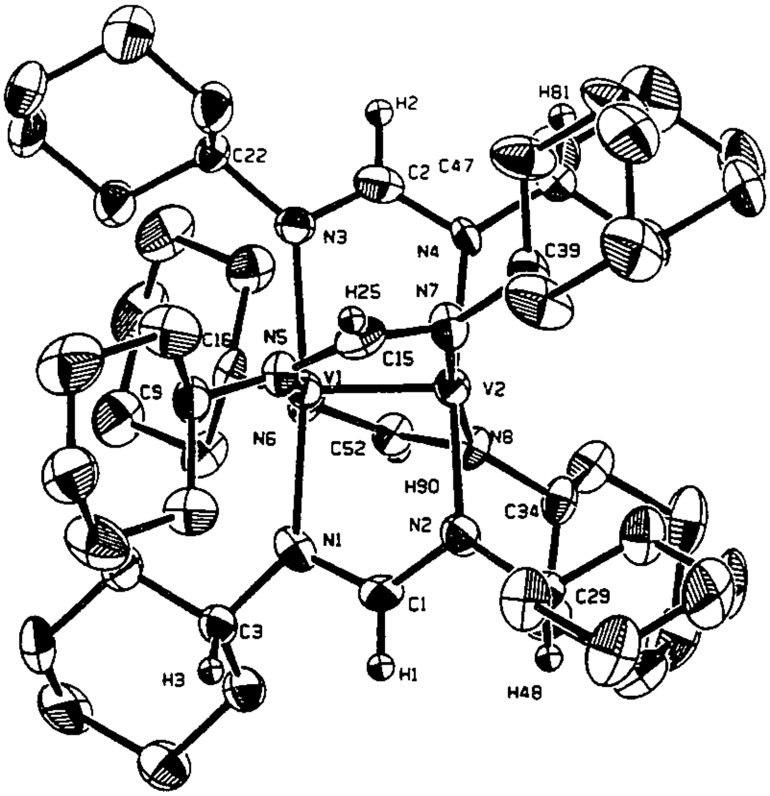


Figure 8-2. ORTEP plot of **8.2**.

8.6 Experimental Section

All operations were performed under inert atmosphere in a nitrogen-filled dry-box (Vacuum Atmosphere) or by using standard Schlenk techniques. VCl_3THF_3, *trans*-$(TMEDA)_2VCl_2$ [TMEDA = N,N,N',N'-tetramethylethylenediamine],[81] $\{[(Me_3Si)N]_2C(Ph)\}Li(TMEDA)$,[219] and CyN(H)-(H)C=NCy,[221] were prepared according to published procedures. CyN=C=NCy and $(Me_3Si)_2NH$ (Aldrich) were used as received. NMR spectra were recorded on a Varian Gemini 200 and on a Bruker AMX-500 spectrometer by using vacuum-sealed samples prepared in a dry-box. Solvents for NMR spectroscopy were dried over the appropriate drying agents, vacuum- transferred into appropriate ampoules and stored inside a dry- box. Infrared spectra were recorded on a Mattson 9000 FTIR instrument from Nujol mulls prepared in a dry-box. Samples for magnetic susceptibility measurements were weighed inside a dry-box equipped with an analytical balance, and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature. The magnetic moment was calculated following standard methods,[111] and corrections for underlying diamagnetism were applied to data.[112] Elemental Analyses were carried out with a Perkin Elmer PE 2400 CHN analyzer.

[CyN-C(H)-NCy]Li

A solution of CyN-C(H)-N(H)Cy (13.3 g, 64 mmol) in hexane (160 mL) was treated with a solution of n-BuLi in hexane (26 mL, 2.5 M, 64 mmol) at room temperature. The resulting light-yellow solution was allowed to stand overnight at room temperature, upon which colorless crystals of [CyN-C(H)-NCy]Li precipitated (11.0 g, 51 mmol, 80%). I.R. [nujol mull, KBr, cm^{-1}] ν: 1565(s), 1330(s), 1295(s), 1260(m), 1230(m), 1150(w), 1100(m), 1060(m), 1030(w), 990(w), 890(m), 840(m), 805(m), 785(w), 720(m), 600(w), 580(m) ^{1}H-NMR [C_6D_6, 200 MHz, 25C^0] δ: 8.38(s, 1H, C-H formamidine), 2.81(pseudoquintet, 2H, cyclohexyl), 1.89(m, 4H, cyclohexyl), 1.71-1.24(series of lines, 16H, cyclohexyl).

[CyN-C(CH_3)-NCy]Li(Et_2O)

A solution of MeLi in ether (7.3 mL, 1.4M, 10.2 mmol) was added to a cooled solution (-70°C) of CyNCNCy (2.1 g, 10.2 mmol) in Et_2O (30 mL). Colorless crystals of [CyN-C(CH_3)-NCy] Li(Et_2O) (2.4 g, 7.9 mmol, 77%) separated from the resulting yellowish solution upon reaching room temperature. I.R. [nujol mull, KBr, cm^{-1}] ν: 1510(vs), 1410(s), 1350(s), 1305(w), 1250(m), 1160(m), 1130(w), 1070(sh), 1050(s), 1020(w), 990m), 1030(w), 990(w), 950(w), 920(m), 890(m), 840(w), 820(w), 795(m), 720(w), 650(m), 600(m), 570(m), 495(br), 460(w), 410(m). ^{1}H-NMR [C_6D_6, 200 MHz, 25C°] δ: 3.26(q. J=7.0Hz, 4H, Et_2O) 3.18(broad s, 2H, cyclohexyl), 1.99(m, 4H, cyclohexyl), 1.89(s, 3H, CH_3), 1.85-1.45 (series of multiplets, 16H, cyclohexyl), 1.09(t J=7.0Hz, 6H, Et_2O).

[CyN-C(CH_2Ph)-NCy]Li(Et_2O)

A solution of CyNCNCy (4.0 g, 19.4 mmol) in ether (70 mL) was cooled to -40C° and treated with PhCH_2Li(TMEDA) (4.25 g, 19.4 mmol). After standing overnight at room temperature, the resulting yellowish solution was concentrated to small volume by evaporation of the solvent in vacuo, and layered with hexane (40 mL). Pale-yellow microcrystalline [CyN-C(CH_2Ph)-NCy]Li(Et_2O) (2.8 g, 7.4 mmol, 38%) separated upon standing at -30°C for 4 days . I.R. [nujol mull, KBr, cm^{-1}] ν: 3077(sh), 3054(sh), 3020(sh), 2788(sh), 1592(s), 1500(s), 1498(s), 1457(s), 1407(m), 1376(m), 1355(s), 1342(m), 1294(m), 1257(m), 1159(s), 1132(m), 1064(m), 1132(m), 1064(m), 1022(m), 944(s), 887(m), 835(w), 790(m), 771(w), 732(s), 703(s), 651(w), 619(w), 582(br), 543(m). ^{1}H-NMR [C_6D_6, 200 MHz, 25C°] δ: 7.50, 7.24, 7.05(m, 5H, phenyl,) 3.79(s, 2H, CH_2benzyl), 3.27(q. J=7.0Hz, 4H, Et_2O), 3.21(broad s, 2H, cyclohexyl), 1.85(m, 4H, cyclohexyl), 1.60(m, 4H, cyclohexyl), 1.31(m, 4H, cyclohexyl), 1.11(t. J=7.0Hz, 6H, Et_2O).

Preparation of [CyN-C(H)-NCy]$_2$V(TMEDA) (8.1)

A suspension of $VCl_2(TMEDA)_2$ (4.44 g, 12.5mmol) in toluene (100 mL) was stirred and boiled in the presence of [CyN-C(H)- NCy]Li (4.33 g, 20.2 mmol). The resulting deep-yellow suspension was cooled to room temperature and filtered to discard white solid. The resulting dark yellow solution was concentrated to small volume until crystallization of dark-yellow solid started. The suspension was boiled to redissolve the solid and slowly cooled to room temperature. Dark-yellow air-sensitive crystals of **8.1** were obtained upon standing two days at room temperature (3.0 g, 5.0 mmol, 40%). I.R. [nujol mull, KBr, cm^{-1}] ν: 3005(m), 1570(s), 1545(s), 1450(s), 1400(m), 1370(s), 1350(m), 1340(s), 1270(s), 1250(m), 1230(s), 1180(sh), 1160(s), 1155(sh), 1120(s), 1110(s), 1090(br), 1060(m), 1040(w), 1020(m), 1010(m), 980(m), 960(sh), 950(m), 880(s), 840(w), 790(s), 770(w), 720(w), 590(w), 565(w), 475(w), 450(w), 440(w), 390(br). μ_{eff}= 3.88 μ_B. El. Anal. Calcd.(found) for $C_{32}H_{62}N_6V$: C 66.06(65.98), H 10.74(10.66), N 14.44(14.11).

Preparation of $[(CyN\text{-}C(H)\text{-}NCy)_2V]_2$ (8.2)

Method A : A suspension of $VCl_2(TMEDA)_2$ (2.23 g, 6.3 mmol) in toluene (100 mL) was refluxed and stirred overnight in the presence of [CyN-C(H)-NCy]Li (2.86 g, 13.4 mmol). The resulting deep-yellow suspension was filtered at 80°C to eliminate a gray solid (0.2 g). The resulting dark yellow solution was concentrated to small volume until crystallization of emerald-green solid started. The suspension was boiled to redissolve the solid and slowly cooled to room temperature. Emerald-green air-sensitive crystals of **8.2** were obtained upon standing two days (0.4 g, 0.4 mmol, 13%). I.R. [nujol mull, KBr, cm^{-1}] ν: 2805 (s), 1585(s), 1550(m), 1460(s), 1370(m), 1360 (m), 1340(s), 1325(s), 1290(m), 1250(m), 1185(w), 1150(s), 1120(m), 1100(s), 1080(m), 1070(sh), 1020(w), 980(m), 890(m), 840(m), 780(w), 725(w), 690(w), 510(m), 490(m), 450(w), 425(s), 390(m). ^{1}H-NMR [C_6D_6, 200 MHz, 25C°] δ: 9.85 (s, 4H, formamidine), 2.75(pseudo-quintet, 8H, cyclohexyl), 1.99(s, 3H, toluene), 1.90(pseudo-d, 16H, cyclohexyl), 1.75(pseudo-d, 16H, cyclohexyl), 1.63(pseudo-d, 8H, cyclohexyl), 1.20(m, 40H, cyclohexyl). El. Anal. Calcd.(Found) for $C_{52}H_{92}V_2N_8$: C 67.07(66.98), H 9.96(9.73), N 12.03(11.89).

Method B : A solution of **8.4** (1.3 g, 1.3 mmol) in THF (50 ml) was boiled and stirred in the presence of potassium metal (0.14 g, 3.6 mmol) for a few minutes and then stirred overnight at room T. The deep red color turned dark green. The solvent was evaporated in vacuo and the residual solid was redissolved in toluene (20 ml). The solution was filtered to remove KCl and the filtrate allowed to stand at -30°C for two days, upon which green microcrystals of **8.2** (0.5 g, 0.54 mmol, 42%) separated.

Method C : A solution of **8.4** (1.71 g, 1.7 mmol) in THF (50 ml) was boiled and stirred in the presence of potassium metal (0.23 g, 5.9 mmol) and TMEDA (2.0 ml, 13.8 mmol) for a few minutes. After overnight stirring at room T, the color turned dark green. The solvent was replaced with toluene (25 ml), and microcrystalline **8.2** (0.7 g, 0.75 mmol, 44%) was obtained by allowing the resulting solution to stand at -30°C for two days.

Method D : A solution of **8.4** (1.22 g, 1.2 mmol) in toluene (50 ml) was heated for a few minutes while stirred to about 100°C in the presence of potassium metal (0.14 g, 3.6

mmol). Stirring was continued overnight at room T. Green microcrystals of **8.2** (0.6 g, 0.65 mmol, 53%) separated after filtration, concentration to about 20 mL and standing at -30°C.

Method E : A solution of **8.1** (1.1 g, 1.9 mmol) in toluene was refluxed overnight. Green crystals of **8.2** (0.6 g, 0.65 mmol, 68%) were obtained from the resulting dark yellow solution upon standing two days at -30°C.

Method F : A deep blue solution of **8.3** (0.3 g, 0.48 mmol) in toluene (20 ml) was refluxed for 30 min. The resulting green solution was concentrated and cooled to -30°C, yielding green crystals of **8.2**. (47%)

Preparation of V(CyN-C(H)-NCy)$_2$Py$_2$ (8.3)

A suspension of **8.2** (0.6 g, 0.65 mmol) in pyridine (15 ml) was heated at about 100°C for 30 min. The resulting deep blue solution separated blue crystals of **8.3** upon slowly cooling to room temperature (0.3 g, 0.48 mmol, 37%). μ_{eff}= 3.81 μ_B. I.R. [nujol mull, KBr, cm^{-1}] : 2747(m), 1664(w), 1565(s), 1480(m), 1453(s), 1436(s), 1376(m), 1364(s), 1344(s), 1311(m), 1258(s), 1228(s), 1171(s), 1145(m), 1118(m), 1088(s), 1064(w), 1040(m), 998(w), 985(w), 956(w), 920(w), 885(m), 842(w), 7499s), 722(w), 685(s), 668(w), 548(w), 455(w). El. Anal. Calcd.(Found) for $C_{36}H_{56}N_6V$: C 69.31(69.22), H 9.05(8.88), N 13.47(13.38).

Preparation of {V[CyN-C(H)-NCy]$_2$Cl}$_2$ (8.4)

A suspension of VCl_3THF_3 (8.25 g, 22.1 mmol) in THF (100 ml) was boiled in the presence of [CyN-C(H)-NCy]Li (9.33 g, 43.6 mmol). After stirring overnight, the solvent was evaporated in vacuo and the resulting deep red solid was extracted from hexane yielding **8.4** as a red microcrystalline solid (7.6 g, 7.6 mmol, 69%). ^{1}H-NMR [C_6D_6, 200 MHz, 25 C] δ: 9.4(1H, $\Delta\nu_{\frac{1}{2}}$ = 40Hz, C-H_{form}), 6.6(2H, $\Delta\nu_{\frac{1}{2}}$ = 63Hz, cyclohexyl), 6.2(2H, $\Delta\nu_{\frac{1}{2}}$ = 50Hz, cyclohexyl), 2.8(4H, $\Delta\nu_{\frac{1}{2}}$ = 15Hz, cyclohexyl), 2.1(2H, $\Delta\nu_{\frac{1}{2}}$ = 15Hz, cyclohexyl), 1.88(2H, $\Delta\nu_{\frac{1}{2}}$ = 9Hz, cyclohexyl), 1.6(4H, $\Delta\nu_{\frac{1}{2}}$ = 20Hz, cyclohexyl), 1.3(4H, $\Delta\nu_{\frac{1}{2}}$ = 10Hz, cyclohexyl), 0.8(4H, $\Delta\nu_{\frac{1}{2}}$ = 20Hz, cyclohexyl). I.R. [nujol mull, KBr, cm^{-1}]: 1558(s), 1529(s), 1454(s), 1411(m), 1374(s), 1364(sh), 1350(m), 1334(m), 1313(m), 1260(s), 1228(s), 1189(m), 1151(m), 1118(m), 1096(s), 1082(sh), 1064(m), 1046(w), 1020(m), 992(w), 968(w), 920(w), 887(m), 845(m), 803(w), 788(w), 764(w), 728(s), 694(m), 680(m), 510(m), 478(w), 464(w), 454(w), 432(s). μ_{eff}= 1.22 μ_B per dimer. El. Anal. Calcd.(Found) for $C_{26}H_{46}N_4ClV$: C 62.32(62.19), H 9.25(9.13), N 11.18(11.01).

[CyNC(Me)NCy]$_2$V(THF)$_2$ (**8.5a**), [CyNC(CH_2Ph)NCy]$_2$V(THF)$_2$ (**8.5b**), [(Me_3Si)NC(Ph)N($SiMe_3$)]$_2$V(THF)$_2$ (**8.5c**), [CyNC(Me)NCy]$_3$V (**8.6**), and [CyNC(Me)NCy]$_2$VCl (**8.7**) were prepared by Ravinder K. Minhas in our group. {[Me_3SiNC(Ph)N$SiMe_3$]$_2$V}$_2$(N_2) (**8.8**), [Me_3SiNC(Ph)N$SiMe_3$]VCl_2(TMEDA) (**8.9**) and [(Me_3Si)NC(Ph)N($SiMe_3$)]$_2$VCl (**8.10**) were synthesized by Pietro Berno in our group.

Chapter 9

Low-spin linear trimeric and high-spin monomeric octahedral V(II) diphenylacetate complexes.

9.1 Introduction

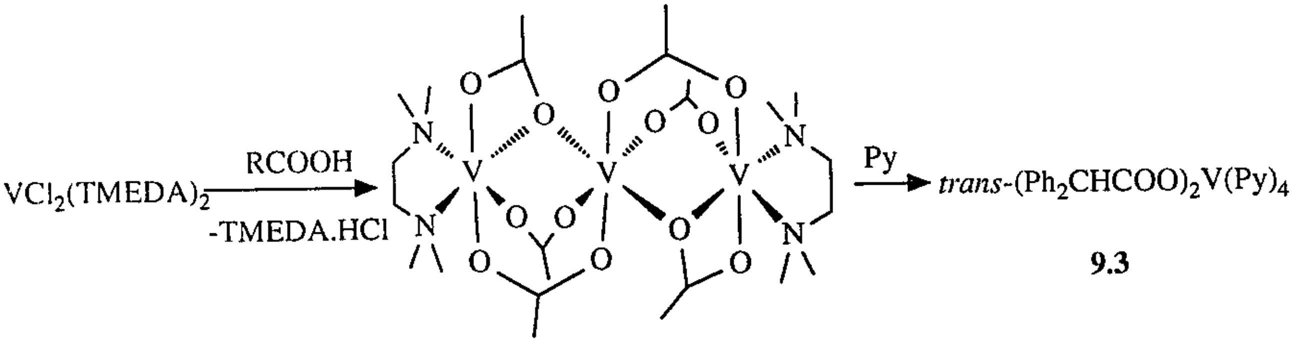
The ability of carboxylate anions to work as bridging three center chelating ligands is an attractive feature of this class of molecules widely employed for the assemblage of di-[2,292-303] and polymetallic units.[304] The most useful characteristics of carboxylate anions as ligands can be summarized in the ability: *i*) to easily form dimers via bridging interactions of the two oxygen donor atoms, each binding one of the two metal centers;[2,292-303] *ii*) to accommodate an enormous range of M-M distances (from very short[61,305] to considerably long non bonding distances)[306-308] and *iii*) to establish efficient magnetic couplings between two metal centers.[59,104, 309,310] Thus, structural investigations on transition metal carboxylates may be helpful for understanding the nature of the M-M interaction.

Among low-valent early transition metals, V(II) carboxylates are especially interesting because of some attractive performances expected or reported for these species, including dinitrogen fixation[311] and formation of short V-V triple bonds.[84,85,91] Early theoretical work has predicted the stability of dimeric V(II) carboxylate with a V-V bonding distance of c.a 2.2 Å.[91] Although initial attempts to preparare V(II) carboxylates have been hampered by the apparent tendency of V(II) to abstract oxygen from the $-COO^-$ group to form a mixed-valence $[V_3O]$ core,[312] an encouraging result describing the preparation of cationic $[V_2(CF_3COO)_2Cl(THF)_6]^+$ has been recently reported.[313] However, no neutral V(II) carboxylates have been reported to date. In this chapter we wish to discuss the preparation and characterization of the first linear trimeric V(II) carboxylates, together with their facile cleavage.

9.2 Results and Discussion

In a standard experiment a solution of $VCl_2(TMEDA)_2$[81] in THF was treated with neat carboxylic acid at room temperature (Scheme 9-1). The color turned rapidly reddish-brown and after elimination of the TMEDA.HCl salt, light brown analytically pure crystals of $V_3(RCOO)_6(TMEDA)_2$ [R = Ph_2CH (**9.1**), $PhCH_2$ (**9.2**)], were obtained by crystallization from toluene at -30 ^{0}C.

Scheme 9-1



R = Ph_2CH (**9.1**)
$PhCH_2$(**9.2**)

9.1, 9.2

The trimeric structure of **9.1** has been demonstrated by an X-ray diffraction analysis. The molecule is constituted by three slightly distorted octahedral vanadium atoms forming an almost linear V_3 core [V2-V1-V3 = 177.34°] (Figure 9-1). Two coplanar TMEDA molecules are attached to each of the two external vanadium atoms forming V-N distances [V2-N1 =

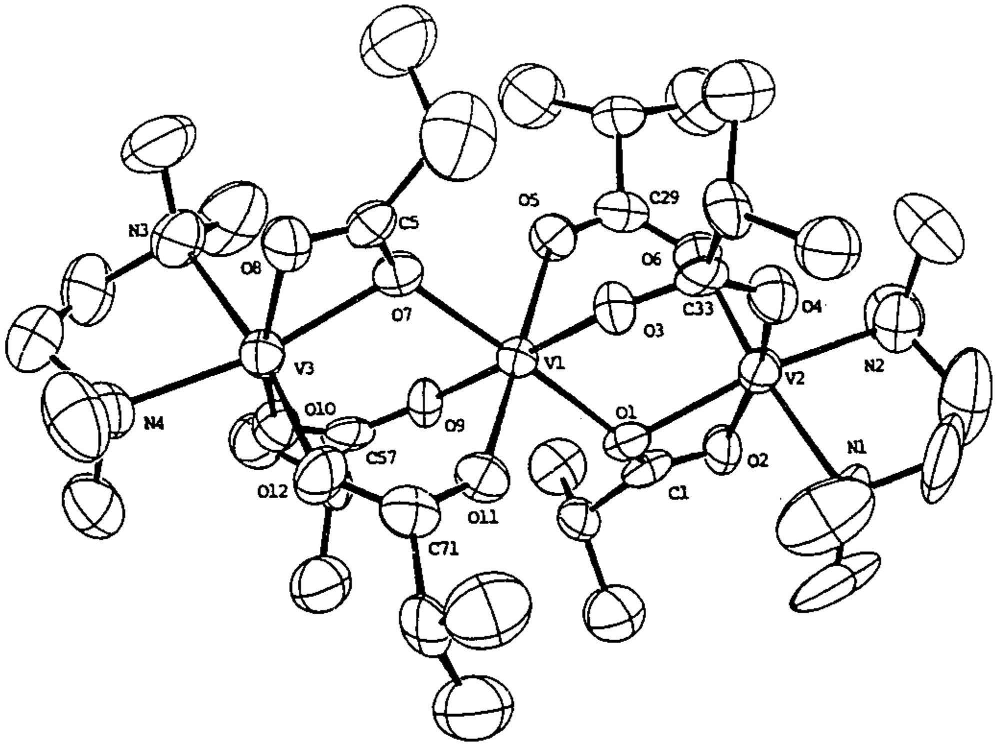


Figure 9-1. ORTEP drawing of **9.1**, showing the labeling scheme.

2.198(9)Å] which compare quite well with those of other V(II) TMEDA complexes.[81,245,288] The linkage between the three vanadium atoms is obtained by six bridging carboxylates. Four carboxylates work as conventional three center chelating ligands adopting the classical *syn-syn* arrangement with each oxygen donor atom bonding one metal center.[314] The V-O distances formed with the terminal and central vanadium atoms are rather similar (ranging from 2.063Å to 2.112Å) and compare well with those observed in $[V_2Cl(CF_3COO)_2]^+$.[313] The angles subtended at the central carbon atom by the two oxygen atoms in each -COO group slightly deviate from the normal angles expected for sp^2 carbon atoms [ranging from 125.1° to 127.6°]. The remaining two carboxylic groups adopted a "tridentate" bonding mode with one oxygen attached to the terminal vanadium [V2-O2 = 2.151(8), V3-O8 = 2.160(7)] and the second oxygen which bridges two metal centers [V1-O1 = 2.195(7), V2-O1 = 2.163(7)]. As a result of the two considerably different bonding modes, the angles subtended at the carbon atoms by the two donor oxygen atoms are significantly narrower [O1-C1-O2 = 117.9(9)°, O7-C43-O8 = 119.7°]. The geometry around the tricoordinated bridging oxygen is pyramidal forming normal tetrahedral angles [V1-O1-V2 = 109.0(3)°, V1-O7-V3 = 113.9(3)°].

Although the acetate ligand in complex **9.1** does not support a V-V multiple bond [V1..V2 = 3.555Å, V1..V3 = 3.549Å], nevertheless it does provide an efficient electronic coupling between the three metal centers. The magnetic moment of the trimer is in fact lower than expected for a high-spin d^3 V(II) [$\mu_{eff} = 5.45\ \mu_B$ per trimer], probably as result of an efficient ligand-mediated superexchange performed by the bridging oxygen donor atom. It is noteworthy that the normal high-spin configuration with three unpaired electrons per vanadium atom has been observed in the dimeric $[V_2Cl(CF_3COO)_2(THF)_6]^+$, having only slightly longer value of the V..V non bonding distance.[313] This suggests that the nature of the bridging ligand and the positioning of the bridging donor atoms around the transition metal as determined by steric factors or geometry optimization, may be responsible, rather than the M-M distance, for the efficiency of the magnetic couplings.

The trimeric aggregation of **9.1** is rather weak, since simple reaction with pyridine cleaves the linear trimer forming the monomeric $(R_2CHCOO)_2V(pyridine)_4$ (**9.3**) (Scheme 9-1).

The structure of **9.3**, as demonstrated by X-ray analysis, showed the unit cell composed of discrete monomeric units with two carboxylate groups occupying the axial

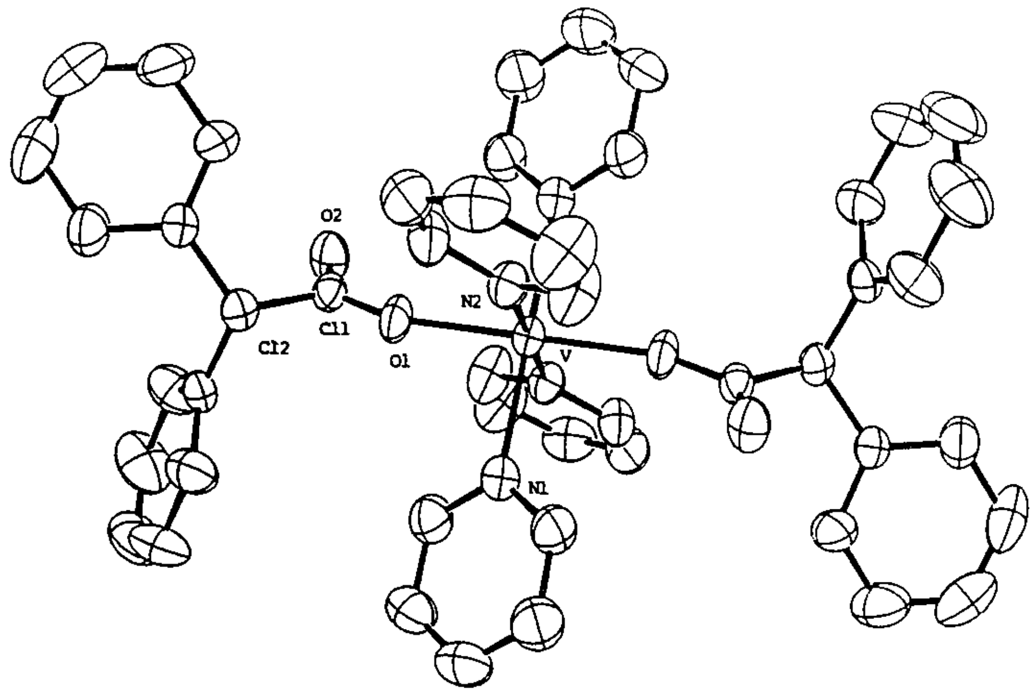


Figure 9-2. ORTEP drawing of **9.3**, showing the labeling scheme.

positions of the ideal octahedron centered on vanadium [O1-V-N1 = 88.28(9)°, O1-V-N2 = 87.6(1)°, N1-V-N2 = 91.6(1)°] (Figure 9-2). The nitrogen atoms of the four pyridine molecules occupy the equatorial plane forming V-N distances [V-N1 = 2.220(3)Å] comparable to those of $VCl_2(pyridine)_4$.[315] The two carboxylate ligands work as a simple monodentate group forming V-O distances [V-O1 = 2.087(2)Å] which fall in the range of those formed by the briging carboxylates in complex **9.1**.

9.3 X-ray crystallography

Refer to Section **2.3**. Details on data collection and structure refinement for **9.1** and

9.3 are reported in Table 9-1. Selected bond distances and angles are given in Table 9-2.

Table 9-1 Crystal Data and Structural Analysis Results

complex	**9.1**	**9.3**
Formula	$C_{110}H_{104}N_4O_{12}V_3$	$C_{48}H_{42}N_4O_4V$
Formula Weight	1632.86	788.98
Crystal system	monoclinic,	monoclinic
Space Group	$P2_1/n$	$P2_1/n$
a, Ä	15.142(7)	9.999(2)
b, Ä	26.543(6)	18.333(7)
c, Å	24.775(22)	11.500(1)
β, deg	101.78(5)	105.53(1)
V, Ä^3	9748(10)	2031.1(9)
Z	4	2
T (°C)	25	25
d_{calcd}, g/cm^{-3}	1.245	1.291
μ_{calcd} (cm^{-1})	1.27	0.26
Radiation, Ä	1.54056	0.70930
R	0.103	0.045
R_w	0.089	0.017

Table 9-2 Selected Bond Distances (Å) and Angles (deg)

9.1	**9.3**
V1..V2 = 3.555(7)	V-O1 = 2.087(2)
V1..V3 = 2.549(7)	V-N1 = 2.220(3)
V2-N2 = 2.198(9)	V-N2 = 2.208(3)
V1-O1 = 2.195(7)	N1-V1-O1 = 88.28(9)
V2-O1 = 2.163(7)	N1-V1-N2 = 91.66(10)
V1-O3 = 2.112(7)	N2-V1-O1 = 87.62(10)
V2-O4 = 2.085(7)	
O1-V1-O7 = 176.7(3)	
O3-V1-O9 = 178.4(3)	
O1-V1-O3 = 93.3(3)	
O3-V1-O5 = 88.7(3)	

9.4 Experimental Section

All operations were performed under inert atmosphere in a dry-box (Vacuum Atmosphere) or using standard Schlenk techniques. $VCl_2(TMEDA)_2$[81,245,288] was prepared according to published procedures. RCOOH (R = Ph_2CH, $PhCH_2$) (Aldrich) were purchased and used without further purification. Infrared spectra were recorded on a Mattson 9000 FT-IR instrument from Nujol mulls prepared in a dry-box. Samples for magnetic susceptibility measurements were weighed inside a dry-box equipped with an analytical balance, and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature. The magnetic moment was calculated according to standard methods,[111] and corrections for underlying diamagnetism were applied to data.[112] Combustion analysis data were obtained which satisfactorily verified the composition of all the complexes.

The preparation of $V_3(Ph_2CHCOO)_6(TMEDA)_2$ (9.1).

$VCl_2(TMEDA)_2$ (2.65 g, 7.5 mmol) in THF (70 mL) was treated with neat diphenylacetic acid (3.17 g, 15.0 mmol) at room temperature. The color turned rapidly reddish-brown upon boiling and the mixture was stirred for 12 hrs. The TMEDA.HCl salt was filtered out from a boiling solution and light brown, analytically pure crystals of $V_3(Ph_2CHCOO)_6(TMEDA)_2$.2 toluene (**9.1**), (3.46 g, 2.1 mmol), were separated upon evaporation and crystallization from toluene at -30°C. I.R. [KBr, nujol mull, cm^{-1}]: 1600 (s), 1545 (m), 1490(w), 1390(s), 1290(w), 1260(w), 1170(w), 1130(w), 1080(m), 1040(m), 1035(m), 950(m), 795(s), 740(s), 730(s), 695(s), 640(s), 560(m), 490(w), 465(m). Anal Calcd (found) for $C_{110}H_{104}N_4O_{12}V_3$: C 72.32(72.31), H 5.74(5.65), N3.07(2.99), V 8.37(8.29). [μ_{eff} = 5.45 μ_B at room T].

The preparation of $V_3(PhCH_2COO)_6(TMEDA)_2$ (9.2).

$VCl_2(TMEDA)_2$ (2.05 g, 5.8 mmol) in THF (70 mL) was treated with neat phenylacetic acid (1.64 g, 12.0 mmol) at room temperature. The color turned rapidly reddish-brown upon boiling and the mixture was stirred for 12 hrs. The TMEDA.HCl salt was filtered out from a boiling solution and light brown, analytically pure crystals of $V_3(PhCH_2COO)_6(TMEDA)_2.2$ toluene (**9.2**) (3.14 g, 2.3 mmol), were separated upon evaporation and crystallization from toluene at -30^{0}C. I.R. [KBr, nujol mull, cm^{-1}]: 1600 (s), 1545 (m), 1490(w), 1390(s), 1290(w), 1260(w), 1170(w), 1130(w), 1080(m), 1040(m), 1035(m), 950(m), 795(s), 740(s), 730(s), 695(s), 640(s), 560(m), 490(w), 465(m). Anal Calcd (found) for $C_{74}H_{74}N_4O_{12}V_3$: C 65.15 (65.12), H 5.43 (5.38), N 4.11 (4.04), V 11.23 (11.08). [μ_{eff} = 5.41 μ_B at room T].

The preparation of $(Ph_2CHCOO)_2V(Py)_4$ (9.3).

The addition of pyridine (5 mL) to a solution of $V_3(Ph_2COO)_6(TMEDA)_2.2C_7H_8$ (2.27 g, 1.31mmol) in THF (50 mL) turned the solution deep purple. The resulting solution was boiled and evaporated to dryness. The solid residue was recrystallized from THF (10 mL) containing 1 mL of pyridine. Black crystals of **9.3** precipitated upon standing at room temperature (1.76 g, 2.65 mmol, 67%). I.R. [KBr, nujol mull, cm^{-1}]: 1610(s), 1595(m), 1495(w), 1480(m), 1450(s), 1415(s), 1375(m), 1370(s), 1345(s), 1270(m), 1220(m), 1175(m_), 1150(m), 1070(m0, 1040(m), 1035(m), 1005(w), 950(w), 880(w), 850(w), 775(m), 760(m), 735(m), 710(s), 700(s), 695(s), 645(s), 625(m), 565(m), 475(w), 445(m). Anal Calcd (found) for $C_{48}H_{42}N_4O_4V$: C 72.32(72.19), H 5.74(5.66), N 3.07(3.00), V 8.37(8.33). [μ_{eff} = 3.73 μ_B at room T].

Chapter 10

Conclusions

New series of divalent chromium and vanadium complexes have been prepared and characterized. These results strongly support the initial hypothesis that, in spite of very short and supershort intermetallic separations, M-M multiple bonds may be artifacts of the bridging ability of ligands employed. In addition to their ability to form dinuclear frame, the ligand geometry is able to determine the extent of intermetallic separation. Finally, our work has confirmed the suspected and debated paradoxical weakness of M-M multiple bonds.

$[(TAA)Cr]_2$ is a sole example of dinuclear Cr(II) complex with no bridging and axial ligands. It demonstrates that the formation of Cr-Cr multiple bonds is indeed possible when chromium d orbitals can be pyramidalized by 'small hole' of macrocyclic ligands. However, the reversible cleavage of $[(TAA)Cr]_2$ via coordination of pyridine indicates that the strength of the Cr-Cr multiple bond in $[(TAA)Cr]_2$ can not exceed four times the energy of a Cr-Py bond. This behavior seems to be a rather general trend, the supershort V-V multiple bond of $V_2(CyNCHNCy)_4$ has also been reversibly cleaved by pyridine.

The reversible cleavage of $Me_8Cr_2Li_4L_4$ (L = Et_2O, THF) via replacement of the Lewis base coordinated to the alkali cation has also confirmed that no significant Cr-Cr bond exists in $Me_8Cr_2Li_4L_4$. Our result indicated that in spite of the supershort Cr-Cr intermetallic distance, no significant Cr-Cr bond exists in $Me_8Cr_2Li_4L_4$ since the equilibrium between dimeric $Me_8Cr_2Li_4L_4$ and monomeric $Me_4CrLi_2(TMEDA)_2$ can shift to either side without modification of the coordination sphere of the chromium atom. The crucial role of the alkali cation in holding together the dinuclear structure through a network of organic interchains has been confirmed not only in $Me_8Cr_2Li_4L_4$ (Cr-Cr = 1.968 Å) but also in a novel series of CrR_2 and CrR_4^{2-} species.

The steric interactions within the ligand was never regarded before as a factor capable of determining nuclearity and of promoting the formation of very short Cr-Cr contacts. The preparation of a consistent series of monomeric and dimeric cyclohexyl amidinate chromium complexes has shown that steric factors indeed control the formation of the dichromium unit. Since similar behavior was observed in the case of V(II), the steric hindrance within the ligand should be considered as a very important factor to promote or disfavor dinuclear aggregation. Our results also imply that theoretical calculations carried out on dinuclear Cr(II) and V(II) complexes may be inadequate, because the model compounds employed in the calculations are usually obtained by simplifying the large substituent groups to a hydrogen atom. The justification for such a simplification is the premise that steric bulk within a ligand is not crucial to the final outcome. Examples include the model compounds $Cr_2(O_2CH)_4$, $V_2(O_2CH)_4$ and $Cr_2[(HN)_2CH]_4$ which represent complexes of the form $Cr_2(O_2CR)_4$, $V_2(O_2CR)_4$ and $Cr_2[(R^1N)_2CR^2]_4$, respectively. Our results show that the above premise is not correct.

In order to understand the nature of the Cr-Cr interaction in lantern-type complexes, we have also studied the role of the electronic configuration of the ligand and the nature of the donor atom in affecting the formation of short Cr-Cr contacts. The conclusions may be summarized as follows:

(i) With the exception of $[(TAA)Cr]_2$, where the Cr(II) has been pyramidalized by the ligand, no significant Cr-Cr multiple bonds have been found in a variety of classes of Cr(II) complexes despite the very short and supershort Cr-Cr intermetallic contacts. Therefore Cr-Cr intermetallic distance is actually a necessary but not sufficient factor to determine the existence of a Cr-Cr bond.

(ii) Ligand features, such as geometry, steric hindrance, electronic configuration, donor atoms, bite, alkali cation etc., determine both the Cr-Cr intermetallic separation and electronic coupling. A similar passive behavior of the metal with respect to the dominance of ligands was also found in some of V(II), V(III) and Ti(III) complexes. However, the generality of these findings for other first row low valent transition metals must await further investigation.

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