



uOttawa

L'Université canadienne
Canada's university

**FACULTÉ DES ÉTUDES SUPÉRIEURES
ET POSTDOCTORALES**



**FACULTY OF GRADUATE AND
POSTDOCTORAL STUDIES**

Indumathi Pihillagawa Gedera
AUTEUR DE LA THÈSE / AUTHOR OF THESIS

M.Sc. (Chemistry)
GRADE / DEGREE

Department of Chemistry
FACULTÉ, ÉCOLE, DÉPARTEMENT / FACULTY, SCHOOL, DEPARTMENT

Metal to Ligand Electron Transfer for Molecular Activation and Catalysis

TITRE DE LA THÈSE / TITLE OF THESIS

Sandro Gambarotta
DIRECTEUR (DIRECTRICE) DE LA THÈSE / THESIS SUPERVISOR

CO-DIRECTEUR (CO-DIRECTRICE) DE LA THÈSE / THESIS CO-SUPERVISOR

Sean Barry

Muralee Murugesu

Gary W. Slater

Le Doyen de la Faculté des études supérieures et postdoctorales / Dean of the Faculty of Graduate and Postdoctoral Studies

***Metal to ligand electron transfer for
molecular activation and catalysis.***

Indu Vidayaratne

Thesis submitted to the

Faculty of Graduate and Postdoctoral Studies

In partial fulfillment of the requirement for the degree of

Master of Science

in Chemistry

Ottawa-Carleton Chemistry Institute

University of Ottawa

Candidate

Supervisor

Indu V. Pihillagawa Gedea

Professor S. Gambarotta

© Indumathi Pihillagawa Gedera, Ottawa, Canada, 2010



Library and Archives
Canada

Published Heritage
Branch

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque et
Archives Canada

Direction du
Patrimoine de l'édition

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file *Votre référence*
ISBN: 978-0-494-73815-3
Our file *Notre référence*
ISBN: 978-0-494-73815-3

NOTICE:

The author has granted a non-exclusive license allowing Library and Archives Canada to reproduce, publish, archive, preserve, conserve, communicate to the public by telecommunication or on the Internet, loan, distribute and sell theses worldwide, for commercial or non-commercial purposes, in microform, paper, electronic and/or any other formats.

The author retains copyright ownership and moral rights in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

AVIS:

L'auteur a accordé une licence non exclusive permettant à la Bibliothèque et Archives Canada de reproduire, publier, archiver, sauvegarder, conserver, transmettre au public par télécommunication ou par l'Internet, prêter, distribuer et vendre des thèses partout dans le monde, à des fins commerciales ou autres, sur support microforme, papier, électronique et/ou autres formats.

L'auteur conserve la propriété du droit d'auteur et des droits moraux qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

In compliance with the Canadian Privacy Act some supporting forms may have been removed from this thesis.

While these forms may be included in the document page count, their removal does not represent any loss of content from the thesis.

Conformément à la loi canadienne sur la protection de la vie privée, quelques formulaires secondaires ont été enlevés de cette thèse.

Bien que ces formulaires aient inclus dans la pagination, il n'y aura aucun contenu manquant.


Canada

Abstract

The ultimate goal of this thesis was to elucidate the metal oxidation state of the active species in the catalytic cycle for ethylene oligo- and polymerization, and understanding the nature of the catalyst/co-catalyst interaction. Central to achieving these goals is of course the judicious choice of the metal and ligand system enabling the isolation and characterization of species arising from the interaction catalyst precursor/activator, and an investigation of their catalytic behaviour.

Early transition metals have been the elements of primary choice for this work given their well established ability to provide both oligomerization and polymerization catalysts. A particular emphasis was placed on chromium which provides commercial catalysts for both processes.

Nitrogen donor based ligand systems were chosen for this thesis work for several reasons. In particular, we have selected molecules which may be easily accessible, inexpensive and effective in terms of supporting high catalytic activity. The possibility of tuning steric and donor properties via relatively simple organic synthesis also was a factor of choice for the selection of the appropriate ligand. Two families of ligands (bis-iminopyridine) and pyrrolide anions have been used for different sets of reasons. The first is by excellence a non-innocent ligand commonly involved in the organometallic chemistry of the metal center, displaying an array of surprising transformations. We also discovered that this ligand is able to stabilize species where the metal deceptively appears in low and unusual oxidation states, the spin density having being transferred to the ligand system instead. Remarkably however, this does not resolve into a quenching of the reactivity of the metal center whose behavior remained in fact as one could expect for genuine low-valent species. We have tried to elaborate further on this information.

Chapter 2 is a study on the divalent chromium complexes of this particular ligand system and on its catalytic behavior. A divalent chromium complex of bis(imino)pyridine, $\{2,6-[2,6-(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]_2(\text{C}_5\text{H}_3\text{N})\}\text{CrCl}_2$ (**2.1**), was prepared with the aim of studying its reactivity with alkylating agents. Upon treatment with MeLi, the metal center was both reduced and alkylated, forming $\{2,6-[2,6-(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]_2(\text{C}_5\text{H}_3\text{N})\}\text{-CrMe}(\mu\text{-Me})\text{Li}(\text{THF})_3$ (**2.2**). Complex **2.1** is also conveniently reduced with either NaH or metallic sodium to give the new species $\{2,6-[2,6-(i-$

Pr)₂PhN=C(CH₃)₂(C₅H₃N)}CrCl (**2.3**). Despite the appearance of the metal center in a rare monovalent oxidation state, the square-planar geometry of the Cr atom suggests that the metal is most likely divalent, with the electron housed in the ligand π^* orbital. When activated with MAO, complex **2.3** is a very and even more active catalyst for the polymerization of ethylene than either the -CrCl₂ or -CrCl₃ derivative of this ligand system and yet produces polymers with similar properties. Subsequent reactivity studies of complex **2.3** have allowed the isolation of several products. Reaction with either LiCH₂Si(CH₃)₃ or MeLi resulted in deprotonation of one of the methyl groups on the ligand backbone, forming {2-[2,6-(*i*-Pr)₂PhN=C(CH₃)]-6-[2,6-(*i*-Pr)₂PhNC=CH₂](C₅H₃N)}Cr(THF) (**2.4**) and {2-[2,6-(*i*-Pr)₂PhN=C(CH₃)]-6-[2,6-(*i*-Pr)₂PhNC=CH₂](C₅H₃N)}Cr(*i*-Me)Li(THF)₃ (**2.5**), respectively. On the other hand, alkylation with AlMe₃ allowed the successful preparation of another organochromium species, {2,6-[2,6-(*i*-Pr)₂PhN=C(CH₃)₂(C₅H₃N)}CrCH₃ (**2.7**), along with small amounts of the byproduct {2,6-[2,6-(*i*-Pr)₂PhN=C(CH₃)₂(C₅H₃N)}Cr(μ -Cl)₂Al(CH₃)₂ (**2.6**). Interestingly, complex **2.7**, which also has the deceiving connectivity of a monovalent species, displays an even greater activity for ethylene polymerization than all of the other species reported herein, again producing a polymer with nearly identical characteristics. Activation with IBAO revealed a deactivation pathway similar to that observed with the FeCl₂ system. In this case, the stronger reducing power of IBAO resulted in the usual reduction not only of the ligand backbone but also of the metal center. As a result of the metal reduction, partial transmetalation of the ligand system occurred, with formation of [η^4 -{2,6-[2,6-(*i*-Pr)₂PhN=C(CH₃)₂(C₅H₃N)}Al₂(*i*-Bu)₃(μ -Cl)]Cr(η^6 -C₇H₈) (**2.8**). By being catalytically inactive, the partly transmetalated **2.8** suggests that ligand demetalation is a possible catalyst deactivation pathway.

In **Chapter 3** we have further elaborated on the concept of electron transfer and explored the direct reduction of the chromium complexes prepared in chapter two. Reduction of {2,6-[2,6-(*i*-Pr)₂PhN=C(CH₃)₂(C₅H₃N)}CrCl (**2.3**) with NaH afforded a rare case of dinitrogen fixation on chromium. The dinuclear dinitrogen complex {[2,6-[2,6-(*i*-Pr)₂PhN=C(CH₃)₂(C₅H₃N)}Cr(THF)]₂(μ -N₂)}·THF (**3.1**) was isolated and characterized. Reaction carried in exclusion of dinitrogen afforded instead deprotonation of the ligand with the formation of {2-[2,6-(*i*-Pr)₂PhN=C(CH₃)]-6-[2,6-(*i*-Pr)₂PhNC=CH₂](C₅H₃N)}Cr(THF) (**2.4**). Further reduction of **3.1** with NaH yielded a curious

dinuclear compound formulated as $\{[2,6-[2,6-(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]_2(\text{C}_5\text{H}_3\text{N})\}\text{Cr}(\text{THF})\}[\{2-[2,6-(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]-6-[2,6-(i\text{Pr})_2\text{PhNC}=\text{CH}_2](\text{C}_5\text{H}_3\text{N})\}\text{Cr}-(\text{THF})](\mu\text{-N}_2\text{H})(\mu\text{-Na})_2$ (**3.2**) containing two sodium atoms only bound to the dinitrogen unit and the π systems of the two diiminepyridine ligands. Subsequent reduction with NaH triggered a complex series of events, leading to the formation of a species formulated as $\{2-[2,6-(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]-6-[2,6-(i\text{-Pr})_2\text{PhNC}=\text{CH}_2](\text{C}_5\text{H}_3\text{N})\}\text{Cr}(\mu\text{-NH})[\text{Na}-(\text{THF})]$ (**3.3**) on the basis of crystallographic, spectroscopic, isotopic labeling, and chemical degradation experiments.

In **Chapter 4** we have extended the concept of reduced species of this ligand system with a brief exploration on vanadium. Reduction of the two trivalent $2,6-\{[2,6-(i\text{-Pr})_2\text{C}_6\text{H}_5]\text{N}=\text{C}(\text{CH}_3)\}_2(\text{C}_5\text{H}_3\text{N})\text{VCl}_3$ and $\{2,6-\{[2,6-(i\text{-Pr})_2\text{C}_6\text{H}_5]\text{N}-\text{C}=(\text{CH}_2)\}_2(\text{C}_5\text{H}_3\text{N})\}\text{VCl}(\text{THF})$ (**4.1**) complexes with excess NaH afforded two corresponding end-on dinitrogen-bridged complexes $[2,6-\{[2,6-(i\text{-Pr})_2\text{C}_6\text{H}_5]\text{N}=\text{C}(\text{CH}_3)\}_2(\text{C}_5\text{H}_3\text{N})\text{V}]_2(\mu\text{-N}_2)\cdot(\text{hexane})$ (**4.2**) and $[\{2,6-\{[2,6-(i\text{-Pr})_2\text{C}_6\text{H}_5]\text{N}-\text{C}=(\text{CH}_2)\}_2(\text{C}_5\text{H}_3\text{N})\}\text{V}]_2(\mu\text{-N}_2)\cdot(\text{hexane})$ (**4.3**). In spite of their very close structural similarity, the two species have completely different nature. The first is paramagnetic and may be regarded as generated by the two-electron attack of two formally zero-valent vanadium moieties on the same N_2 unit. In the nearly diamagnetic **4.3** instead, the N_2 unit has been reduced by two vanadium atoms, formally divalent. Structural analysis and DFT calculations have indicated that partial reduction of the bridging nitrogen occurred for both complexes while, in the case of **4.1**, substantial metal-to-ligand electron transfer also occurs.

The second family of ligand systems examined in this thesis work was provided by pyrrolide-based organic molecules. The motif of electron storage has been further investigated by using a dianionic ligand bearing a central π -system which can be constrained by sterics at bonding distance to the metal center. The Cp-like features of pyrrolide anions and the fact that pyrrole/chromium provides a catalytic system for the commercial production of 1-hexene prompted this study reported in **Chapter 5**. By using a mixture of $\text{CrCl}_3(\text{THF})_3$, 2,3,4,5-tetramethylpyrrole and Me_3Al , the complex $[\eta^5\text{-}2,3,4,5\text{-Me}_4\text{C}_4\text{N}(\text{AlClMe}_2)]_2\text{Cr}$ (**5.1**) with a chromocene-like sandwich structure has been isolated and fully characterized. Unlike the real chromocene, this species acts as a single-component polymerization catalysts producing UHMWPE with good activity and very

narrow polydispersity. Oxidation of the complex was carried out with azobenzene affording the pentavalent $\{[\eta^5\text{-}2,3,4,5\text{-Me}_4\text{C}_4\text{N}(\text{AlClMe}_2)] \text{CrMe}(\mu\text{-NPh})_2\text{AlMe}_2\} \cdot [\text{Me}_3\text{Al}(\text{THF})]$ (**5.2**) after addition of a stoichiometric amount of THF to help crystallization. This species also is a single component ethylene polymerization catalysts producing HDPE albeit of substantially lower molecular weight. If for the preparation of **5.1**, $\text{CrCl}_2(\text{THF})_2$ instead of the trivalent salt was used, the result of the reaction was completely different affording the divalent $\{[\eta^5\text{-}2,3,4,5\text{-Me}_4\text{C}_4\text{N}(\text{AlClMe}_2)]\text{Cr}\}_2(\mu\text{-Me})_2$ (**5.3**) with short Cr...Cr contact. In spite of the divalent state and the close relationship with **5.1**, complex **5.3** is not a polymerization catalyst. Instead it is a single-component ethylene trimerization catalysts producing 1-hexene in high purity and activity if methyl cyclohexane is used as a solvent. Employing toluene as a solvent spectacularly decreased both catalytic activity and selectivity.

In **Chapter 6** we have introduced an electron storage device in the pyrrole based ligand system and report a study for their use in vanadium and titanium chemistry. The deprotonation of the tripyrrole MeTPH_2 $[\text{MeTPH}_2]_{2,5}\text{-}[(2\text{pyrrolyl})(\text{C}_6\text{H}_5)_2\text{C}]_2(\text{MeN C}_4\text{H}_2)]$, containing one N-methylated pyrrolyl ring, was carried out with 2 equiv of KH. The corresponding dipotassium salt reacted with $\text{VCl}_3(\text{THF})_3$ and $\text{TiCl}_3(\text{THF})_3$ to afford the complex $[(\text{MeTP})\text{VCl}(\text{THF})] \cdot \text{THF}$ (**6.1**) and $\{2,5\text{-}[(\text{C}_4\text{H}_3\text{N})\text{CPh}_2]_2[\text{C}_4\text{H}_2\text{N}(\text{Me})]\} \text{TiCl}$ respectively. In both cases, while the two lateral pyrrolide rings are *o*-bonded, the central one is perpendicularly oriented in a sort of π -fashion. However, the bond distances clearly indicated that only the quaternized N atom is forming a bonding contact. Subsequent reduction of **6.1** with Na yielded the corresponding divalent complex $[(\text{MeTP})\text{V}(\text{THF})] \cdot (\text{C}_7\text{H}_8)_{0.5}$ (**6.2**) where the central N-methylated ring adopted a more regular π -orientation. When treated with a strong Lewis acid (AlMe_3), THF was extracted from the vanadium coordination sphere, forming the dinuclear dinitrogen complex $[(\text{MeTP})\text{V}(\mu\text{-N}_2)]_2 \cdot (\text{C}_7\text{H}_8)_{2.9}$ (**6.3**). Reduction of **6.3** with potassium graphite gave cleavage of dinitrogen, affording the mixed-valent nitride-bridged complex $[(\text{MeTP})\text{V}(\mu\text{-N})]_2 \cdot (\text{THF})$ (**6.4**). Reduction of the Ti(III) complex $\{2,5\text{-}[(\text{C}_4\text{H}_3\text{N})\text{CPh}_2]_2[\text{C}_4\text{H}_2\text{N}(\text{Me})]\} \text{TiCl}$ with Na/Hg under nitrogen atmosphere in either DME or THF afforded the dinuclear and tetravalent $[\text{Na}(\text{DME})_3][\{2,5\text{-}[(\text{C}_4\text{H}_3\text{N})\text{CPh}_2]_2[\text{C}_4\text{H}_2\text{N}(\text{Me})]\} \text{Ti}_2(\mu\text{-NH})(\mu\text{-N})]$ (**6.5**) In the anionic unit of the complex, the two identical $\{2,5\text{-}$

$[(C_4H_3N)CPh_2]_2[C_4H_2N(Me)]\}$ Ti moieties are bridged by one nitride atom and one NH group. Isotopic labelling experiments as well as NMR spectroscopy and chemical degradation clearly indicated that the bridging nitrogen atoms were originated from nitrogen gas cleavage. The hydrogen atom on the imide residue was provided by the solvent most likely via a radical-type of attack of an intermediate reduced species.

Dedication

*To my beloved mom who is no longer
here to witness my graduation*

Acknowledgements

There are many people I have to thank over the course of my existence at the University of Ottawa. First and foremost would be Professor Sandro Gambarotta. A better supervisor could not be had. His support, dedication, intellect, wit and habitual anecdotes have made the experience that much more worthwhile. He has always kept the door open and is always there to listen. I am eternally grateful for all the opportunities that he had given to me, encouragement and advice.

Dr. Rob Duchateau took his time out of his busy schedule to help me for some of the work in this thesis work. arrange some of catalytic testing in this thesis, which I am very grateful.

There are other important people from whom I have attained a greater understanding of Chemistry and I am indebted to Dr. Jennifer Scott, Dr. A. Athimoolam, Dr. Ilia korobkov for frequent gems of knowledge. I would like to thank the Dean of the Faculty of Science Dr. Christian Detellier.

Numerous other individuals in the department have helped me immeasurably. Ilia, Athi and Patrick for all the lithium and potassium chloride structures and as well as the more useful ones. Dr. Glenn Facey for performing the NMR experiments that were necessary for my research. Annette and Linda for all the administrative work (including appointing me as a TA and specially for giving me my salary on time).

There are also many grad students and post docs that I have to thank. Particular special attention should go to Dr. Patrick Crewdson, , Dr. Balamurugan, Indira Thapa, Khalid Albahily, Dr. G. B. Nikiforov, and Dr. Amir Jabri.

Special thanks to Ludmila Scoles who had encouraged and supported me in writing process of this thesis. Not only that, her support, encouragement and valuable advices help me to go through very difficult times in my life. Ludi, you will remain in my heart forever as a true friend.

Many thanks to all of my friends without whom my life would be very dull. To my late beloved mother Kusuma and my father Vidyaratne for courage, compassion and continual support for me in all my pursuits. To my brother, Donald who was always with

me in spirit and keep me on track by listening to the frustration of my chemistry and discussing new advancements in my research project. To my son Gayashan who always keeps me happy by being a good child.

List of Publication.

- (1) Nikiforov, G. B.; Vidyaratne, I.; Sandro Gambarotta, S.; Ilia Korobkov, I.; *Angew. Chem. Int. Ed.* **2009**, *48*, 7415.
- (2) Vidyaratne, I.; Nikiforov, G. B.; Gambarotta, S.; Robbert Duchateau, R.; Ilia Korobkov, I.; *Angew. Chem.Int.Ed.* **2009**, *48*, 1.
- (3) Scott, J.; Vidyaratne, I.; Gambarotta, S.; Budzelaar, P. *Inorg. Chem.* **2008**, *47*, 896 (most accessed article Jan-Apr 2008).
- (4) Vidyaratne, I.; Crewdson, P.; Lefebvre, E.; Gambarotta, S. *Inorg. Chem.* **2007**, *46*, 8836.
- (5) Vidyaratne, I.; Scott, J.; Gambarotta, S.; Budzelaar, P. *Inorg. Chem.* **2007**, *46*, 7040.
- (6) Vidyaratne, I.; Scott, J.; Gambarotta, S.; Budzelaar, P. *Organometallics* **2007**, *26*, 3201.
- (7) Vidyaratne, I.; Gambarotta, S. Korobkov, I.; Budzelaar, P.; *Inorg. Chem.* **2007**, *46*, 1187.

Contents

Chapter 1-Introduction	200
Introduction.....	211
Characteristics of Transition Metal complex Catalysts	211
Ziegler-Natta Polymerization Catalysts.....	233
Ethylene Oligomerization.....	28
Development of Oligomerization Catalyst.....	29
References	333
Chapter 2: Reactivity of Chromium Complexes of a Bis(imino)pyridine Ligand: Highly Active Ethylene Polymerization Catalysts Carrying the Metal in a Formally Low Oxidation State	366
Introduction.....	37
Experimental Section	39
Preparation of {2, 6-[2, 6-(<i>i</i>-Pr)₂PhN=C(CH₃)₂(C₅H₃N)}CrCl₂. 0.75THF (2.1)	39
Preparation of {2,6-[2,6-(<i>i</i>-Pr)₂PhN=C(CH₃)₂(C₅H₃N)}CrMe-(μ-Me)Li(THF)₃ (2.2).....	40
Preparation of {2,6-[2,6-(<i>i</i>-Pr)₂PhN=C(CH₃)₂(C₅H₃N)}CrCl (2.3).....	400
Preparation of {2-[2,6-(<i>i</i>-Pr)₂PhN=C(CH₃)₂]-6-[2,6-(<i>i</i>- Pr)₂PhNC=CH₂](C₅H₃N)}Cr(μ-Me)Li(THF)₃.0.66(toluene) (2.5)	411
Preparation of {2,6-[2,6-(<i>i</i>-Pr)₂PhN=C(CH₃)₂(C₅H₃N)}Cr-(μ-Cl)₂Al(CH₃)₂ (2.6)	411
Preparation of {2,6-[2,6-(<i>i</i>-Pr)₂PhN=C(CH₃)₂(C₅H₃N)}- CrCH₃.0.5(hexane) (2.7).....	422
Preparation of {[η⁴-{2,6-[2,6-(<i>i</i>-Pr)₂PhN=C(CH₃)₂(C₅H₃N)}- Al₂(<i>i</i>-Bu)₃(μ- Cl)]Cr(η⁶-C₇H₈)} .0.66(hexane) (2.8)	422
Polymerization.....	433
X-ray Crystallography.....	433
Results and Discussion.....	544
Polymerization Results	67
Conclusion	70
Reference	71
Chapter 3: Dinitrogen Activation, Partial Reduction, and Formation of Coordinated Imide Promoted by a Chromium Diiminepyridine Complex. ...	76
Introduction.....	77
Experimental Section.....	78
Preparation of {2[2,6(<i>i</i>-Pr)₂PhN=C(CH₃)₂]₆[2,6(<i>i</i>- Pr)₂PhNC=CH₂](C₅H₃N)}Cr(THF) (3.1)	79

Preparation of $\{[2,6-[2,6-(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]_2(\text{C}_5\text{H}_3\text{N})\}\text{Cr}(\text{THF})_2(\mu\text{-N}_2)\cdot\text{ether}$ (3.2)	79
Preparation of $[2,6-[2,6-(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]_2(\text{C}_5\text{H}_3\text{N})\}\text{Cr}(\text{THF})][2,6-(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]-6-[2,6-(i\text{-Pr})_2\text{PhNC}=\text{CH}_2](\text{C}_5\text{H}_3\text{N})\}\text{Cr}(\text{THF})(\mu\text{-N}_2\text{H})(\mu\text{-Na})_2$ (3.3)	80
Preparation of $\{2-[2,6-(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]-6-[2,6-(i\text{-Pr})_2\text{PhNC}=\text{CH}_2](\text{C}_5\text{H}_3\text{N})\}\text{Cr}(i\text{-NH})[\text{Na}(\text{THF})]$ (3.4)	81
Degradation of 3.4 and Isolation of NH_4BPh_4	82
X-ray Crystallography	82
Results and Discussion	89
Electronic Structure of Mononuclear Chromium Complexes	91
Calculation	93
Dinitrogen Activation	95
Electronic Structure of Dinuclear Chromium Complexes	97
Cleavage of Dinitrogen	99
Conclusions	103
Reference	104
Chapter 4: Dinitrogen Partial Reduction by Formally Zero- and Divalent Vanadium Complexes Supported by the Bis-iminopyridine System.	108
Introduction	109
Experimental Section	110
Preparation of $[2,6-\{[2,6-(i\text{-Pr})_2\text{C}_6\text{H}_5]\text{N}=\text{C}(\text{CH}_3)\}_2(\text{C}_5\text{H}_3\text{N})\text{V}]_2(\mu\text{-N}_2)\cdot(\text{hexane})$ (4.1)	110
Preparation of $\{[2,6-(i\text{-Pr})_2\text{C}_6\text{H}_5]\text{N}=\text{C}(\text{CH}_3)\}_2(\text{C}_5\text{H}_3\text{N})\text{V}(\text{THF})\}\text{Cl}\cdot 1.5\text{Tol}$ (4.2)	111
Preparation of $[2,6-\{[2,6-(i\text{-Pr})_2\text{C}_6\text{H}_5]\text{N}=\text{C}(\text{CH}_3)\}_2(\text{C}_5\text{H}_3\text{N})\text{V}]_2(\mu\text{-N}_2)\cdot(\text{hexane})$ (4.3)	111
X-ray Crystallography	111
Results and Discussion	115
Conclusion	121
References	122
Chapter 5: Isolation of a Self-Activating Ethylene Trimerization Catalyst.	125
Introduction	126
Experimental Section	127
Preparation of $[\{\eta^5\text{-}2,3,4,5\text{-Me}_4\text{C}_4\text{N}(\text{AlClMe}_2)\}_2\text{Cr}]$ (5.1)	12727
Preparation of $[\{\eta^5\text{-}2,3,4,5\text{-Me}_4\text{C}_4\text{N}(\text{AlMe}_2\text{Cl})\}\text{CrMe}(\mu\text{-NPh})_2\text{AlMe}_2][\text{Me}_3\text{Al}(\text{THF})]$ (5.2)	12828
Preparation of $[\{\eta^5\text{-}2,3,4,5\text{-Me}_4\text{C}_4\text{N}(\text{AlClMe}_2)\text{Cr}\}_2(\mu\text{-Me})_2]$ (5.3)	129

Polymerization / Oligomerization:	12929
X-ray Cryatallography	130
Resuts and Discussion	133
Conclusion	145
Reference	14646
Chapter 6: Dinitrogen Coordination and Cleavage Promoted by Vanadium and Titanium Complexes of a σ,π,σ- Donor Ligand: Partial Hydrogenation, and Silylation.	
Introduction	150
Experimental Section	153
Preparation of 2, 5-[(C ₆ H ₅) ₂ C(OH)] ₂ (N-Me-pyrrole)	15454
Preparation of 2,5-[(2-pyrrolyl) (C ₆ H ₅) ₂ C] ₂ (MeNC ₄ H ₂)(MeTPH ₂)	15555
Preparation of [(MeTP)VCl(THF)].THF (6.1)	15555
Preparation of [(MeTPH ₂)V(THF)].(C ₇ H ₈) _{0.5} (6.2)	156
Preparation of [(MeTP)V(μ -N ₂)].(C ₇ H ₈) _{2.9} (6.3)	15656
Preparation of [(MeTP)V] ₂ (μ -N)].(THF) (6.4)	15656
Degradation of 6.4.....	157
Preparation of [Na(dme) ₃] ₄ {LNa} ₂][(LTi) ₂ (μ -N) ₂].2dme (6.5).....	15757
Degradation of 6.5.....	15858
Preparation of [Na(DME) ₃] ₄ [LNa] ₂ [LTi(N) ₂ TiL](DME) ₂ (6.6).....	15959
Preparation of [Na(dme) ₃] ₂ [(LTi) ₂ (μ -N) ₂] (6.7)	15959
Preparation of LTiNSiMe ₃ (6.8)	16060
X-ray Crystallography.....	16161
Results and Discussion.....	167
Conclusion	180
Reference	181

List of Common Abbreviations.

<i>Acac</i>	acetylacetonato
Å	angstrom
atm	atmosphere
oC	degrees Celsius
Calcd.	Calculated
cm-1	wave number
Cp	cyclopentadienyl
δ	chemical shift
D _{calcd}	calculated density
Et	ethyl
EP	ethylene propylene elastomers
EPDM	ethylene propylene diene elastomers
F ₀₀₀	electronic density
FTIR	Fourier transform infrared spectroscopy
F.W.	Formula weight
g	grams
G.o.F	goodness of fit
GPC	gel permeation chromatography
h	hour
<i>i</i> -Pr	isopropyl
K	Kelvin
kg	kilograms
L	ligand

μ_{calcd}	absorption coefficient
μ_{eff}	effective magnetic moment in Bohr magnetons
M	molar
MAO	methylalumoxane
mM	millimolar
Me	methyl
min	minute
ml	milliliter
mmol	millimole
m.p.	melting point
NMR	nuclear magnetic resonance
ORTEP	Oak Ridge thermal ellipsoid program
PD	polydispersity(M_w/M_n)
Ph	phenyl
ppm	parts per million
R	alkyl group (found in reaction schemes)
R	reliability factor (ceystallographic tables)
T	temperature
THF	tetrahydrofuran
Me_3Al	trimethylaluminium
X	halogen
XRD	X-ray diffraction
TMS	tetramethylsilane
TMA	trimethylaluminum

List of Figures.

Figure 2.1	Thermal ellipsoid plot for 2.1 with ellipsoids drawn at the 50 % probability level.	38
Figure 2.2	Thermal ellipsoid plot for 2.2 with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.	39
Figure 2.3	Thermal ellipsoid plot for 2.3 with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.	40
Figure 2.4	Thermal ellipsoid plot for 2.5 with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.	43
Figure 2.5	Thermal ellipsoid plot for 2.6 with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.	45
Figure 2.6	Thermal ellipsoid plot for 2.7 with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.	45
Figure 2.7	Thermal ellipsoid plot for 2.8 with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.	47
Figure 2.8	Gel permeation chromatograms of selected polymer samples.	50
Figure 3.1	Thermal ellipsoid plot for 3.1 with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.	73
Figure 3.2	Calculated (♦) C=N and C _{im} -C _{py} distances for complexes 3.1 , 2.1 , 2.3 and 3.4a/3.4b , compared to reference values (●) for the transfer of zero to three electrons. ¹³ⁱ	76
Figure 3.3	Thermal ellipsoid plot for 3.2 with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.	77

Figure 3.4	Thermal ellipsoid plot of 3.3 with ellipsoids drawn at 50% probability. Hydrogen atoms have been omitted for clarity.	78
Figure 4.1	Thermal ellipsoid plot of 4.1 with ellipsoids drawn at 50% probability. Hydrogen atoms have been omitted for clarity.	98
Figure 4.2	Thermal ellipsoid plot of 4.2 with ellipsoids drawn at 50% probability. Hydrogen atoms have been omitted for clarity.	100
Figure 4.3	Thermal ellipsoid plot of anion of 4.3 with selected ellipsoids drawn at 50% probability. Hydrogen atoms have been omitted for clarity.	101
Figure 4.4	Observed and <i>calculated</i> bond lengths (Å) for complexes 4.1 ($S = 1$) and 4.3 ($S = 0$).	103
Figure 5.1	Thermal ellipsoid plot of 5.1 with selected ellipsoids drawn at 50% probability. Hydrogen atoms have been omitted for clarity	116
Figure 5.2	Thermal ellipsoid plot for 5.2 with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.	118
Figure 5.3	Thermal ellipsoid plot for 5.3 with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.	120
Figure 6.1	Thermal ellipsoid plot for 6.1 with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity	148
Figure 6.2	Thermal ellipsoid plot for 6.2 with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity	149
Figure 6.3	Thermal ellipsoid plot for 6.3 with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity	150
Figure 6.4	Thermal ellipsoid plot for 6.4 with ellipsoids drawn at the 50	151

	% probability level. Hydrogen atoms have been omitted for clarity	
Figure 6.5	Thermal ellipsoid plot for 6.5 with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity	154
Figure 6.6	Thermal ellipsoid plot for 6.6 with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity	155
Figure 6.7	Thermal ellipsoid plot for 6.8 with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity	156

List of Tables

Table 2.1	Crystal Data and Structure Analysis Results for 2.1 - 2.8	45
Table 2.2	Selected Bond Distances (Å) and Angles (deg) for 2.1 - 2.8	47
Table 2.3	Comparative Bond Distances (Å).	66
Table 2.4	Ethylene polymerization results.	69
Table 3.1	Crystal Data and Structure Analysis Results for 3.1 – 3.3	84
Table 3.2	Selected Bond Distances (Å) and Angles (deg) for 3.1 - 3.3	85
Table 3.3	Calculated and Observed Bond Lengths for Mononuclear Chromium Complexes	92
Table 4.1	Crystal Data and Structure Analysis Results for 4.1 – 4.3	113
Table 4.2	Selected Bond Distances (Å) and Angles (deg) for 4.1 - 4.3	114
Table 5.1	Crystal Data and Structure Analysis Results for 5.1 – 5.3	131
Table 5.2	Selected Bond Distances (Å) and Angles (deg) for 5.1 – 5.3	132
Table 5.3	Ethylene polymerization by 5.1 and 5.2	137
Table 5.4	Ethylene oligomerization by 5.3.[a]	140
Table 5.5	Calculated thermodynamic parameters. [a]	143
Table 6.1	Crystal Data and Structure Analysis Results for 6.1 – 6.4.	163
Table 6.2	Crystal Data and Structure Analysis Results for 6.5 – 6.8.	164
Table 6.3	Selected Bond Distances (Å) and Angles (deg) for 6.1- 6.4.	165
Table 6.4	Selected Bond Distances (Å) and Angles (deg) for 6.5- 6.8.	166

Chapter 1-Introduction

Introduction

Characteristics of Transition Metal complex Catalysts

In the early development of the science of microbiology, researchers came to the realization that many specific cellular functions are regulated by enzymatic reactions, which could be described as mother nature's own catalysts. Many of these enzymes were revealed to be dependent on transition metals to render the high efficiency and high selectivity of the thousands of reactions that occur daily, under mild conditions, in living organisms. These catalytic reactions span a wide range of uses, from the most spectacular transformation of solar energy into chemical energy, as in the photosynthetic systems found in the plant kingdom mediated by manganese porphyrin complexes, to the transformations of atmospheric dinitrogen into ammonia by a complex series of reactions mediated by iron/sulphur and molybdenum/sulphur cluster-based enzymes and co-enzymes found in certain types of bacteria.¹

These naturally occurring catalysts have inspired the industrial use of catalysts to accelerate industrial process to promote a wide variety of chemical reactions. In this context, the catalyst can be more specifically defined as a substance in which a transition metal complex serves as an active site that will influence the rate of the reaction and reduce the activation energy barrier without itself being consumed during the reaction. The catalyst can therefore also be considered as both a reactant and a product.

Catalysts are classified as belonging to two major categories namely, homogeneous and heterogeneous. Transition metal complexes are in the greater scheme of things, classified as homogeneous catalysts, and have certain advantages over heterogeneous catalysts such as metal and metal oxides. High catalytic activity is the most common advantage displayed by homogeneous catalysts. The heterogeneous catalyst usually activated the substrate via surface high-reactivity that in turn allows specific reactions to occur even in the absence of solvent. One of the many advantages of the heterogeneous catalyst lies simply in the fact that they are relatively easy to prepare, inexpensive and may work even in the absence of solvent. In addition, these catalysts are thermally robust and less sensitive to "poisoning" or decomposition when compared to the homogeneous early transition metal complex catalysts. However, the fact that

heterogeneous catalyst in nature directly depend on physical and chemical structure of the surface, makes the study of catalytic reaction difficult to characterize.

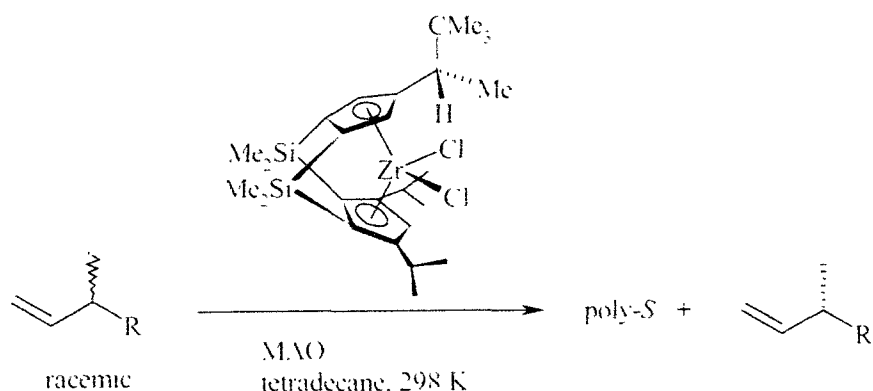
The homogeneous catalytic systems, on the other hand, have a great advantage that their discrete molecular structure can be monitored and characterized in the dynamic catalytic process. In order to characterize the catalytically active species, a wide variety of spectroscopic methods have been developed to describe the structure and nature of transition metal complexes. Major advances in the field of organometallic chemistry have come about since the advent of single crystal X-ray structural analysis, which plays an important role in revealing the structure of transition metal complexes. The structures obtained from X-ray diffraction studies enable organometallic chemists to determine transition metal complex geometries including bond distances and bond angles, yielding important information on how ligand's features affect the catalytic process. This possibility turns out to be particularly important in the case of paramagnetic complexes where nuclear magnetic resonance spectroscopy not always allows unambiguous conclusions.

The catalytic processes originally targeted by this thesis work were polymerization and oligomerization of olefins mediated by vanadium, chromium and iron organometallic complexes supported by nitrogen donor based ligand systems. We were particularly interested in investigating the role of low oxidation state vis-à-vis the selectivity of the particular catalytic behavior of these elements. These findings are presented and discussed in Chapter 2, 3 and 4. The enormous reactivity of the low oxidation states makes of course possible molecular activation processes which, albeit interesting, may detract from the target of finding catalytic behavior. As a matter of fact, we have encountered with these three metals during this thesis work examples of activation, cleavage and protonation of dinitrogen. This was also largely anticipated and since our laboratory has a long-lasting interest in dinitrogen activation chemistry, this behavior was also regarded as worth of investigating. These findings are discussed in chapter 5 and 6.

As mentioned above, homogeneous catalysis opens the door to endless synthetic possibilities to tune and induce selectivity by choosing the right metal in the appropriate oxidation state. By allowing detailed mechanistic studies, a homogenous system allows to

tailor suitable supporting ligand systems, a feature which is less accessible despite recent advances in surface organometallic chemistry. Among many examples of diversified reactivity existing in the literature about tunable selectivity of homogeneous catalysts, a particularly good example is provided by the kinetic resolution of racemic 3-substituted α -olefins with zirconocene catalysts² (Scheme 1.1) as enabled by the judicious design of the steric environment.

Scheme 1.1 Example of the Tunable Selectivity of a Homogeneous Catalyst



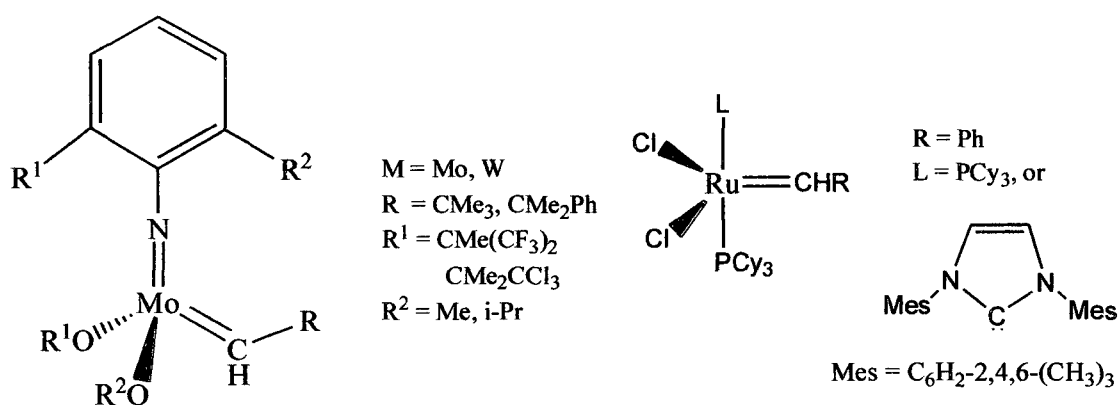
Ziegler-Natta Polymerization Catalysts

The discovery by Ziegler and Natta in the 50's concerning the ability of a catalytic mixture of $\text{MCl}_x/\text{AlEt}_3$ ($\text{M} = \text{Ti, Zr, V}$; $x = 3, 4$) to produce large amount of high value polymers from inexpensive α -olefin had an enormous impact in the literature and directly affected our modern lifestyle. Since then, this great catalytic process has been the target of a tremendous amount of research. Earlier developments in this field include the synthesis of stabilized group IV metallocenes in high oxidation states developed for polymerization in the late 1970's, and the well-known constrained geometry catalysts.³ In combination with the development of novel co-catalysts such as methylalumoxane⁴ and "cationizing" reagents such as $\text{Na}[\text{B}\{3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3\}_4]$ or $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ ⁵ a phenomenal increase of activity, extended catalyst life, control over polymer molecular weight distributions have been obtained.

Research in the development of this field has grown towards synthesizing catalysts that can tailor polymer properties. Competing with other methods of

polymerization, such as ring opening olefin metathesis (ROMP) based on the molybdenum (VI) Schrock type catalysts⁶ or the ruthenium (IV) Grubbs type catalysts (scheme 1.2),⁷ the field of cationic Ziegler –Natta polymerization catalyst design is today gearing towards the synthesis of new organometallic complexes having the capacity of inserting functionalized monomers in order to synthesize novel polymers tailored to specific industrial needs .

Scheme 1.2 ROMP Catalysts

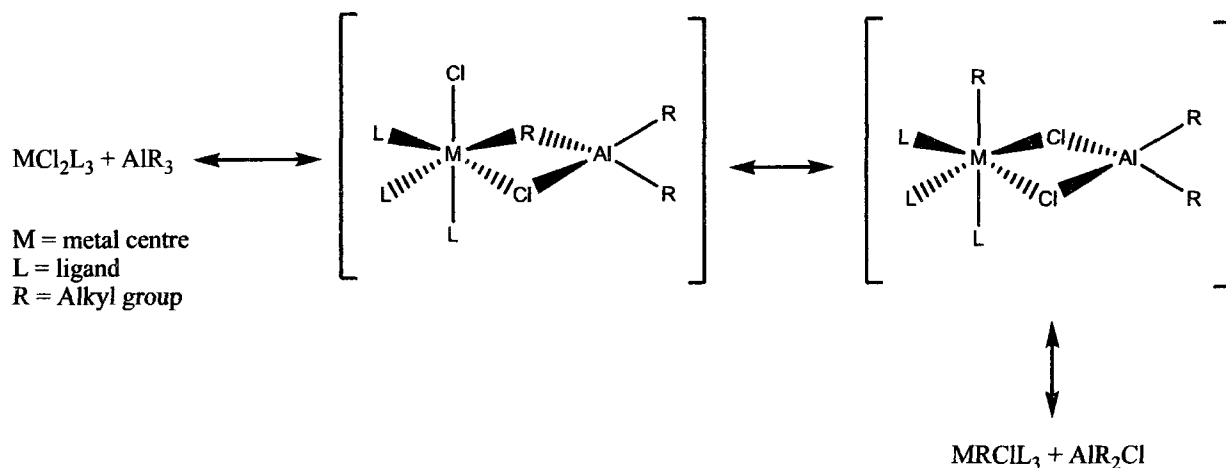


Schrock –type Catalyst

Grubbs-type Catalyst

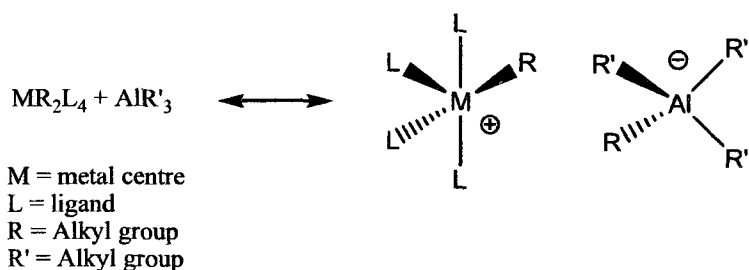
Conventional cationic Ziegler-Natta polymerization systems are based on electron- deficient group IV metals such as Ti (IV) and Zr (IV). Organometallic complexes synthesized for polymerization have strong Lewis acid properties and require a co-catalyst for two purposes. The first is to alkylate the metal centre in the case where the complex does not bear any alkyls to initiate chain growth (Scheme 1.3)

Scheme 1.3 Alkylation of a catalyst by the co-catalyst



The second is to cationize the metal centre to coordinate α -olefins, an important intermediate step discovered by Jordan in the mid 80's and improved by other groups (Scheme 1.4). Subsequently, Erker's group⁵ had demonstrated that the formation of the cation can not only be obtained with the use of an aluminium-based co-catalyst but also by using a borane based reagent, to form an analogous species in solution.

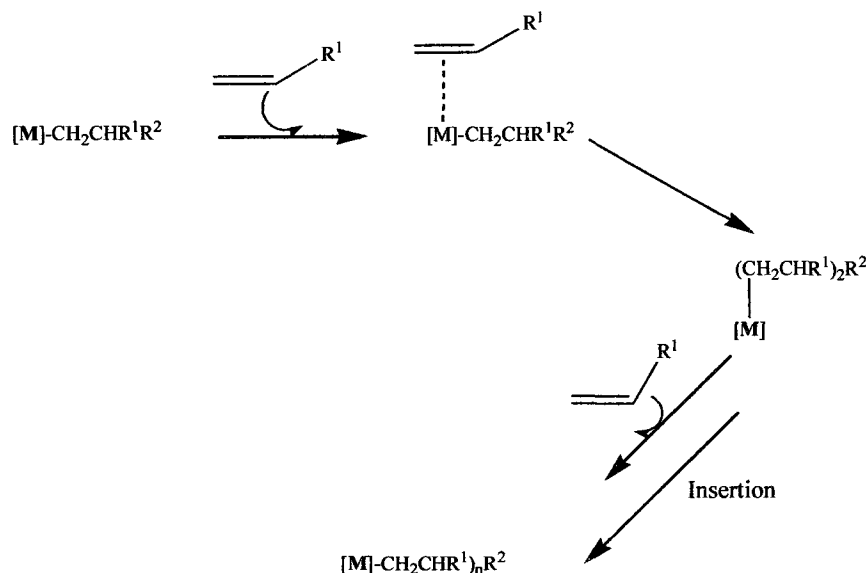
Scheme 1.4 Formation of the Cationic Catalytic Species



It is generally agreed that the initial insertion of α -olefin into the metal-carbon bond occurs through coordination of the olefin at the empty coordination site of the organometallic complex. Migration of the alkyl to the olefin follows forming an alkyl chain augmented by a minimum of two carbons depending on which α -olefin

is inserted (Scheme 1.5). Subsequent insertions of the olefin into the growing alkyl propagate the chain (Scheme 1.4) until chain termination events occur through processes such as β -H elimination or chain transfer.

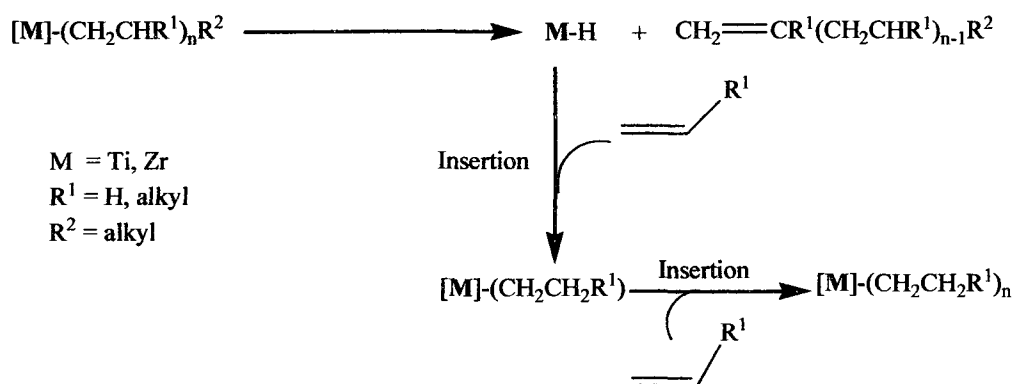
Scheme 1.5 Initial Olefin Insertion in to the Metal – Carbon Bond



The key to high chain propagation and therefore to high molecular weight fractions lies in the stability of the metal-carbon bond and how susceptible the complex is to β -H elimination of the growing alkyl chain. Once the alkyl chain has undergone β -H elimination, olefin insertion can continue via insertion into the metal-hydrogen (Scheme 1.6) until the catalyst is deactivated or chain termination occurs once again.

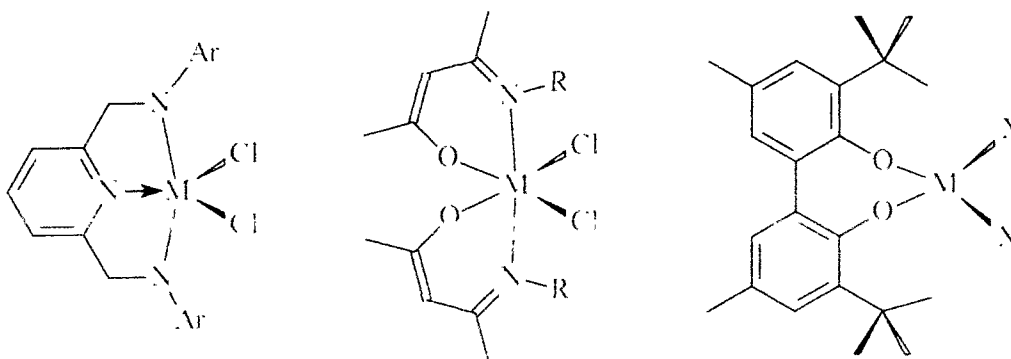
Given the tremendous activity of Cp-based group IV catalysts towards α -olefin polymerization, development of novel supporting ligand systems has been a growing field of research since the original discovery. Good alternatives to the cyclopentadienyl systems were obtained with the oxygen and nitrogen donor based ligands, that can be related by isolobality to the Cp anions. These “alternative” ligands have demonstrated to possess activities quite comparable to those displayed by the metallocenes.

Scheme 1.6 Chain Termination through β -H Elimination.



Examples of successful group IV transition metal catalysts supported by oxygen/nitrogen ligand systems are highlighted in scheme 1.7⁶

Scheme 1.7 Alternative Group iv Catalysts to the Conventional Metallocenes.⁶

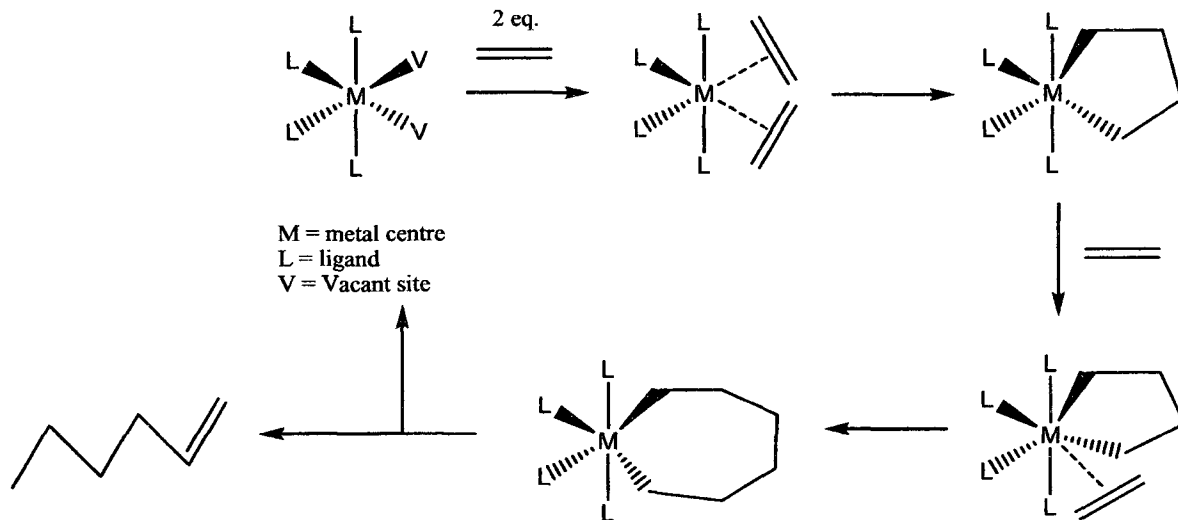


M = Ti, Zr, Hf.

Ethylene Oligomerization

The search for finding new olefin polymerization catalysts led to the unexpected discovery of selective ethylene trimerization to 1-hexene by Manyik in 1967⁷. In a patent related to olefin polymerization with homogeneous chromium catalyst based on mixture of $\text{Cr}(\text{octanoate})_3$ and $(\text{Al}^i\text{Bu}_2)_2\text{O}$, a small amount of 1-hexene and branched decene isomers were isolated along with polymer. The ethylene concentration dependence of the 1-hexene product was later reported to be second order⁸ while the polymer product was first order, in ethylene indicating different mechanisms for the formation of the two products. Based on this evidence, the authors proposed that 1-hexene is produced by an unprecedented metallacycle mechanism. (scheme 1.8) However the paramagnetic nature of chromium limited any mechanistic analysis at that time, and no further progress in understanding ethylene trimerization catalysis was made for another 25 years. Yet convenient and useful catalytic processes have been developed and patented. A process producing Shultz-Flory⁹ distribution of α -olefins ranging from C_4 - C_{20} (eg. SHOP¹⁰ process) was patented by Shell although the production remains rather inconvenient, as a sophisticated distillation is required in order to adequately separate the desired fractions. The highest market demand is currently for 1-butene, 1-hexene and 1-octene. While satisfactory processes for production of 1-butene are conveniently available by using Ni-based catalyst systems, a selective system for producing 1-hexene has been commercialized by Chevron Phillips in Qatar based on a pyrrole/chromium/aluminate system.

Scheme 1.8 Manyik Metallacycle Mechanism

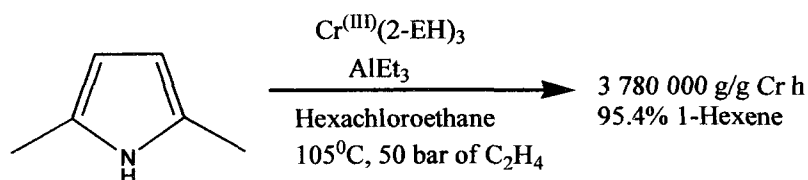


Development of Oligomerization Catalyst

Since the original discovery of selective oligomerization, a tremendous increase in interest geared towards the direction of developing commercial catalyst resulting over 200 patents since 1987. In 2004 John Dixon of Sasol Technology published the most comprehensive review of both patent and academic literature to date.¹¹

Reagan described in a patent in 1971 the reaction of sodium pyrrolide with different stoichiometric ratios of Cr^{II} and Cr^{III} reagents obtaining a selective and active catalytic system for ethylene trimerization.¹² Even though the complexes generated from the catalytic mixture were not characterized, they all had one feature in common which is all these complexes performed oligomerization in the presence of ethylene and various alkylating agents. Subsequently, the Phillips company utilized 2-5 dimethylpyrrole, along with $[\text{Cr}^{\text{(III)}}(2\text{-EH}_3)]$ (2-EH = 2-Ethylhexanoate) which would soon become a standard source of Cr for oligomerization catalyst. This system produced 156 666 (g/g.Cr.h) at 115°C with 93% yield of 1-hexene.¹³ Furthermore, the activity of this system was optimized by the judicious use of activator and additives to be one of the most active catalyst for 1-hexene production to date (scheme 1.9).¹⁴

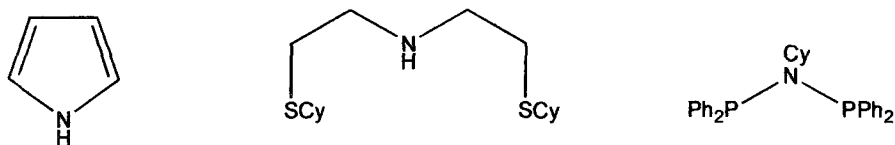
Scheme 1.9 Optimized Philips system



The interest in selective olefin trimerization catalysts has been increasing in the recent past. This can be visualized by the number of patents and publications for selective catalysts filed each year.¹⁵

Even though there were trimerization catalyst based on titanium and tantalum reported^{16,17,18} chromium-based catalysts are the most preferred in industry since they have some synthetic advantages. For example, the polymer byproduct of the chromium system is a soluble low MW PE, while titanium catalyst produced a significant quantity of insoluble HDPE.¹⁹ There are many patents for chromium trimerization catalyst based on large variety of ligand such as pyrrole, SNS, PNP. (scheme 1.10)^{20,21,22,23,24,25}

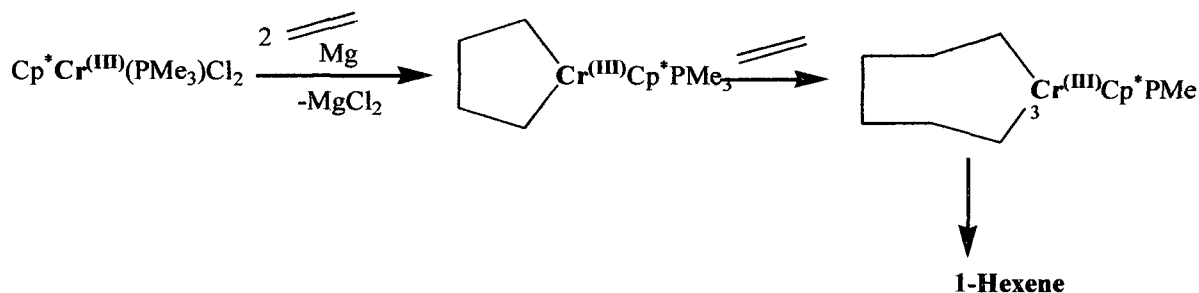
Scheme 1.10 Pyrrole, SNS and PNP based trimerization catalyst.



Later on, a significant amount of research has been directed towards theoretical and experimental mechanistic studies aiming at understanding the selectivity of the oligomerization process. The primary tasks are understanding the mechanism of the catalytic cycle and nature of the catalytic intermediates. Jolly and co-workers have

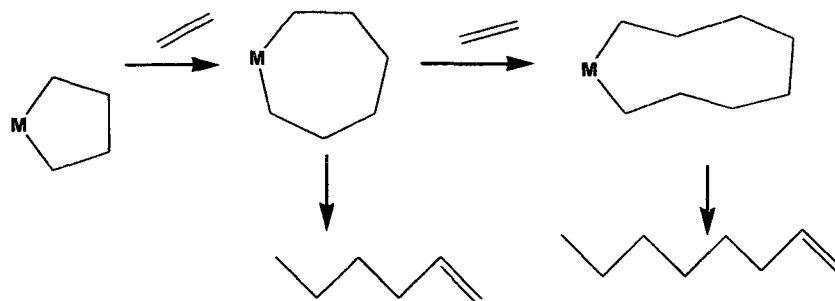
studied the reactivity of model chromacyclopentane and chromacycloheptane complexes and provided compelling evidence for the chromium (I-III) redox couple being responsible for the selectivity. (scheme 1.11)²⁶ A major drawback of the choice of $\text{Cp}^*\text{Cr}(\text{III})(\text{PMe}_3)_2\text{Cl}_2$ as a model for mechanistic studies of ethylene trimerization is that they are not catalytically active. A major breakthrough was recently made in our group by isolating and characterizing catalytically active species from an actual selective chromium trimerization catalytic cycle.²⁷

Scheme 1.11 Jolly's Chromocycle Model



SASOL research group discovered an outstanding chromium diphosphine catalyst capable of producing octene in 70% yield. This discovery brings to question the possibility that the original metallacycle mechanism²⁸ might also “extend” to metallocyclononane (scheme 1.12) to rationalize the formation of octene. This extended metallacycle mechanism was supported by related isotopic labelling studies of some non selective chromium oligomerization catalyst.^{29,30}

Scheme 1.12 The “extended” metallacycle mechanism



In the process of polymerization, elements such as Ti, Zr, V, Cr and Fe are the most preferred for their activity, performance and rheology of the polymer produced. Instead all the academic and patent literature of ethylene oligomerization is largely dominated by chromium. With the exception of zirconium, all these elements may easily span a large range of oxidation states, therefore raising question about the true state of the catalytically active species. In turn, addressing this point would enable a more rational targeting of new catalysts of high activity and selectivity. Given the common belief that a selective oligomerization process proceeds via preliminary reduction of the metal center followed by oxidative coupling of two molecules of ethylene, it is conceivable that a low oxidation state might be the critical state of the catalytically active species. For this reason we have focused with this thesis work on the preparation and characterization of metal complexes of V, Cr, and Ti with appropriate ligand systems for a broad-scoped investigation with several activator. Reduction was of course much anticipated as well as the possibility of parallel nitrogen activation processes. Also common reductant different from the traditional alkyl aluminum activators have in fact be widely probed in this thesis work. Finally, we have mainly focused, as ligand systems, on molecules that were already known to support outstanding catalytic behavior although no clear idea was available in the literature with the purpose of elucidating which makes these ligands so performing. The rationale for the use of each of these ligands is offered in each chapter detailing the findings.

References

1. Georgiadis, M. M.; Komiya, H.; Chakrabarti, P.; Woo, D.; Kornuc, J. J.; Rees, D. *C. Science* **1992**, *257*, 1653.
2. a) Herzog, T. A.; Zubris, D. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 11988
b) Veghini, D.; Henling, L. M.; Burkhardt, T. J.; Bercaw, J. E. *J. Am. Chem. Soc.*, **1999**, *121*, 564.
3. a) Bochman, M. *J. Chem. Soc. Dalton Trans.* **1996**, 255.
b) Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Reiger, B.; Waymouth, R.M.; *Angew. Chem.* **1995**, *107*, 1255.
c) Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Reiger, B.; Waymouth, R.M. *Angew. Chem.* **1995**, *34*, 1143.
(d) Mohring, P. C.; Coville, N. J. *J. of Organomet, Chem.* **1994**, *479*, 1.
(e) Guptha, V. K.; Satish, S.; Bhardwaj I. S. *Rev. Macromol. Mol. Chem. Phys.C*, **1994**, *34*, 439.
d) Kaminsky, W. *J. chem.. Soc. Dalton Trans.* **1998**, 1413.
e) Soga, K.; Shiono, T. *Prog. polym. Sci.* **1997**, *22*, 1503.
f) Jordan, R.F. *Adv. Organomet. Chem.* **1991**, *32*, 325.
4. Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 39205.
a) Temme, B.; Erker, G.; Karl, J.; Luftmann, H.; Frohlich, R.; Kotila, S.; *Angew Chem*, **1995**, *107*, 1867.
b) Temme, B.; Erker, G.; Karl, J.; Luftmann, H.; Frohlich, R.; Kotila, S.; *Angew Chem, Int Ed. Engl.* **1995**, *34*, 1755.
c) Temme, B.; Erker, G.; Karl, J. *Chem. Eur. J.* **1995**, *2*, 919.
d) Erker, G.; Karl, J.; *Chem. Eur. J.* **1997**, *130*, 1261.
6. a) Schaverien, C. J. *J. Mol. Catal.* **1994**, *90*, 177-183.
b) *Chem. Eng. News.* **1978**, *56(31)*, 24.
c) Pelletier, J. F.; Mortreux, A.; Petit, F.; Olonde, X.; Bujadoux, K. *stud. Surf. Sci. Catal.* **1994**, *89*, 249.
7. Manyik, R.; walker, W.; Wilson, T. *US Pat.* 3300458, **1967**.
8. Manyik, R.; walker, W.; Wilson, T. *Journal of Catalysis* **1977**, *47*, 197.

9. a) Flory, P. J. *J. Am. Chem. Soc.* **1940**, 62, 1561.
 b) Schulz, G. V. *Z. Phys. Chem. Abt. B.* **1939**, 43, 25.
 c) Schulz, G. V. *Z. Phys. Chem. Abt. B.* **1935**, 30, 379.
10. Thomas, J. M.; Thomas, W. J. *Principals and Practice of heterogeneous Catalysis* VCH; Weinheim, **1997**.
11. Dixon, J. T.; Green, M. J.; Hess, F. M.; Morgan, D.H. *J. Organomet. Chem.* **2004**, 689, 3641.
12. Regan, W. K. EU Pat. 0417 477 (Phillip Petroleum Company), **1991**.
13. Freeman, J. W.; Buster, J. L.; Knudsen, R. D. US Pat. 5 856 257 (Phillip Petroleum Company), **1999**.
14. Araki, Y.; Nakamura, H.; Nanba, Y.; Okanu, T. US Pat. 5 856 612 (Mitsubishi Chemical Company), **1994**.
15. Dixon, J. T. et al., *Journal of Organometallic Chemistry*, **2004**, 689(23), 3641.
16. Deckers, P.; Hessen, B.; Teuben, J. *Angew. Chem, Int Ed. Engl.* **2001**, 40, 2516.
17. Murtuza, S.; Harkins, S.; Long, G.; Sen, A. *J. Am. Chem Soc* **2000**, 122, 1867.
18. Andes, C.; Harkins, S.; Murtuza, S.; Oyler, K.; Sen, A. *J. Am. Chem Soc* **2001**, 123, 7423.
19. Kohn, R.; Haufe, M.; Kociok-Kohn, G.; Grimm, S.; Wasserscheid, P.; Keim, W. *Angew. Chem, Int Ed. Engl.* **2000**, 39, 4337.
20. Hagen, H.; Kretschmer, W.; Van Buren, F.; Hessen, B.; Van Oeffelen, D. *J. of Molecular catalysis a- chemical* **2006**, 248, 237.
21. McGuinness, D.; Wasserscheid, P.; Keim, W.; Morgan, D.; Dixon, J.; Bollmann, A.; Maumela, H.; Hess, F.; Englert, U. *J. Am. Chem Soc.* **2003**, 125, 5272.
22. McGuinness, D.; Wasserscheid, P.; Morgan, D.; Dixon, J.; *Organometallics* **2005**, 24, 552.
23. Agapie, T.; Day, M. W.; Henling, L. M.; Labinger, J. A.; Bercaw, J. E.; *Organometallics* **2006**, 25, 2733.
24. Tkach, V. S.; Suslov, D. S.; Myagmarsuren, G.; Shmidt, F. K. *Russian Journal of Applied Chemistry* **2007**, 80, 1419.
25. Zhang, J.; Braunstein, P.; Hor, T. S. A. *Organometallics* **2008**, 27, 4277.
26. Emrich, R.; Heinemann, O.; Jolly P.; Kruger, C.; Verhovnik, G. *Organomettalics* **1997**, 16, 1511.

27. Jabri, A.; Mason, C. B.; Sim, Y.; Gambarotta, S.; Burchell, T. J.; Duchateau, R. *Angew. Chem. Int. Ed.* **2008**, *47*, 9717.
28. Bollmann, A.; Blann, K.; Dixon, J.; Hess, F.; Killian, E.; Maumela, H.; McGuinness, D.; Morgan, D.; Neveling, A.; Otto, S.; Overett, M.; Slawin, A.; Wasserscheid, P.; Kuhlmann, S. *J. Am. Chem Soc.* **2004**, *126*, 14712.
29. McGuinness, D. S.; Suttill, J. A.; Gardiner, M.G.; Davies, N. W. *Organometallics* **2008**, *27*, 4238.
30. Tomov, A.; Chirinos, J.; Jones, D.; Long, R.; Gibson, V. *Am. Chem Soc.* **2005**, *127*, 10166.

***Chapter 2:* Reactivity of Chromium Complexes of a
Bis(imino)pyridine Ligand: Highly Active Ethylene
Polymerization Catalysts Carrying the Metal in a
Formally Low Oxidation State**

(Published in *Organometallics* **2007**, 26, 3201)

Introduction

Chromium is the key element in the silica-supported Phillips¹ and Union Carbide² catalytic systems commercially used for the polymerization of olefins. The importance of these catalysts has provided a compelling rationale for the development of homogeneous Cr(III) catalysts supported by a variety of ligands, including both cyclopentadienyl-based³ and non-cyclopentadienyl-based systems.⁴⁻¹⁰ These catalyst precursors are usually well-defined, and yet the metal oxidation state of the catalytically active species remains debatable, the most commonly accepted being either Cr(III) or Cr(II).

After the initial discovery by Brookhart and Gibson that bis- (imino)pyridine ligands enable high activity when coordinated to unconventional Ziegler-Natta metals,¹¹ extensive investigations were undertaken to unveil the properties of this fascinating ligand system.¹²⁻²⁹ Attempts to isolate possible active species gradually revealed the direct involvement of the ligand in a variety of transformations, including attack at the imino C atom^{14,16} or at any position of the pyridine ring,^{12,13b,14,16c,17} single^{17bc,18} or double deprotonation^{13b,14,19,20} of the imino methyl protons, and dimerization through either the ring meta C atoms^{13b,16c} or the imino methyl groups.^{13b,14,15,21} Perhaps most unusual was the possibility of storing up to three electrons in its delocalized δ system.¹⁸ This behavior allows the preparation of complexes in which the metal deceptively appears in unusual low oxidation states but where in reality the frontier orbitals are ligand-centered molecular orbitals.²¹ Therefore, the low valency of the metal in these complexes should be regarded as purely formal. Remarkably, however, these species retain the high reactivity expected for a low-valent compound.^{21,22-26} The recurrence of dinitrogen fixation among these derivatives^{24,25} is the most compelling evidence of this behavior.

The ability of this ligand system to undergo facile electrontransfer processes is perhaps the key to understanding why reduction of the metal center occurs so readily upon alkylation^{12-14,26-28} or activation with Alalkyls^{13b,28a,b,29} without apparently affecting the catalytic activity of these derivatives. As mentioned above, the metal-to-ligand electron transfer does not necessarily imply quenching of the chemical reactivity. The “low-valent” Fe²⁶ and Co²⁸ complexes maintain the same high activity and polymer quality as the divalent precursors, suggesting the formation of an even lower valent

electron-rich catalytically active species. An exception to this trend involves vanadium,¹² whose facile reduction upon activation provides a deactivation pathway.

When tested in our laboratory, the Cr(III) bis(imino)pyridine complex displayed, upon activation with MAO at room temperature and under ethylene at atmospheric pressure, disappointingly low catalytic activity.^{13b} On the other hand, at higher temperatures and increased pressures of ethylene, Esteruelas⁹ and Small¹⁰ observed that the Cr(III) catalyst displays much higher, but varying, degrees of activity. On the basis of the results obtained with the Co and Fe analogues, it is possible that activation of the precursor with MAO involves an initial reduction to Cr(II). The Cr(II) derivative was also found to be catalytically active, initially as a polypropylene catalyst by Dow,³⁰ but also for ethylene polymerization by Small¹⁰ and Esteruelas.⁹ The observation by Esteruelas suggested that activation of the Cr(III) precursor does not involve reduction to Cr(II). However, by using UV-vis and analysis of the resulting polymers, Small et al. concluded that the Cr(II) and Cr(III) precursors generate the same active species after reaction with MAO. Attempts in our laboratory to elucidate the organometallic chemistry of the Cr(III) precursor with BzMgCl and AlMe₃ did indeed show a facile reduction toward divalent complexes.^{13b} While the alkylation with BzMgCl led to a slew of transformations, the reaction with AlMe₃ instead resulted in immediate reduction of the metal center. Both products were inactive, possibly suggesting that, similar to the case of vanadium, the reduction toward the divalent state is a catalyst deactivation pathway. However, the reactions were not carried out under polymerization conditions (e.g., alkylaluminum reagents) and it should be noted that the presence of ethylene may hinder reduction or promote different transformations.

Herein, we describe the reduction of the divalent 2,6-[2,6-(i-Pr)₂PhN=C(CH₃)]₂ (C₅H₃N)CrCl₂ catalyst precursor, affording reduced chromium species as might be present in the catalytic cycle and which display very high catalytic activity for ethylene polymerization.

Experimental Section

All operations were performed either under a nitrogen atmosphere using standard Schlenk techniques or in a purified nitrogen-filled drybox. The THF complexes of CrCl_3 and CrCl_2 were prepared according to the standard procedure. The ligand 2,6-[2,6-(*i*-Pr) $_2$ PhN=C(CH $_3$)] $_2$ (C $_5$ H $_3$ N),^{11,31} the complex {2,6[2,6 (*i*-Pr) $_2$ PhN=C(CH $_3$)] $_2$ (C $_5$ H $_3$ N)} CrCl_3 ,^{13b} LiCH $_2$ Si(CH $_3$) $_3$,^{3,32} and {2-[2,6-(*i*-Pr) $_2$ Ph N=C(CH $_3$)]-6-[2,6-(*i*-Pr) $_2$ PhN C=CH $_2$](C $_5$ H $_3$ N)}Cr(THF)(2.4)³³ were prepared according to published procedures. Solutions of 1.6 M MeLi in ether, 2 M AlMe $_3$ in toluene, and 10 wt % IBAO in toluene (purchased from Aldrich) and 10 wt % of MAO in toluene (purchased from Chemtura) were used as received. Infrared spectra were recorded on a Mattson 9000 and Nicolet 750-Magna FT-IR instrument from Nujol mulls prepared in a drybox. Samples for magnetic susceptibility measurements were weighed inside a drybox equipped with an analytical balance and sealed into calibrated tubes, and the measurements were carried out at room temperature with a Gouy balance (Johnson Matthey). Magnetic moments were calculated following standard methods, and corrections for underlying diamagnetism were applied to the data. NMR spectra were recorded with a Varian AMX-500 spectrometer. Elemental analyses were performed with a Perkin-Elmer 2400 CHN analyzer. Data for X-ray crystal structure determinations were obtained with a Bruker diffractometer equipped with a Smart CCD area detector.

Preparation of {2, 6-[2, 6-(*i*-Pr) $_2$ PhN=C(CH $_3$)] $_2$ (C $_5$ H $_3$ N)}CrCl $_2$ ·0.75THF (2.1)

A suspension of 2,6-[2,6-(*i*-Pr) $_2$ PhN=C(CH $_3$)] $_2$ -(C $_5$ H $_3$ N) (0.90 g, 1.87 mmol) and CrCl $_2$ (THF) $_2$ (0.50 g, 1.87 mmol) was refluxed in toluene (150 mL) overnight. The resulting purple solid was isolated by decanting the solution and washing with hexane. Excess fresh THF (200 mL) was added and the suspension boiled, followed by a hot filtration to obtain a clear purple solution. The purple solution was slowly cooled to room temperature, upon which time small purple crystals of **2.1** formed (1.07 g, 1.77 mmol, 95%). Anal. Calcd (found after drying) for C $_{33}$ H $_{43}$ N $_3$ Cl $_2$ Cr: C, 65.55 (65.48); H, 7.17 (7.12); N, 6.95 (6.91). IR (Nujol mull, cm $^{-1}$): ν 3081 (w), 3062 (w), 2910 (s), 2853 (s), 1587 (m), 1553 (s), 1528 (s), 1409 (w), 1318 (s), 1277 (s), 1253 (m), 1242 (w), 1210 (s), 1187 (m), 1148 (w), 1117 (w), 1103 (m), 1069 (s), 1057 (m), 1041 (m), 1025 (m), 984

(w), 937 (m), 909 (m), 839 (w), 817 (s), 809 (s), 800 (s), 780 (s), 762 (m), 741 (m), 725 (s), 694 (m). $\mu_{\text{eff}} = 3.6 \mu_{\text{B}}$.

Preparation of {2,6-[2,6-(*i*-Pr)₂PhN=C(CH₃)₂(C₅H₃N)]₂CrMe- (μ -Me)Li(THF)₃ (2.2)

A suspension of **2.1** (0.25 g, 0.41 mmol) in diethyl ether (20 mL) was cooled to -35 °C and treated with a cold solution of MeLi (0.54 mL, 0.87 mmol) in ether (1.6 M). The resulting dark greenish brown solution was warmed to room temperature overnight. The solvent was evaporated to dryness and the residue re-suspended in hexane (15 mL). Most of the solid dissolved, affording a dark greenish brown solution with a colorless precipitate. The supernatant was separated by centrifugation and stored at -35 °C for 2 days, at which time dark block like crystals of **2.2** were isolated (0.11 g, 0.14 mmol, 35% yield). Anal. Calcd (found) for C₄₇H₇₃CrLiN₃O₃: C, 71.73 (71.66); H, 9.35 (9.31); N, 5.34 (5.28). IR (Nujol mull, cm⁻¹): ν 2973-2845 (b, s), 1575 (s), 1493 (w), 1469 (s), 1377 (m), 1355 (w), 1332 (m), 1316 (m), 1280 (w), 1244 (s), 1204 (s), 1176 (w), 1143 (m), 1133 (m), 1100 (w), 1078 (m), 1044 (s), 990 (s), 935 (m), 887 (s), 872 (s), 839 (w), 807 (s), 776 (s), 748 (s), 730 (s), 715 (w), 693 (w), 662 (m), 646 (w). $\mu_{\text{eff}} = 4.24 \mu_{\text{B}}$.

Preparation of {2,6-[2,6-(*i*-Pr)₂PhN=C(CH₃)₂(C₅H₃N)]₂CrCl (2.3)

Method 1. A suspension of **2.1** (0.25 g, 0.41 mmol) with 2.2 equiv of NaH (0.022 g, 0.91 mmol) in THF (25 mL) was stirred at room temperature for approximately 4 days. During this time, the mixture changed from purple to dark green. After 4 days, the solvent was evaporated in vacuo and the solids were redissolved in toluene (20 mL). The dark green solution was centrifuged to remove a small amount of precipitate and concentrated to approximately 5 mL. Dark green crystals of **2.3** grew after standing at room temperature for 3 days (0.19 g, 0.34 mmol, 83% yield). Anal. Calcd (found) for C₃₃H₄₃N₃ClCr: C, 69.64 (69.59); H, 7.62 (7.61); N, 7.38 (7.40). IR (Nujol mull, cm⁻¹): ν 2854 (s), 1578 (w), 1501 (w), 1462 (s), 1377 (s), 1331 (w), 1315 (m), 1237 (s), 1185 (m), 1177 (m), 1106 (s), 1092 (s), 1024 (m), 948 (s), 827 (s), 756 (s), 727 (s), 693 (s). $\mu_{\text{eff}} = 3.57 \mu_{\text{B}}$.

Method 2. A suspension of $\{2,6-[2,6-(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]_2-(\text{C}_5\text{H}_3\text{N})\}\text{CrCl}_3$ (0.43 g, 0.67 mmol) in THF (15 mL) was reacted with NaH (0.05 g, 2.0 mmol) over a period of 1 week, during which time the mixture became dark green. After evaporation to dryness and addition of toluene, the dark green solution was centrifuged to remove a small amount of insoluble solid and allowed to stand at room temperature. Dark green crystals of **2.3** precipitated after approximately 3 days (0.076 g, 0.15 mmol, 22%).

Preparation of $\{2-[2,6-(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]-6-[2,6-(i\text{-Pr})_2\text{PhNC}=\text{CH}_2](\text{C}_5\text{H}_3\text{N})\}\text{Cr}(\mu\text{-Me})\text{Li}(\text{THF})_3\cdot 0.66(\text{toluene})$ (2.5**)**

A cold solution of MeLi in diethyl ether (1.6 M, 0.58 mL, 0.92 mmol) was added to a suspension of **2.3** (0.25 g, 0.44 mmol) in ether (25 mL) at $-35\text{ }^\circ\text{C}$. The resulting dark reddish brown solution was stirred and warmed to room temperature for 4 h. After the solvent was evaporated, ether (20 mL) was added to the residue. The dark reddish brown supernatant was separated from the precipitates by centrifugation and dark reddish brown block crystals of **2.5** were grown after standing for 2 days at $-35\text{ }^\circ\text{C}$. The remaining precipitates were dissolved in toluene and centrifuged. Dark reddish brown crystals of **2.5** were grown from a toluene solution (0.17 g, 0.21 mmol, 48%). Anal. Calcd (found after drying) for $\text{C}_{46}\text{H}_{69}\text{N}_3\text{O}_3\cdot\text{CrLi}$: C, 71.66 (71.61); H, 9.02 (8.97); N, 5.45 (5.44). IR (Nujol mull, cm^{-1}): ν 2975-2838 (b, s), 1602 (w), 1585 (m), 1563 (m), 1508 (w), 1468 (s), 1378 (s), 1302 (m), 1240 (s), 1193 (m), 1171 (m), 1155 (w), 1144 (m), 1110 (w), 1099 (m), 1044 (s), 967 (s), 910 (w), 887 (s), 828 (s), 799 (m), 770 (m), 742 (m), 726 (s), 693 (m), 666 (m). $\mu_{\text{eff}} = 3.81\text{ }\mu_{\text{B}}$.

Preparation of $\{2,6-[2,6-(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]_2-(\text{C}_5\text{H}_3\text{N})\}\text{Cr}(\mu\text{-Cl})_2\text{Al}(\text{CH}_3)_2$ (2.6**)**

A solution of Me_3Al in toluene (2 M, 2.20 mL, 4.39 mmol) was added to a solution of complex **2.3** (0.25 g, 0.44 mmol) in the same solvent (20 mL) at $-35\text{ }^\circ\text{C}$. The mixture immediately changed from dark green to dark brownish green. After the mixture was stirred overnight, the solvent was evaporated and cold hexane (10 mL) added to the residue. The resulting suspension was centrifuged, and the dark green solution, separated from the dark precipitates, afforded dark green crystals of **2.6** upon standing for 2 days at $35\text{ }^\circ\text{C}$ (0.044 g, 0.066 mmol, 15% yield based on chromium). Anal. Calcd (found) for $\text{C}_{35}\text{H}_{49}\text{AlCl}_2\text{CrN}_3$: C, 63.53 (63.47); H, 7.46 (7.41); N, 6.35 (6.33). IR (Nujol mull, cm^{-1}): ν 2963-2855 (s), 1576 (m), 1468 (s), 1377 (s), 1232 (s), 1147 (s), 1104 (s), 1093 (s), 1055

(s), 935 (s), 860 (s), 827 (s), 805 (m), 776 (s), 757 (m), 721 (m), 694 (s), 690 (s). $\mu_{\text{eff}} = 3.86 \mu_{\text{B}}$.

Preparation of {2,6-[2,6-(*i*-Pr)₂PhN=C(CH₃)₂(C₅H₃N)]₂- CrCH₃·0.5(hexane) (2.7)

The preparation was carried out as for complex 2.6, using the same amounts, except that the remaining hexane-insoluble portion was dissolved first in ether, evaporated to dryness, and then dissolved in toluene (15 mL). After centrifugation, the dark greenish brown solution was concentrated to 5 mL, layered with hexane, and allowed to stand at room temperature for 4 days, upon which time dark brown crystals of 2.7 precipitated (0.18 g, 0.33 mmol, 75% yield based on chromium). Anal. Calcd (found after drying) for C₃₄H₄₆N₃Cr: C, 74.42 (74.39); H, 8.45 (8.41); N, 7.66 (7.60). IR (Nujol mull, cm⁻¹): ν 2900-2849 (s, b), 1633 (m), 1584 (w), 1565 (w), 1464 (s), 1377 (s), 1318 (w), 1303 (w), 1222 (s), 1204 (m), 1150 (m), 1087 (s), 931 (s), 881 (w), 855 (s), 804 (w), 796 (w), 779 (w), 7556 (s), 726 (s), 705 (m), 665 (w). $\mu_{\text{eff}} = 3.54 \mu_{\text{B}}$.

Preparation of {[η^4 -{2,6-[2,6-(*i*-Pr)₂PhN=C(CH₃)₂(C₅H₃N)]₂- Al₂(*i*-Bu)₃(μ -Cl)]Cr(η^6 -C₇H₈)}·0.66(hexane) (2.8)

A solution of IBAO in toluene (10 w/w %, 6.55 g, 2.20 mmol) was added dropwise to a solution of complex 2.3 (0.12 g, 0.220 mmol) in toluene (15 mL) at -35 °C. The mixture immediately turned deep brownish red and was slowly warmed to room temperature. The solvent was evaporated in vacuo, and the residue was redissolved in hexane (20 mL), forming a deep brown-red solution which was separated by centrifugation from a substantial amount of insoluble material. Very dark block like crystals of 2.8 were formed after standing for 5 days at room temperature (0.056 g, 0.068 mmol, 31%). A noncharacterizable oily material was also present. The crystals were isolated in pure form by careful washing with small portions of cold hexane to remove the oily contaminant. Anal. Calcd (found upon drying) for C₄₈H₆₉N₃ClCrAl₂: C, 69.50 (69.45); H, 8.38 (8.31); N, 5.07 (5.09). IR (Nujol mull, cm⁻¹): ν 2949-2861 (b,s), 1610 (w), 1564 (w), 1462 (s), 1405 (w), 1377 (s), 1318 (m), 1253 (w), 1230 (w), 1179 (s), 1161 (m), 1116 (w), 1066 (m), 1018 (s), 944 (w), 918 (w), 869 (m), 814 (m), 804 (m), 759 (w), 724 (m), 708 (m), 681 (s). $\mu_{\text{eff}} = 1.73 \mu_{\text{B}}$.

Polymerization

The catalytic testing was performed under two sets of conditions for the purposes of comparison. The trivalent precursor LCrCl_3 was also prepared and tested for comparison under the same conditions. Polymerization under atmospheric ethylene pressure at room temperature proceeded in a Schlenk flask on a vacuum-nitrogen line. Samples were also tested at 40 atm and 50 °C in a 200 mL high-pressure reactor containing a heating/cooling jacket. In both cases, a preweighed amount of catalyst was dissolved in 100 mL of toluene under N_2 prior to loading the reaction vessel. A solution of 500 equiv of MAO in toluene was added to the catalyst, and the mixture was stirred for 10 min. The Schlenk-line polymerizations were run for 60 min under a continuous flow of ethylene, after first evacuating the nitrogen. High-pressure polymerization mixtures were heated to 50 °C using a thermostatic bath and charged with 40 atm of ethylene, maintaining the pressure throughout the run. In both procedures polymerizations were quenched by addition of MeOH and HCl. The resulting polymer was isolated by filtration, sonicated with a solution of HCl, rinsed, and thoroughly dried prior to measuring the mass. Gel permeation chromatography (GPC) analysis of the polyethylene was carried out by A. Jekel (University of Groningen) on a Polymer Laboratories Ltd. (PL-GPC210) chromatograph using 1,2,4-trichlorobenzene (TCB) as the mobile phase at 150 °C. The samples were prepared by dissolving the polymer in the mobile-phase solvent in an external oven at 0.1% (w/v) and were run using a 4PL-Gel Mixed A column. The molecular weight was referenced to polystyrene ($M_w = 65500$, $\text{PDI} = 1.02$) standards.

X-ray Crystallography

All of the compounds consistently yielded crystals that diffracted weakly, and the results presented are the best of several trials. The crystals were mounted on thin glass fibers using paraffin oil and cooled to the data collection temperature. Data were collected on a Bruker AXS SMART 1k CCD diffractometer. Data for the compounds **2.1**, **2.2**, and **2.5 – 2.8** were collected with a sequence of 650 scans per set at 0.3° ω scans at 0, 120, and 240° in ϕ . To obtain acceptable redundancy data for compound **2.3**, the sequence of 650 scans per set with 0.3° ω scans at 0, 90, 180, and 270° in ϕ was used. Initial unit cell parameters were determined from 60 data frames collected at the different sections of

the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.³⁴ Systematic absences in the diffraction data set and unit-cell parameters were consistent with monoclinic $P2_1/c$ for **2.1**, orthorhombic $Pna21$ for **2.2**, triclinic $Pna2_1$ for **2.3**, monoclinic $P2_1/n$ for **2.5**, monoclinic $P2_1$ for **2.6**, monoclinic $C2/c$ for **2.7**, and monoclinic $P2_1/n$ for **2.8**. Solutions in centrosymmetric space groups for compounds **2.1**, **2.3**, **2.5**, **2.7**, and **2.8** and noncentrosymmetric space groups for compounds **2.2** and **2.6** yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed with difference Fourier synthesis, and refined with full-matrix least squares procedures based on F^2 . The compound molecules were located in common positions in the structures of the complexes **2.1**- **2.6** and **2.8**. In complex **2.7**, a half-occupancy ether solvent molecule is located on the 2-fold axis of the symmetry element and the Cr molecule is located in the common position ($1/4$ ether molecules per chromium center). In complex **2.5**, the initial solution suggested two cocrystallized, severely disordered toluene solvent molecules. The data set was treated with the Squeeze routine of PLATON³⁵ with a refined void space per cell of 1246.2 Å³ and an electron count per cell of 133, consistent with $8/3$ toluene molecules per cell. In compound **6**, the asymmetric unit contains 2 molecules of the Cr complex, which brings the Z' number to 2. Complex **2.8** contains a partially occupied molecule of hexane. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. All scattering factors are contained in several versions of the SHELXTL program library, with the latest version used being v.6.12.³⁶ Crystallographic data and relevant bond distances and angles are reported in Tables 1 and 2.

Table 2.1 Crystal Data and Structure Analysis Results for **2.1, 2.2, 2.3, 2.5.**

	2.1	2.2	2.3	2.5
Formula	$C_{36}H_{49}Cl_2CrN_3O_{0.75}$	$C_{47}H_{73}CrLiN_3O_3$	$C_{33}H_{43}ClCrN_3$	$C_{50.62}H_{74.28}CrLiN_3O_3^b$
FW	658.68	787.02	569.15	831.79
space group	Monoclinic $P2_1/c$	Orthorhombic $Pna2_1$	Triclinic P_1	Monoclinic $P2_1/n$
a (Å)	13.644(4)	28.334(12)	8.528(19)	13.217(14)
b (Å)	15.007(4)	12.367(5)	8.731(19)	17.70(2)
c (Å)	18.454(5)	13.407(6)	23.05(5)	22.278(12)
α (deg)	90	90	95.08(4)	90
β (deg)	100.880(5)	90	95.40(4)	95.46(8)
γ (deg)	90	90	109.66(3)	90
V (Å ³)	3710.7(18)	4698(3)	1595(6)	5187(9)
Z	4	4	2	4
radiation (K λ , Å)	0.71073	0.71073	0.71073	0.71073
T (K)	213(2)	208(2)	210(2)	203(2)
D _{calcd} (g cm ⁻³)	1.179	1.113	1.185	1.065
μ _{calcd} (mm ⁻¹)	0.481	0.283	0.467	0.290
F ₀₀₀	1400	1708	606	1800
R, R _w ^{2 a}	0.0800, 0.1237	0.0762, 0.1130	0.0606, 0.1557	0.0588, 0.1426
GoF	1.009	1.012	1.031	1.005

Table 2.1 Crystal Data and Structure Analysis Results for **2.6 – 2.8**.

	2.6	2.7	2.8
Formula	$C_{70}H_{98}Al_2C_{14}Cr_2N_6$	$C_{35}H_{48.50}CrN_3O_{0.25}$	$C_{52}H_{78}Al_2ClCrN_3$
FW	658.68	787.02	569.15
space group	Monoclinic, $P2_1$	Monoclinic, $C2/c$	Monoclinic, $P21/n$
a (Å)	14.337(17)	27.8(3)	10.895(6)
b (Å)	14.879(17)	14.95(14)	19.206(11)
c (Å)	17.38(2)	21.6(2)	23.981(14)
α (deg)	90	90	90
β (deg)	98.86(2)	126.86(15)	101.029(11)
γ (deg)	90	90	90
V (Å ³)	3663(7)	7190(117)	4925(5)
Z	2	8	4
radiation ($K\alpha$, Å)	0.71073	0.71073	0.71073
T (K)	207(2)	208(2)	203(2)
D_{calcd} (g cm ⁻³)	1.200	1.048	1.196
μ_{calcd} (mm ⁻¹)	0.509	0.343	0.359
F_{000}	1404	2444	1912
R, R_w^{2a}	0.0736, 0.1469	0.0650, 0.1507	0.0741, 0.1626
GoF	1.031	1.038	1.050

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

Table 2.2 Selected Bond Distances (Å) and Angles (deg) for **2.1, 2.2, 2.3, 2.5.**

1	2	3	5
Cr1 - N1 = 2.118(7)	Cr1 - N1 = 2.045(8)	Cr1 - N1 = 2.045(8)	Cr1 - N1 = 2.034(4)
Cr1 - Cl1 = 2.299(2)	Cr1 - C35 = 2.062(8)	Cr1 - C35 = 2.062(8)	Cr1 - C34 = 2.129(4)
C1 - C2 = 1.470(10)	C1 - C2 = 1.473(12)	C1 - C2 = 1.473(12)	N1 - C14 = 1.383(5)
N1 - C2 = 1.294(9)	N1 - C2 = 1.376(10)	N1 - C2 = 1.376(10)	C19 - C20 = 1.461(6)
Cr1 - N2 = 1.993(6)	Cr1 - N2 = 1.921(8)	Cr1 - N2 = 1.921(8)	Cr1 - N2 = 1.993(3)
Cr1-Cl2 = 2.416(3)	Cr1 - C34 = 2.134(9)	Cr1 - C34 = 2.134(9)	C13 - C14 = 1.465(6)
C8 - C9 = 1.495(10)	C8 - C9 = 1.477(12)	C8 - C9 = 1.477(12)	N3 - C20 = 1.381(5)
N3 - C8 = 1.298(9)	N3 - C8 = 1.379(10)	N3 - C8 = 1.379(10)	N2 - C15 = 1.372(5)
Cr1 - N3 = 2.118(6)	Cr1 - N3 = 2.045(8)	Cr1 - N3 = 2.045(8)	C20 - C21 = 1.387(6)
N1-Cr1-N2 = 75.4(3)	Li1 - C34 = 2.362	Li1 - C34 = 2.362	C14 - C15 = 1.409(6)
N1 -Cr1-Cl1 = 101.77(19)	N1 -Cr1-N2 = 77.8(4)	N1 -Cr1-N2 = 76.66(16)	N2 - C19 = 1.359(5)
N1 -Cr1-Cl2 = 98.11(18)	N1 -Cr1-C34 = 100.5(4)	N3 -Cr1-Cl1 = 102.29(11)	N1 -Cr1-N2 = 77.72(16)
N3 -Cr1-Cl2 = 100.89(18)	C35 -Cr1-N1 = 98.2(3)	N1 -Cr1-N3 = 154.46(14)	N3 -Cr1-C34 = 101.54(16)
N2 -Cr1-N3 = 76.2(3)	C35 -Cr1-C34 = 97.1(4)	N2 -Cr1-Cl1 = 175.61(10)	N1 -Cr1-N3 = 155.13(14)
N2 -Cr1-Cl1 = 160.95(19)	N2 -Cr1-N3 = 77.2(4)	N2 -Cr1-N3 = 77.95(13)	N2 -Cr1-C34 = 172.97(16)
N2 -Cr1-Cl2 = 93.16(18)	Cr1 -C34-Li1 = 166.73	N1 -Cr1-Cl1 = 103.24(13)	N2 -Cr1-N3 = 77.55(16)
Cl1 -Cr1-Cl2 = 105.88(10)	N3 -Cr1-C34 = 101.1(3)		N1 -Cr1-C34 = 103.32(17)
N3 -Cr1-Cl1 = 99.2(2)	N2 -Cr1-C34 = 168.6(3)		
N1 -Cr1-N3 = 146.5(3)	C35 -Cr1-N3 = 101.1(3)		

Table 2.2 Selected Bond Distances (Å) and Angles (deg) for **2.6 – 2.8.**

6	7	8
Cr1 - N1 = 2.105(8)	Cr1 - N1 = 1.947(16)	Al1 - N1 = 2.140(5)
Cr1 - Cl2 = 2.526(4)	C1 - C2 = 1.532(16)	Al2 - C49 = 1.952(7)
Al1 - C34 = 1.957(11)	N1 - C2 = 1.356(12)	Cr1 - C37 = 2.060(7)
C8 - C9 = 1.509(13)	Cr1 - N2 = 1.877(12)	C4 - C5 = 1.395(9)
Cr1 - N2 = 1.923(8)	Cr1 - C34 = 1.971(13)	Al1 - N2 = 2.002(5)
Cl1-Al1 = 2.248(5)	C8 - C9 = 1.500(10)	Cr1 - C3 = 2.119(6)
Al1 - C35 = 1.948(12)	N3 - C8 = 1.356(10)	Cr1 - C38 = 2.073(7)
N1 - C2 = 1.327(12)	Cr1 - N3 = 1.930(12)	C5 - C6 = 1.438(10)
Cr1 - N3 = 2.131(8)	N1 - Cr1 - N2 = 81.4(7)	Al1 - N3 = 1.924(5)
Cl1-Al1 = 2.248(5)	N1 - Cr1 - C34 = 98.3(8)	Cr1 - C4 = 1.952(7)
Al1 - C35 = 1.948(12)	N1 - Cr1 - N3 = 163.11(15)	Cr1 - C39 = 2.088(7)
N1 - C2 = 1.327(12)	N2 - Cr1 - C34 = 178.96(18)	C6 - C7 = 1.440(9)
Cr1 - N3 = 2.131(8)	N2 - Cr1 - N3 = 81.7(8)	Al1 - C41 = 1.967(6)
Cl2 - Al1 = 2.233(5)		Cr1 - C5 = 2.000(7)
C1 - C2 = 1.497(14)		C1 - C2 = 1.512(9)
N3 - C8 = 1.334(11)		N2 - C7 = 1.457(7)
N1 - Cr1 - Cl1 = 144.7(2)		Al1 - Cl = 2.393(3)
N1 - Cr1 - N2 = 77.6(3)		Cr1 - C6 = 2.158(7)
N1 - Cr1 - Cl2 = 99.9(2)		N1 - C2 = 1.300(7)
N3 - Cr1 - Cl2 = 99.9(3)		C7 - C8 = 1.343(8)
N2 - Cr1 - N3 = 77.6(3)		Al2 - Cl = 2.291(3)
N1 - Cr1 - N2 = 77.6(3)		Cr1 - C34 = 2.094(7)
N2 - Cr1 - Cl2 = 133.2(2)		C2 - C3 = 1.435(9)
Cl1 - Cr1 - Cl2 = 82.11(11)		C8 - C9 = 1.508(9)
N3 - Cr1 - Cl1 = 99.2(2)		Al2 - N2 = 1.963(5)
N1 - Cr1 - N3 = 154.9(3)		Cr1 - C35 = 2.064(7)
N2 - Cr1 - Cl1 = 109.8(4)		N2 - C3 = 1.459(8)
N1 - Cr1 - N2 = 98.6(2)		N3 - C8 = 1.378(8)
Cl2 - Al1 - C35 = 110.0(4)		Al2 - C45 = 1.968(7)
Cl1 - Al1 - C34 = 106.3(4)		Cr1 - C36 = 2.083(7)
C34 - Al1 - C35 = 123.0(5)		C3 - C4 = 1.428(8)

N2 - Al1 - C41 = 172.3(3)
N2 - Al1 - N3 = 82.4(2)
N2 - Al2 - C45 = 111.9(3)
C3 - N2 - Al1 = 116.1(4)
N1 - Al1 - N3 = 142.7(2)
C41 - Al1 - Cl = 98.2(2)
N2 - Al2 - C49 = 116.3(3)
C3 - N2 - Al2 = 113.7(4)
N3 - Al1 - Cl = 104.56(17)
C41 - Al1 - N1 = 94.9(2)
Cl - Al2 - C45 = 108.5(2)
C7 - N2 - Al1 = 109.7(4)
N1 - Al1 - Cl = 104.55(16)
C41 - Al1 - N3 = 103.4(3)
Cl - Al2 - C49 = 104.0(2)
C7 - N2 - Al2 = 105.1(4)
N2 - Al1 - Cl = 85.09(16)
Al1 - Cl - Al2 = 82.97(8)
C45 - Al2 - C49 = 121.4(3)
Al1 - N2 - Al2 = 103.0(2)
N2 - Al1 - N1 = 77.5(2)
N2 - Al2 - Cl = 88.80(16)
C3 - N2 - C7 = 108.6(5)

Complex 2.1

The structure of complex 2.1 (Figure 2.1) is very similar to those of the Fe,¹¹ Co,¹¹ and Mn¹³ bis(imino)pyridine analogues. The coordination geometry around the Cr center is defined by the three N atoms of the ligand [Cr1-N1 = 2.118(7) Å, Cr1-N2 = 1.993(6) Å, Cr1-N3 = 2.118(6) Å] and two terminal Cl atoms (Cr1-Cl1 = 2.299(2) Å, Cr1-Cl2 = 2.416(3) Å) in an overall distorted-square-pyramidal arrangement. The basal plane is occupied by the nitrogen donor atoms of the tridentate ligand and one chlorine [N1-Cr1-N2 = 75.4(3)°, N2-Cr1-N3 = 76.2(3)°, N3-Cr1-Cl1 = 99.2(2)°, N(1)-Cr1-Cl1 = 101.77(19)°, N2-Cr1-Cl1 = 160.95(19)°]. The second Cl is located on the apical position [N1-Cr1-Cl2 = 98.11(18)°, N2-Cr1-Cl2 = 93.16(18)°, N3-Cr1-Cl2 = 100.89(18)°, Cl1-Cr1-Cl2 = 105.88(10)°]. The other bond distances and angles do not show any distinguishing features and compare well with those found in the Fe, Co, and Mn derivatives.^{11,13}

Complex 2.2

The complex consists of a pentacoordinate Cr center surrounded by the ligand's three donor atoms [Cr1-N1 = 2.045(8) Å, Cr1-N2 = 1.921(8) Å, Cr1-N3 = 2.045(8) Å] and two methyl groups in an overall distorted-square-pyramidal geometry ($\tau = 0.31$)³⁶ (Figure 2.2). One methyl group, located in the axial position [C35-Cr1-N1 = 98.2(3)°, C35-Cr1-N2 = 94.3(3)°, C35-Cr1-N3 = 101.1(3)°, C35-Cr1-C34 = 97.1(4)°], is terminally bound [Cr1-C35 = 2.062(8) Å]. The carbon of a second methyl group [Cr1-C34 = 2.134(9) Å] occupies the fourth equatorial position [N1-Cr1-N2 = 77.8(4)°, N2-Cr1-N3 = 77.2(4)°, N3-Cr1-C34 = 101.1(3)°, N1-Cr1-C34 = 100.5(4)°, N1-Cr1-N3 = 149.3(3)°, N2-Cr1-C34 = 168.6(3)°] and is bridging a THF solvated lithium cation, forming an almost linear Li-C-Cr array [Li1-C34 = 2.362 Å, Cr1-C34-Li1 = 166.73°]. An examination of the ligand parameters shows a slight shortening in the C_{Me}-C_{imino} bonds [C1-C2 = 1.473(12) Å, C8-C(9) = 1.477(12) Å], paralleled by a lengthening in the imino C-N bonds [N1-C2 = 1.376(10) Å, N3-C8 = 1.379(10) Å]. Other modifications include a shortening of the C_{imine}-C_{ortho} bond lengths [C2-C3 = 1.417(11) Å, C7-C8 = 1.403(13) Å] and a lengthening of the C_{ortho}-N_{pyr} bond distances [N2-C3 = 1.380(11) Å, N2-C7 = 1.392(11) Å] relative to those of the divalent precursor.

Complex 2.3

Complex 2.3 (Figure 2.3) consists of a Cr center bound to the three N atoms of the ligand [Cr1-N1 = 2.092(5) Å, Cr1-N2 = 1.934(4) Å, Cr1-N3 = 2.062(5) Å] and a terminal Cl atom [Cr1-Cl1 = 2.287(4) Å] in an overall distorted-square planar geometry [N1-Cr1-N2 = 76.66(16)°, N2-Cr1-N3 = 77.95(13)°, N1-Cr1-N3 = 154.46(14)°, N1-Cr1-Cl1 = 103.24(13)°, N3-Cr1-Cl1 = 102.29(11)°, N2-Cr1-Cl1 = 175.61(10)°]. Some of the bond distances and angles of the ligand backbone are different from those of complex 2.2. The C=N and the N_{pyr}-C_{ortho} bonds have been lengthened, by an average of approximately 0.025 Å and 0.035 Å, respectively, and the C_{imine}-C_{ortho} bond length has been lengthened correspondingly, by approximately 0.035 Å.

Complex 2.5

Complex 2.5 (Figure 2.4) consists of a tetracoordinate Cr center bound to the three nitrogen atoms of the ligand system [Cr1-N1 = 2.034(4) Å, Cr1-N2 = 1.993(3) Å, Cr1-N3 = 2.028(4) Å] and a methyl group [Cr1-C34 = 2.129(4) Å]. In turn, the methyl group bridges a THF-solvated Li cation [Li1-C34 = 2.391 Å, Cr1-C34-Li1 = 172.28°]. The geometry about the Cr center is distorted square planar, with the methyl group raised slightly from the plane defined by the ligand [N1-Cr1-N2 = 77.72(16)°, N1-Cr1-N3 = 155.13(14)°, N1-Cr1-C34 = 103.32(17)°, N2-Cr1-N3 = 77.55(16)°, N2-Cr1-C34 = 172.97(16)°, N3-Cr1-C34 = 101.54(16)°]. Similar to the case for complex 2.4, the C_{methyl}-C_{imine} bond lengths have been shortened to an average of 1.426 Å [C13-C14 = 1.465(6) Å, C20-C21 = 1.387(6) Å]. Consequently, the C=N bond distances have also been lengthened [N1-C14 = 1.383(5) Å, N3-C20 = 1.381(5) Å]. Other modifications to the ligand backbone include a degree of elongation and contraction slightly larger than that seen for complex 2.4 in the N_{pyr}-C_{ortho} and C_{imine}-C_{ortho} distances.

Complex 2.6

The structure of complex 2.6 (Figure 2.5) consists of a pentacoordinate Cr center bound to the tridentate ligand [Cr1-N1 = 2.105(8) Å, Cr1-N2 = 1.923(8) Å, Cr1-N3 = 2.131(8) Å] and two Cl atoms (Cr1-Cl1 = 2.468(4) Å, Cr1-Cl2 = 2.526(4) Å) in a

severely distorted square pyramidal geometry ($\tau = 0.17$).³⁶ The axial site is occupied by the second Cl atom [N1-Cr1-Cl2 = 99.9(2)⁰, N2-Cr1-Cl2 = 133.2(2)⁰, N3-Cr1-Cl2 = 99.9(3)⁰], even though the angle subtended at the chromium atom by the two Cl atoms is narrow [Cl1-Cr1-Cl2 = 82.11(11)⁰]. The other atoms occupy the equatorial positions [N1-Cr1-N2 = 77.6(3)⁰, N1 - Cr1-N3 = 154.9(3)⁰, N1-Cr1-Cl1 = 98.6(2)⁰, N2-Cr1-N3 = 77.6(3)⁰, N2-Cr1-Cl1 = 144.7(2)⁰, N3-Cr1-Cl1 = 99.2(2)⁰]. In turn, the Cl atoms are bridging one -AlMe₂ unit [Cl1-Al1 = 2.248(5) Å, Cl2-Al1 = 2.233(5) Å, Al1-C34 = 1.957(11) Å, Al1-C35 = 1.948(12) Å] in which the Al center is found in a distorted-tetrahedral geometry [Cl1 - Al1-Cl2 = 94.11(16)⁰, Cl1-Al1-C34 = 106.3(4)⁰, Cl1-Al1-C35 = 109.8(4)⁰, Cl2-Al1-C34 = 109.7(4)⁰, Cl2-Al1-C35 = 110.0(4)⁰, C34-Al1-C35 = 123.0(5)⁰]. The bond distances of the backbone are similar to those of complex **2.3**.

Complex 2.7

The Cr center of complex **2.7** adopts a distorted-square-planar arrangement (Figure 6) very similar to those observed in **2.3** and **2.4**. The square plane is formed by the three nitrogen donor atoms of the ligand [Cr1-N1 = 1.947(16) Å, Cr1-N2 = 1.877(12) Å, Cr1-N3 = 1.930(12) Å] and a terminal methyl group [Cr1-C34 = 1.971(13) Å, N1-Cr1-N2 = 81.4(7)⁰, N2-Cr1-N3 = 81.7(8)⁰, N3-Cr1-C34 = 98.3(8)⁰, N1-Cr1-C34 = 98.6(7)⁰, N1-Cr1-N3 = 163.11(15)⁰, N2-Cr1-C34 = 178.96(18)⁰]. The ligand system appears to deviate slightly from that of complex **2.3**, showing a curious lengthening of all bonds of the backbone. The largest stretch is in the C=N bond distance, from an average of 1.321 Å to 1.356 Å. However, the most extreme modification is a parallel elongation of approximately 0.03 Å in the C_{imine}-C_{ortho} bond length, as opposed to an equivalent contraction of the distance.

Complex 2.8

The crystal structure of **2.8** shows the ligand system connected to a toluene-solvated chromium atom and a 'Bu₂Al(μ - Cl)Al'Bu unit bound to the nitrogen atoms of the folded ligand (Figure 7). One Al is found coordinated to all three nitrogens of the ligand [Al1-N1 = 2.140(5) Å, Al1-N2 = 2.002(5) Å, Al1-N3 = 1.924(5) Å], an 'Bu

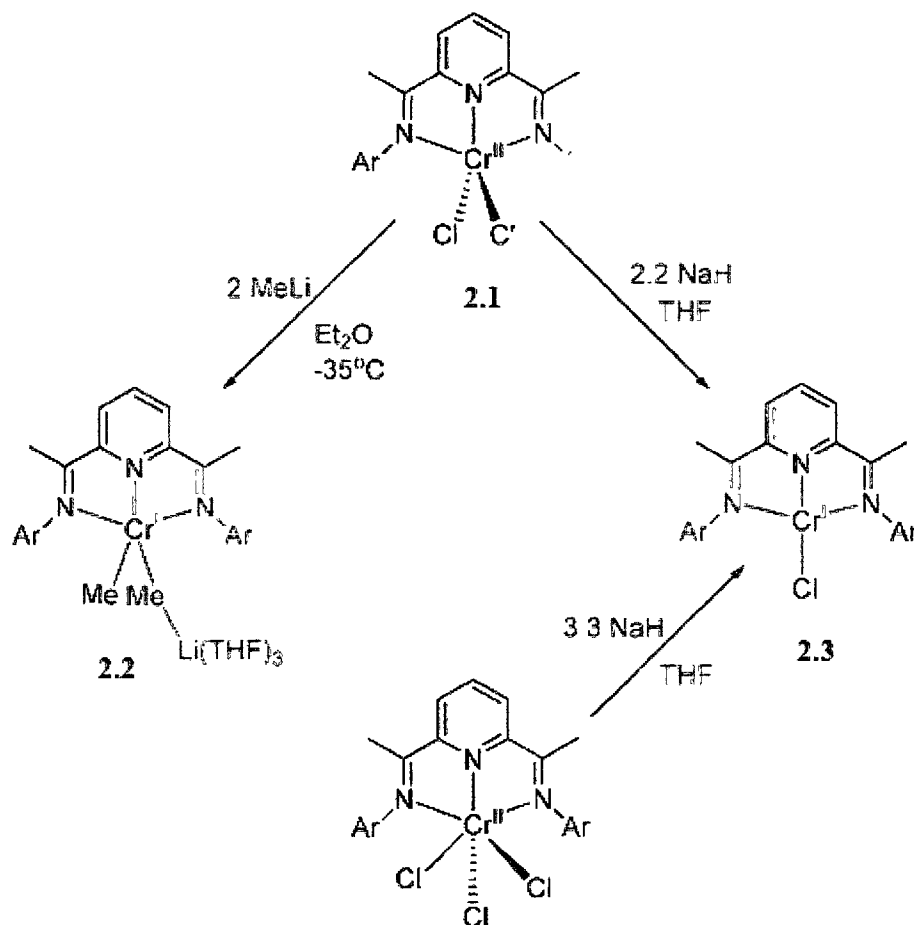
moiety [Al-C41 = 1.967(6) Å], and a chlorine atom (Al1-Cl = 2.393(3) Å) in a geometry which can be described as either distorted trigonal bipyramidal or square pyramidal ($\tau = 0.493$)³⁶ [N1-Al1-N2 = 77.5(2)°, N1-Al1-N3 = 142.7(2)°, N1-Al1-Cl1 = 104.55(16)°, N1-Al1-C41 = 94.9(2)°, N2-Al1-N3 = 82.4(2)°, N2-Al1-Cl1 = 85.09(16)°, N2-Al1-C41 = 172.3(3)°, N3-Al1-Cl1 = 104.56(17)°, N3-Al1-C41 = 103.4(3)°, Cl1-Al1-C41 = 98.2(2)°].

The Cl atom and the N of the pyridine ring in turn bridge the second Al atom (Al2-Cl = 2.291(3) Å, Al2-N2 = 1.963(5) Å), whose coordination is completed by two ⁱBu groups [Al2-C45 = 1.968(7) Å, Al2-C49 = 1.952(7) Å] in a distorted-tetrahedral arrangement [N2-Al2-Cl = 88.80(16)°, N2-Al2-C45 = 111.9(3)°, N2-Al2-C49 = 116.3(3)°, Cl-Al2-C45 = 108.5(2)°, Cl-Al2-C49 = 104.0(2)°, C45-Al2-C49 = 121.4(3)°]. The ligand appears folded, and the major distortion is observable around the pyridine ring, which adopts an η^4 coordination with a Cr atom [Cr1-C3 = 2.119(6) Å, Cr1-C4 = 1.952(7) Å, Cr1-C5 = 2.000(7) Å, Cr1-C6 = 2.158(7) Å]. In turn, the Cr atom is η^6 bound to a molecule of toluene with a distance to the centroid of 1.541(7) Å. The pyridine ring is no longer planar [N2-C3-C4 = 117.4(5)°, C3-C4-C5 = 112.8(6)°, C4-C5-C6 = 117.7(6)°, C5-C6-C7 = 121.1(6)°, C6-C7-N2 = 113.9(5)°, C3-N2-C7 = 108.6(5)°], with the largest deviation occurring at the N of the ring. Bound to the ring and two Al atoms, the N is now clearly sp³ [C3-N2-C7 = 108.6(5)°, C3-N2-Al1 = 116.1(4)°, C3-N2-Al2 = 113.74°, C7-N2-Al1 = 109.7(4)°, C7-N2-Al2 = 105.1(4)°, Al1-N2-Al2 = 103.0(2)°]. In comparison to the bond distances observed in all other complexes, drastic modifications are apparent in the ligand backbone. First of all, the disruption of aromaticity in the pyridine ring, due to the sp³ nature of the N atom and the η^4 coordination of the Cr atom, has resulted in lengthening of all bonds in the pyridine ring [N2-C3 = 1.459(8) Å, C3-C4 = 1.428(8) Å, C4-C5 = 1.395(9) Å, C5-C6 = 1.438(10) Å, C6-C7 = 1.440(9) Å, N2-C7 = 1.457(7) Å]. The fact that the Cr atom is only bound to two-thirds of the ring creates an asymmetric localization of the electron density throughout the rest of the ligand backbone. On the half of the ligand in which the pyridine ortho C is bound to the Cr, the C=N and C_{imine}-C_{ortho} bonds assume semi-normal distances [N1-C2 = 1.300(7) Å, C2-C3 = 1.435(9) Å], as expected for localization of the double bond on the imine function. However, the other half of the ligand backbone, that further away from the Cr coordination, assumes the opposite arrangement [N3-C8 = 1.378(8) Å, C8-C7 = 1.343(8) Å].

Results and Discussion

Alkylation of trivalent chromium compounds often affords reduction toward the divalent state.³⁸ The trivalent (bis(imino)-pyridinato)chromium(III) complexes seem to follow the same trend in spite of the unique electronic flexibility of this particular ligand system. We have previously described that treatment with a mild reducing agent such as Me₃Al yields a divalent complex in crystalline form.^{13b} Therefore, the starting point of this work, aimed at investigating the oxidation state of the catalytically active species, was to use a complex already containing the metal in its divalent state. The synthesis of the divalent {2,6-[2,6-(*i*-Pr)₂PhN=C(CH₃)₂](C₅H₃N)}CrCl₂ (**2.1**) was carried out in a straightforward manner by refluxing CrCl₂(THF)₂ in toluene and in the presence of the 2,6-diisopropylphenylbis(imino)-pyridine ligand. Purple microcrystals of **2.1** were isolated in 95% yield from THF, while slow crystallization afforded X-ray quality crystals. The crystal structure (Figure 2.1) confirmed that the complex possesses the same structure as the previously reported FeCl₂ and CoCl₂ adducts with an overall square-pyramidal arrangement of the metal center.¹¹ The magnetic moment at room temperature ($\mu_{\text{eff}} = 3.6 \mu_{\text{B}}$) was substantially lower than that expected for the d⁴ configuration of high-spin divalent chromium, diagnosing the presence of metal to ligand charge transfer as previously observed with other metal complexes of this ligand.^{21,29,39}

Scheme 2.1



As mentioned above, the reaction of the trivalent chromium derivative with Me₃Al affords reduction to a divalent complex where two Me₃Al residues are bridged to the metal center via bridging chlorines.^{13b} Different from the case of vanadium, we find no evidence for straightforward alkylation at the divalent center^{13b} and, therefore, we have now attempted to form Cr-C bonds by reacting 2.1 with MeLi. It is worth remembering that, in the case of the Fe analogue, the reaction of MeLi afforded a range of derivatives, including a formally zero valent species which has the same catalytic ethylene polymerization activity and produced the same polymer as the starting divalent precursor.²⁶

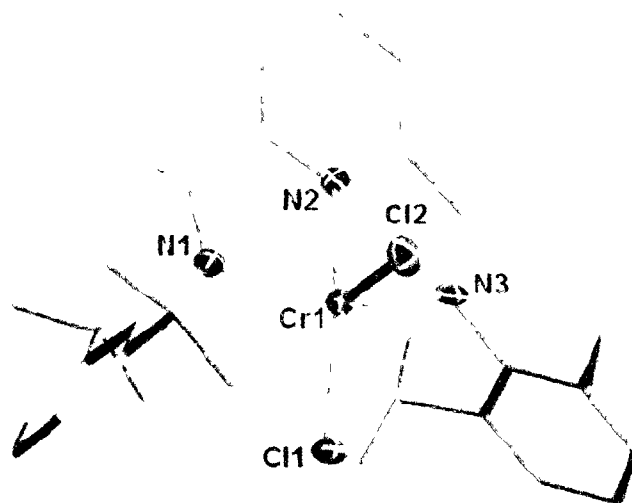


Figure 2.1 Thermal ellipsoid plot for **2.1** with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.

The reaction with 2 equiv of MeLi was carried out at $-35\text{ }^{\circ}\text{C}$ in ether (Scheme 2.1), affording $\{2,6-[2,6-(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]_2(\text{C}_5\text{H}_3\text{N})\}\text{CrMe}(\mu\text{-Me})\text{Li}(\text{THF})_3$ (**2.2**) in crystalline form (Figure 2.2). The presence of two Me groups and one lithium cation assigns the *formal* monovalent state to the chromium atom. Similar to the case of Fe, however, the appearance of this complex as a rare case of monovalent organochromium is probably deceiving, as complex **2.2** can more realistically be described as a divalent chromium center coupled to a ligand radical anion. Accordingly, the ligand backbone shows the same small and yet reproducible modifications of bond distances (Table 2.3) normally observed in the case of a one-electron reduction of the ligand.⁴⁰ The room-temperature magnetic moment ($\mu_{\text{eff}} = 4.2\ \mu_{\text{BM}}$) again suggests the presence of a high-spin d^4 electronic configuration of a Cr(II) center antiferromagnetically coupled to a ligand radical anion.

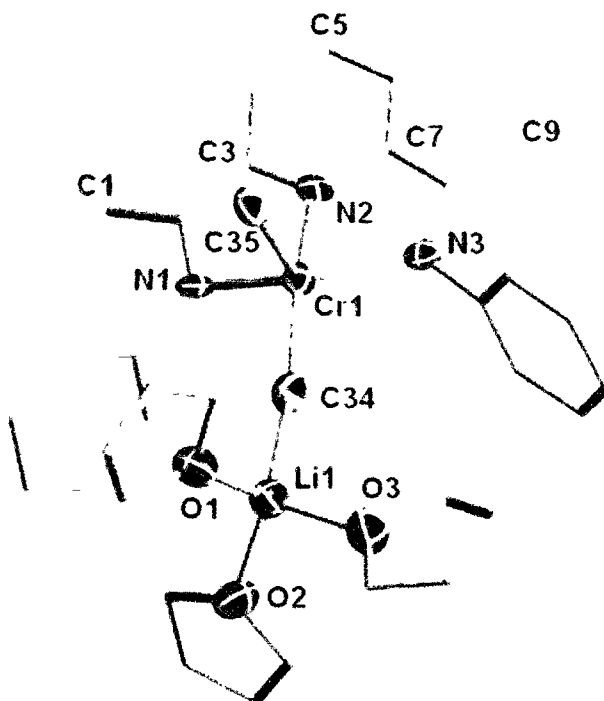


Figure 2.2 Thermal ellipsoid plot for 2.2 with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.

Regardless of how we consider the oxidation state of the chromium center, the result of the alkylation reaction is the formation of a “reduced” species containing one additional electron with respect to the initial divalent complex. Previous work has demonstrated that deliberate reduction of the FeCl_2 ²⁴ and VCl_3 ²⁵ precursors may lead to the formation of species with an overall zerovalent appearance. The remarkable feature of these species is that, although the low-valent appearance is purely formal, given the very substantial metal to ligand electron transfer, the chemical reactivity remained that expected of a low-valent metal species. The recurrence of dinitrogen fixation in the case of Fe,²⁴ V,²⁵ Co,^{15,28b} and even Cr³³ speaks for the genuine low-valent type of behavior of these reduced complexes. Even more remarkably, the reduction does not appear to affect the catalytic behavior in ethylene polymerization, since the two electron- reduced Fe species can produce not only dinitrogen complexes but can also be activated to perform very fast polymerizations and form the same type of polymer as its divalent precursor.²⁶

Reduction of complex **2.1** was further attempted with 2.2 equiv of NaH as a reductant. The slow reaction was carried out in THF over a period of 1 week, affording dark green X-ray-quality crystals of $\{2,6-[2,6-(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]_2(\text{C}_5\text{H}_3\text{N})\}\text{CrCl}$ (**2.3**) (Scheme 2.1) in good yield. Complex **2.3**, whose appearance is also that of a monovalent chromium complex (Figure 2.3), could also be prepared, albeit in lower yield, by reducing the CrCl_3 derivative with excess of NaH. The square-planar geometry strongly suggests the presence of a divalent metal center. Even in this case, the room-temperature magnetic susceptibility ($\mu_{\text{eff}} = 3.57 \mu_{\text{B}}$) can be explained in terms of a high-spin d^4 Cr(II) center in a square-planar ligand field that is magnetically coupled to a radical anion.

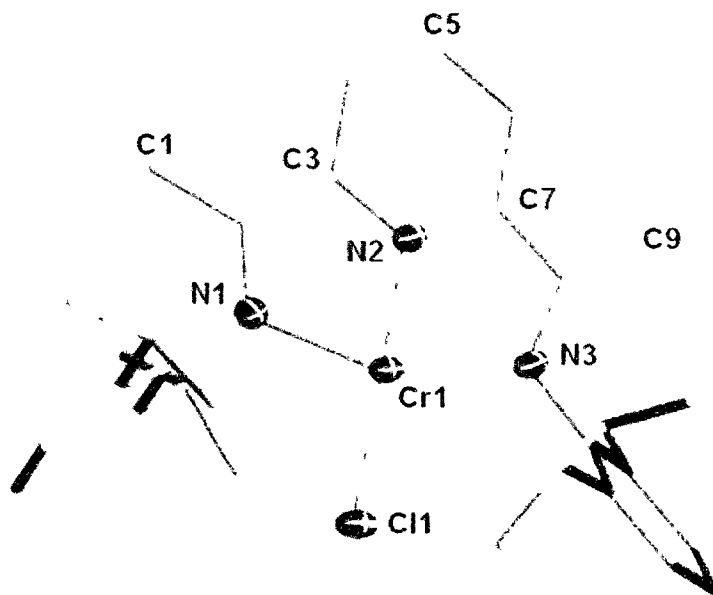


Figure 2.3 Thermal ellipsoid plot for **2.3** with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.

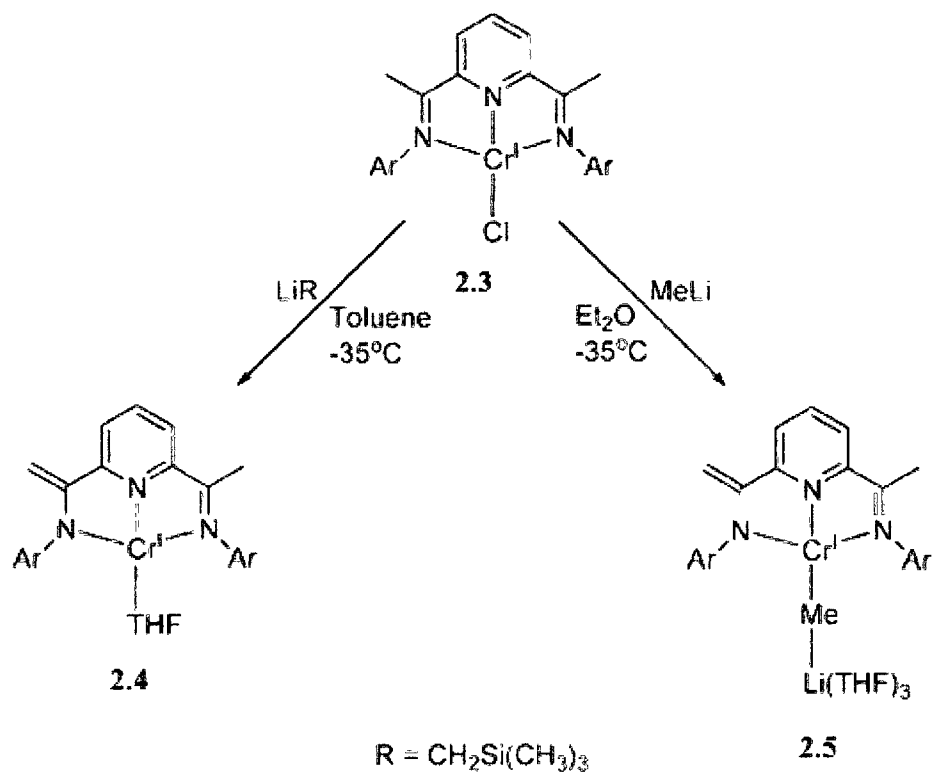
In line with the behavior of the reduced Fe analogue,²⁶ **2.3** is an extremely active polymerization catalyst (vide infra). Thus, we have attempted further alkylation in order to probe the stability of the “monovalent” oxidation state while in the presence of alkylating agents (as for example during the polymerization reaction). The reaction of **2.3** with 1 equiv of $\text{LiCH}_2\text{Si}(\text{CH}_3)_3$ or MeLi afforded $\{2-[2,6-(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]-6-[2,6-(i\text{-Pr})_2\text{PhNC}=\text{CH}_2](\text{C}_5\text{H}_3\text{N})\}\text{Cr}(\text{THF})$ (**2.4**) and $[\{2,6-[2,6-(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]_2(\text{C}_5\text{H}_3\text{N})\}\text{CrCH}_3][\text{Li}(\text{THF})_4]$ (**2.5**), respectively (Scheme 2.2). Complex **2.4** was previously

obtained in crystalline form via reduction of **2.3** with NaH under Ar³³ (chapter 5). In both of these species (Figure 2.4)³³ one of the two methyl groups has undergone deprotonation, thus making the ligand monoanionic in the process. This is clearly indicated by a decrease in the ketimine bond length corresponding to an increase in the C=N bond distance (Table 2.3). The fourth coordination site of **2.4** contains a molecule of THF, while complex **2.5** is bound by a bridging Me-Li unit. Therefore, it appears that the extent of reduction has remained unmodified as the result of the alkylation reaction.

Accordingly, the magnetic moments ($\mu_{\text{eff}} = 3.51$ and $3.81 \mu_{\text{B}}$) are similar to that of **2.3** and fall in the range expected for a d^4 high-spin square-planar divalent chromium coupled to the ligand radical anion. A small contraction in the C_{imine}-C_{ortho} bond distances, paralleled by an elongation of the N_{pyr}-C_{ortho} bond lengths, is also in agreement with partial reduction of the ligand.^{39,40}

The involvement of the imino methyl groups in acid-base type reactions with alkylating agents, forming singly and doubly deprotonated forms of the ligand, is well-documented in the chemical reactivity of this particular ligand system.^{13b,14,17b,c,18-20} In most cases, the single deprotonation precludes a dimerization via formation of a C-C bond between the CH₂= moieties of two different molecules. This process engages the redoxchemistry of the metal center. Therefore, the isolation of a complex in which the ligand has undergone only single deprotonation is a rare event, having only been witnessed for Li^{17b,c,18} and Ga.⁴¹

Scheme 2.2



As briefly mentioned above, complex **2.3** is a potent polymerization catalyst while in combination with MAO. Since the reaction with MAO did not lead to isolable products, the reaction of **2.3** with AlMe_3 may be regarded as a viable alternative in the pursuit of a potential active species for the polymerization reaction. When complex **2.3** was reacted with excess AlMe_3 in hexane, two products, $\{2,6\text{-}[2,6\text{-(}i\text{-Pr)}_2\text{PhN}=\text{C}(\text{CH}_3)]_2(\text{C}_5\text{H}_3\text{-N})\}\text{Cr}(\mu\text{-Cl})_2\text{Al}(\text{CH}_3)_2$ (**2.6**) and $\{2,6\text{-}[2,6\text{-(}i\text{-Pr)}_2\text{PhN}=\text{C}(\text{CH}_3)]_2\text{-(C}_5\text{H}_3\text{N)}\}\text{CrCH}_3$ (**2.7**), were isolated and separated by fractional crystallization from hexane and toluene, respectively (Scheme 2.3). Both complexes have been characterized by X-ray crystallography (Figures 2.5 and 2.6).

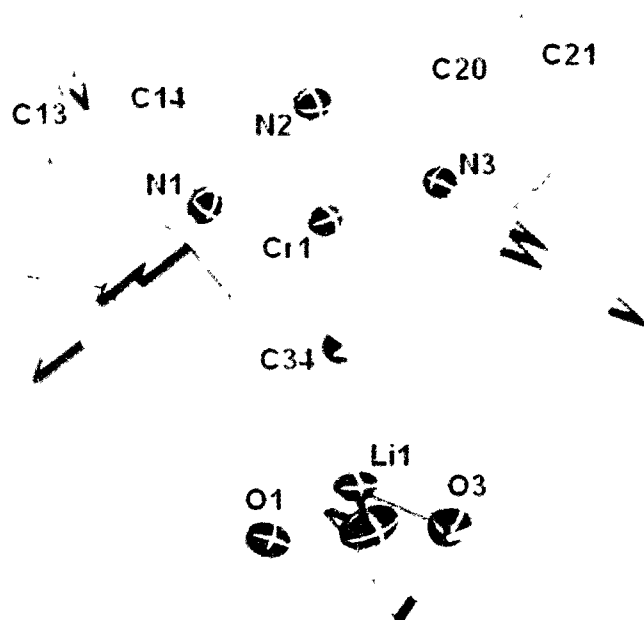
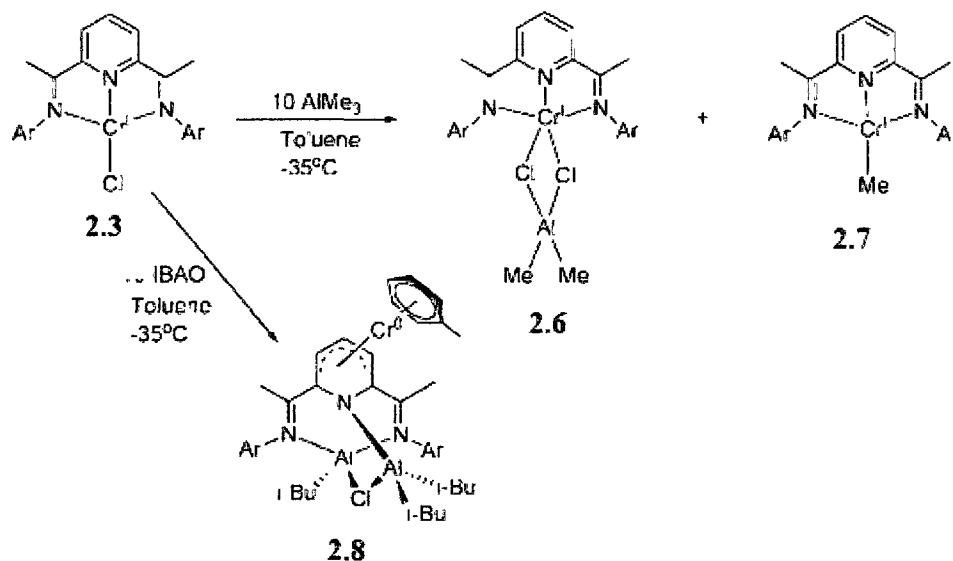


Figure 2.4 Thermal ellipsoid plot for 2.5 with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.

Scheme 2.3



Complex **2.6**, featuring the Cr center surrounded by the ligand and bound to an -AlMe_2 unit by two bridging Cl atoms, again suggests a formal monovalent state for the Cr center. Therefore, the formation of **2.6** is simply the result of coordination of an AlClMe_2 unit to **2.3**. This is substantiated by the value of the magnetic moment ($\mu_{\text{eff}} = 3.86 \mu_{\text{B}}$), which is very similar to that of **2.3**. The presence of an aluminum-bound chlorine atom may be a consequence of the formation of complex **2.7**, which is a direct replacement of the Cl atom on the metal center with a CH_3 unit. Again, the ligand backbone deformations of both compounds suggest reduction of the ligand by one electron (Table 2.3)^{39,40} and can therefore be described as Cr(II) centers bound to ligand radical anions.

It is interesting to note that addition of Me_3Al to the highly active catalyst precursor **2.3** does not result in further reduction of the metal center, in contrast to the case of $\text{Co}^{28\text{ab}}$ or Fe .²⁹ However, addition of a different activator, namely IBAO, indeed led to reduction of the metal center and partial transmetalation (Scheme 2.3), forming

$[\eta^4\{2,6-[2,6-(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]_2(\text{C}_5\text{-H}_3\text{N})\}\text{Al}_2(i\text{-Bu})_3(\mu\text{-Cl})]\text{Cr}-(\eta^6\text{-C}_7\text{H}_8)$ (2.8) (Figure 2.7)

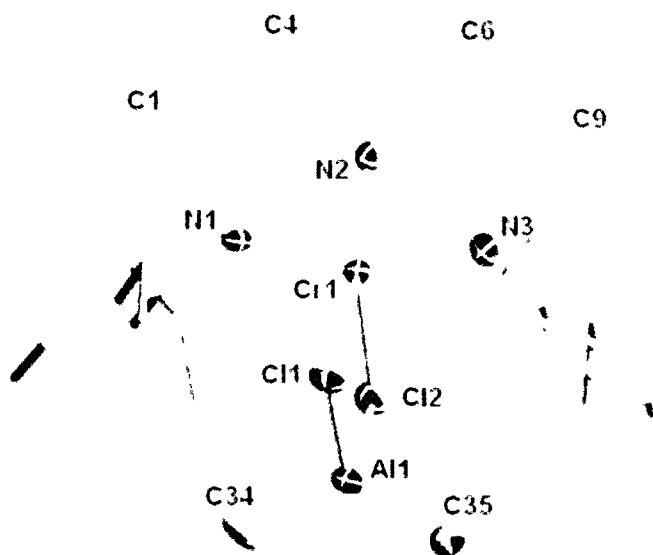


Figure 2.5 Thermal ellipsoid plot for 2.6 with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.

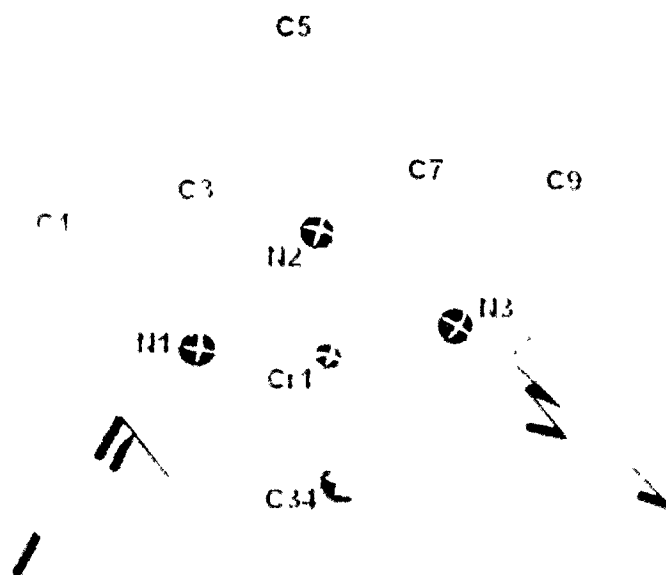


Figure 2.6 Thermal ellipsoid plot for 2.7 with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.

The structure involves three metal centers: two aluminum atoms and one chromium. The chromium atom has been partially dislodged from the ligand system and appears to be exclusively η^5 bound to part of the pyridine ring but not to the N donor atom. The three ligand N donor atoms are instead used to hold an $\text{Al}_2(i\text{-Bu})_3\text{Cl}$ unit. The fact that the Al-containing unit is dicationic suggests that the ligand system is dianionic. The Cr center, on the other hand, could reasonably be regarded as present in the zerovalent state. The η^6 coordination of one molecule of toluene is also another indicating factor, given the well-established ability of zerovalent chromium to form arene complexes. Taken together, the formation of **2.8** is the result of a three-electron reduction, with two electrons located on the ligand and the other one on the Cr center, and a partial transmetalation of the ligand system from Cr to Al. Similar to the case for the closely related Fe analogue,²⁹ complex **2.8** is paramagnetic, with a room-temperature value of the magnetic susceptibility of $1.73 \mu_{\text{B}}$. Calculations performed on the Fe analogue indicated that the electrons stored on the ligand can be found in either the singlet or the triplet state,²⁹ and the paramagnetism in this case also suggests the presence of a mixing of the two states at room temperature. Although the NMR spectrum of **2.8** is contained within the range expected for a diamagnetic system, the peaks are very broad and overlapping, making their convincing assignment on the basis of position and integration impossible. Having observed the partial transmetalation of the transition metal for the second time, and with a metal of a very different nature, it is tempting to speculate that this might be a general behavior for complexes of this ligand system. The reaction pathway leading to the final metal extrusion and formation of (bis(imino)pyridinato)Al derivatives certainly may be, rather than metal reduction, responsible for catalyst deactivation and decomposition in these highly active systems.

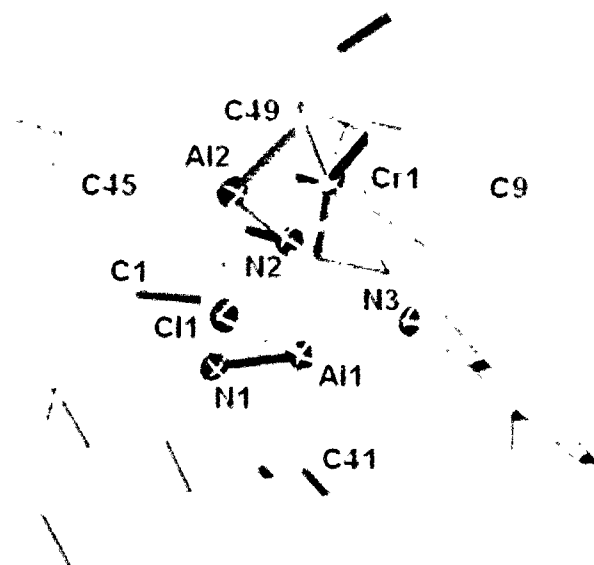


Figure 2.7 Thermal ellipsoid plot for **2.8** with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.

Table 2.3 Comparative Bond Distances (Å).

Complex	Cr-N	N _{imine} -C _{imine}	C _{imine} -C _{ortho}	C _{ortho} -N _{pyr}	C _{methyl} -C _{imine}
Complex 2.1-LCrCl₂	1.993(6)	1.294(9)	1.484(10)	1.329(9)	1.470(10)
	2.118(7)	1.298(9)	1.463(10)	1.359(9)	1.495(10)
	2.118(6)				
Complex 2.2	1.921(8)	1.376(10)	1.417(11)	1.380(11)	1.473(12)
	2.045(8)	1.379(10)	1.403(13)	1.392(11)	1.477(12)
	2.045(8)				
Complex 2.3-LCrCl	1.934(4)	1.311(5)	1.447(6)	1.374(5)	1.504(6)
	2.062(5)	1.331(5)	1.429(6)	1.384(5)	1.497(6)
	2.092(5)				
Complex 2.4⁴⁰	1.953(4)	1.374(6)	1.459(6)	1.360(6)	1.416(7)
	2.020(4)	1.372(6)	1.436(6)	1.366(6)	1.443(7)
	2.022(4)				
Complex 2.5	1.993(3)	1.383(5)	1.409(6)	1.359(5)	1.465(6)
	2.028(4)	1.381(5)	1.461(6)	1.372(5)	1.387(6)
	2.034(4)				
Complex 2.6	1.923(8)	1.327(12)	1.422(13)	1.377(11)	1.404(11)
	2.105(8)	1.334(11)	1.417(13)	1.404(11)	1.509(13)
	2.131(8)				
Complex 2.7	1.877(12)	1.356(10)	1.469(12)	1.384(10)	1.532(16)
	1.930(12)	1.356(10)	1.468(17)	1.393(15)	1.500(10)
Complex 2.8		1.300(7)	1.435(9)	1.459(8)	1.512(9)
		1.378(8)	1.343(8)	1.457(7)	1.508(9)

Polymerization Results

Table 4 outlines the results of the catalytic testing. It can be observed that, in all cases, raising the pressure (1 $\rightarrow$ 40 bar) and temperature (23 $\rightarrow$ 50 $^{\circ}$ C) of the reaction increased the activity of the catalyst significantly, normally by at least 1 order of magnitude or greater. The most intriguing trend, however, is the increase in activity with a decrease of the *formal* oxidation state (runs 1/2, 3/4, and 7/8). The activity of the Cr(III) precursor under 40 atm of ethylene (357 g of PE/mmol), is only half that of the “monovalent” **2.3** at atmospheric pressure (759 g of PE/mmol). The difference in activity between **2.3** and **2.2**, both of which contain Cr in the *formal* monovalent oxidation state, could be ascribed either to the different geometry and coordination number of the metal centers, with square planar being more active than square pyramidal, or perhaps to the presence of a weakly bound MeLi unit able to afford additional transformations (i.e., reduction). The highest activity was observed with complex **2.7**. It remains very active even at atmospheric ethylene pressure (1200 g of PE/mmol), being even more active than the corresponding (bis(imino)-pyridine)FeCl₂ precursor (650 g of PE/mmol) under identical conditions. Runs 10 and 11 compare the results of varying the amount of cocatalyst, showing a slight decrease in the catalytic activity upon doubling the MAO concentration. The increased amount of MAO may lead to an increase in the rate of deactivation or possibly coordination of excess TMA to a dormant species of the type [Cr](μ -Me)₂AlMe₂.⁴³

Most of the polymer samples were analyzed by GPC (Figure 2.8). All samples display the same broad distribution of molecular weights common among complexes of this ligand system,^{12,29} sometimes even exhibiting bi- or polymodal behavior. The main trend to be observed is an increase in the molecular weight of the polymer with an increase in pressure for the Cr(III) and Cr(II) adducts, both displaying very similar GPC Traces. The GPC of the polymer produced by **2.3** is also very similar to those produced by the Cr(III) and Cr(II) species but undergoes a decrease in molecular weight upon an increase in ethylene pressure. The similarities in the GPC and the increase in activity from Cr(III) to Cr(I) suggest potentially the same active species in all three cases. Complex **7**, the main product of activation of **2.3** with AlMe₃, interestingly produced a

polymer sample almost identical with that produced by **2.3**, suggesting the formation of the same active species. In turn, this suggests that complex **2.3** is a precursor to complex **7**, which is a precursor to the active species for the Cr(I) catalyst. Complexes **2.2** and **2.4**, on the other hand, have a similar bimodal distribution, indicative of competing active species, or a change in the active species with time.⁴³ According to previous results, the formation of the =CH₂ function, as resulting from single deprotonation, makes the complex susceptible to reductive dimerization. This transformation may be possible even during the catalytic cycle. The similarities between the polymers produced by **2.2** and **2.4** suggest that the presence of a weakly bound MeLi unit in **2.2** could result in deprotonation of one of the methyl groups, as witnessed in the formation of complex **2.5**. Therefore, complexes **2.2** and **2.4** may undergo the same type of catalyst activation. Complex **2.8** is catalytically inactive.

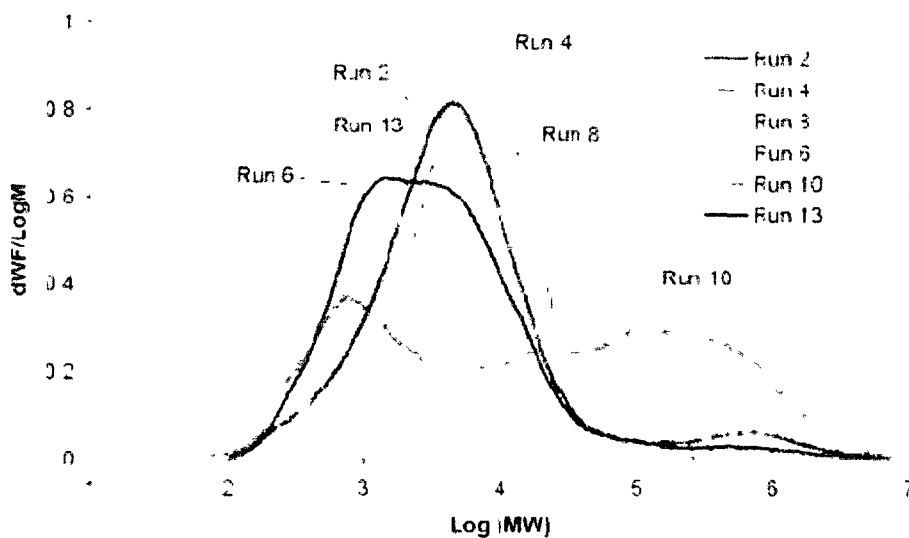


Figure 2.8. Gel permeation chromatograms of selected polymer samples

Table 2.4 Ethylene polymerization results.

run no.	complex	Amt of cat. (μmol)	Amt of MAO (equivs)	P(C ₂ H ₄) (atm)	Temp (°C)	Time (min)	Yield of PE (g)	Activity (g of PE /((mmol of cat.)/h/atm))	M _w	M _n	PDI
1	LCrCl ₃	15.6	500	1	23	60	1.39	89	28 500	1 640	17.4
2	LCrCl ₃	20.3	500	40	50	60	7.24	357	57 400	2 060	27.9
3	2.1	19.7	500	1	23	60	3.05	155	8 250	1 100	7.5
4	2.1	22.8	500	40	50	30	28.24	2477	9 280	2 650	3.5
5	2.2	15.2	500	1	23	60	1.74	114	26 600	1 580	16.8
6	2.2	10.2	500	40	50	60	9.82	966	34 200	1 970	17.4
7	2.3	13.2	500	1	23	60	10.04	759	8 010	3 090	2.6
8	2.3	22.8	500	40	50	60	68.71	3014	41 000	1 710	24.0
9	2.4	16.5	500	1	23	60	2.72	165			
10	2.4	23.1	500	40	50	60	61.23	2645	202 100	1 810	111.7
11	2.4	31.4	1000	40	50	60	67.8	2160			
12	2.7	17.1	500	1	23	60	19.2	1200			
13	2.7	18.8	500	40	50	60	79	4202	27 600	1 650	16.7

All attempts to copolymerize ethylene with a range of terminal olefins failed, in spite of the very promising high activity. High temperature NMR of the polymer samples in 1,3,5-trichlorobenzene revealed that all of the polymers are highly linear with no assignable presence of branching. In those cases when bimodality was observed (Figure 2.8), diffusion order spectroscopy (DOSY) NMR experiments revealed the presence of highly linear oligomers containing terminal olefinic groups. The presence and the absence of long chain branching are direct consequences of the lack of copolymerization of R-olefins.

From the results presented above, it appears that reduction of these chromium complexes, implying electron transfer to the ligand at the expense of the metal center, leads to a more active catalyst precursor. In other words, formation of the active species appears to involve reduction of the ligand system as well as alkylation, in line with previous observations with the Fe and Co systems.^{26,28,29} Therefore, it is tempting to speculate that the high catalytic activity of complexes of this ligand system is dominated by the ability of the ligand to accept negative charge and that formation of the active species requires the presence of electron density on the ligand backbone.

Conclusion

Cr species supported by the bis(imino)pyridine ligand system with low-valent appearance have been isolated and characterized. These complexes are highly active ethylene polymerization catalyst precursors. The activities of the monovalent Cr complexes were found to be much higher than those of the Cr(III) or Cr(II) precursors, indicating that overall reduction of the system (with electron density mainly located on the ligand) enhances the catalytic activity. The presence of the electron on the ligand backbone seems to be an important factor for increased activity by bis(imino)pyridine catalysts. Similar to the case for Fe, the deactivation pathway has been established, involving reduction and transmetalation of the ligand system to the Al cocatalyst.

Reference

- (1) Hogan, J. P.; Banks, R. L. (Phillips Petroleum Co.) U.S. Patent 2,825,721, **1958**.
- (2) a) Karapinka, G. L. (Union Carbide Corp.) Ger. Offen. D. E. 1,808,388, **1970**.
b) Karol, F. J.; Karapinka, G. L.; Wu, C.; Dow, A. W.; Johnson, R. N.; Carrick, W. L. *J. Polym. Sci., Polym. Chem. Ed.* **1972**, *10*, 2621.
c) Karapinka, G. L. (Union Carbide Corp.) U.S. Patent 3,709,853 **1973**.
- (3) a) Thomas, B. J.; Noh, S. K.; Schulte, G. K.; Sendlinger, S. C.; Theopold, K. H. *J. Am. Chem. Soc.* **1991**, *113*, 893.
b) Bhandari, G.; Kim, Y.; McFarland, J. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1995**, *14*, 738.
c) Liang, Y.; Yap, G. P. A.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1996**, *15*, 5284.
d) White, P. A.; Calabrese, J.; Theopold, K. H. *Organometallics* **1996**, *15*, 5473.
e) Theopold, K. H. *CHEMTECH* **1997**, *27*, 26.
f) Emrich, R.; Heinemann, O.; Jolly, P. W.; Kru"ger, C.; Verhownik, G. P. J. *Organometallics* **1997**, *16*, 1511.
g) Theopold, K. H. *Eur. J. Inorg. Chem.* **1998**, 15.
h) Do"hring, A.; Go"hre, J.; Jolly, P. W.; Kryger, B.; Rust, J.; Verhownik, G. P. J. *Organometallics* **2000**, *19*, 388.
i) Jensen, V. R.; Angermund, K.; Jolly, P. W.; Børve, K. J. *Organometallics* **2000**, *19*, 403.
j) Do"hring, A.; Jensen, V. R.; Jolly, P. W.; Thiel, W.; Weber, J. C. *Organometallics* **2001**, *20*, 2234.
k) Enders, M.; Ferná'ndez, P.; Ludwig, G.; Pritzkow, H. *Organometallics* **2001**, *20*, 5005.
l) Do hring, A.; Jensen, V. R.; Jolly, P. W.; Thiel, W.; Weber, J. C. In *Organometallic Catalysts and Olefin Polymerization*; Blom, R., Follestad, A., Rytter, E., Tilset, M., Ystenes, M., Eds.; Springer-Verlag: Berlin, **2001**; p 127.
- (4) a) Coles, M. P.; Gibson, V. C. *Polym. Bull.* **1994**, *33*, 529.
b) Coles, M. P.; Dalby, C. I.; Gibson, V. C.; Little, I. R.; Marshall, E. L.; Ribeiro da Costa, M. H.; Mastroianni, S. *J. Organomet. Chem.* **1999**, *591*, 78.

- (5) a) Gibson, V. C.; Maddox, P. J.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 1651.
 b) Kim, W.-K.; Fevola, M. J.; Liable-Sands, L. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1998**, *17*, 4541.
 c) Gibson, V. C.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Eur. J. Inorg. Chem.* **2001**, 1895.
 d) McAdams, L. A.; Kim, W.-K.; Liable-Sands, L. M.; Guzei, A. I.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **2002**, *21*, 952.
- (6) a) Gibson, V. C.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1999**, 827.
 b) Gibson, V. C.; Mastroianni, S.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Dalton Trans.* **2000**, 1969.
 c) Jones, D. J.; Gibson, V. C.; Green, S. M.; Maddox, P. J. *Chem. Commun.* **2002**, 1038.
- (7) a) Kořhn, R. D.; Haufe, M.; Mihan, S.; Lilge, D. *Chem. Commun.* **2000**, 1927.
 b) Kořhn, R. D.; Haufe, M.; Kociok-Kořhn, G.; Grimm, S.; Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 4337.
 c) Kořhn, R. D.; Seifert, G.; Kociok-Kořhn, G.; Mihan, S.; Lilge, D.; Mass, H. In *Organometallic Catalysts and Olefin Polymerization*; Blom, R., Follestad, A., Rytter, E., Tilset, M., Ystenes, M., Eds.; Springer-Verlag, Berlin, 2001; p 147.
- (8) Ikeda, H.; Manoi, T.; Nakayama, Y.; Yasuda, H. *J. Organomet. Chem.* **2002**, *648*, 226.
- (9) Esteruelas, M. A.; Lopez, A. M.; Mendez, L.; Oliva'n, M.; Onate, E. *Organometallics* **2003**, *22*, 395.
- (10) Small, B. L.; Carney, M. J.; Holman, D. M.; O'Rourke, C. E.; Halfen, J. A. *Macromolecules* **2004**, *37*, 4375.
- (11) a) Small, B. L.; Brookhart, M.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049.
 b) Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 849.

- (12) Reardon, D.; Conan, F.; Gambarotta, S.; Yap, G.; Wang, Q. *J. Am. Chem. Soc.* **1999**, *121*, 9318.
- (13) a) Reardon, D.; Aharonian, G.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2002**, *21*, 786.
 b) Sugiyama, H.; Aharonian, G.; Gambarotta, S.; Yap, G. P. A.; Budzelaar, P. H. M. *J. Am. Chem. Soc.* **2002**, *124*, 12268.
- (14) Scott, J.; Gambarotta, S.; Korobkov, I.; Budzelaar, P. H. M. *J. Am. Chem. Soc.* **2005**, *127*, 13019.
- (15) Scott, J.; Gambarotta, S.; Korobkov, I. *Can. J. Chem.* **2005**, *83*, 279.
- (16)a) Bruce, M.; Gibson, V. C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. *J. Chem. Commun.* **1998**, 2523.
 b) Milione, S.; Cavallo, C.; Tedesco, C.; Grassi, A. *Dalton Trans.* **2002**, 1839.
 c) Knijnenburg, Q.; Smits, J. M. M.; Budzelaar, P. H. M. *C. R. Chim.* **2004**, *7*, 865.
- (17) a) Clentsmith, G. K. B.; Gibson, V. C.; Hitchcock, P. B.; Kimberley, B. S.; Rees, C. W. *Chem. Commun.* **2002**, 1498.
 b) Khorobkov, I.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2002**, *21*, 3088.
 c) Blackmore, I. J.; Gibson, V. C.; Hitchcock, P. B.; Rees, C. W.; Williams, D. J.; White, A. J. P. *J. Am. Chem. Soc.* **2005**, *127*, 6012.
- (18) Enright, D.; Gambarotta, S.; Yap, G. P. A.; Budzelaar, P. H. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3873.
- (19) Sugiyama, H.; Gambarotta, S.; Yap, G. P. A.; Wilson, D. R.; Thiele, S. K. H. *Organometallics* **2004**, *23*, 5054.
- (20) Bouwkamp, M. W.; Lobkovsky, E.; Chirik, P. J. *Inorg. Chem.* **2006**, *45*, 2.
- (21) Sugiyama, H.; Korobkov, I.; Gambarotta, S.; Mo"ller, A.; Budzelaar, P. H. M. *Inorg. Chem.* **2004**, *43*, 5771.
- (22) a) de Bruin, B.; Bill, E.; Bothe, E.; Weyhermu"ller, T.; Wieghardt, K. *Inorg. Chem.* **2000**, *39*, 2936.
 b) Budzelaar, P. H. M.; de Bruin, B.; Gal, A. W.; Wieghardt, K.; van Lenthe, J. H. *Inorg. Chem.* **2001**, *40*, 4649.
- (23) Knijnenburg, Q.; Hetterscheid, D.; Kooistra, T. M.; Budzelaar, P. H. M. *Eur. J. Inorg. Chem.* **2004**, 1204.

- (24) Bart, S. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 13794.
- (25) Vidyaratne, I.; Gambarotta, S.; Korobkov, I.; Budzelaar, P. H. M. *Inorg. Chem.* **2005**, *44*, 1187.
- (26) Scott, J.; Gambarotta, S.; Korobkov, I.; Budzelaar, P. H. M. *Organometallics* **2005**, *24*, 6298.
- (27) Bouwkamp, M. W.; Bart, S. C.; Hawrelak, E. J.; Trovitch, R. J.; Lobkovsky, E.; Chirik, P. J. *Chem. Commun.* **2005**, 3406.
- (28) a) Kooistra, T. M.; Knijnenburg, Q.; Smits, J. M. M.; Horton, A. D.; Budzelaar, P. H. M.; Gal, A. W. *Angew. Chem., Int. Ed.* **2001**, *40*, 4719.
 b) Gibson, V. C.; Humphries, M. J.; Tellmann, K. P.; Wass, D. F.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2001**, 2252.
 c) Steffen, W.; Blo"mker, T.; Kleigrew, N.; Kehr, G.; Fro"hlich, R.; Erker, G. *Chem. Commun.* **2004**, 1188.
 d) Kleigrew, N.; Steffen, W.; Blo"mker, T.; Kehr, G.; Fro"hlich, R.; Wibbeling, B.; Erker, G.; Wsilke, J.-C.; Wu, G.; Bazan, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 13955.
- (29) Scott, J.; Gambarotta, S.; Korobkov, I.; Knijnenburg, Q.; de Bruin, B.; Budzelaar, P. H. M. *J. Am. Chem. Soc.* **2005**, *127*, 17204.
- (30) Devore, D.; Feng, S. S.; Frazier, K. A.; Patton, J. T. (Dow Chemical) World Pat. WO0069923, 2000. 3202 *Organometallics*, Vol. 26, No. 13, **2007** Vidyaratne et al.
- (31) a) Johnson, L. K.; Killian, C. M.; Brookhart, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 6414.
 b) Killian, C. M.; Tempel, D. J.; Johnson, L. K.; Brookhart, M. S. *J. Am. Chem. Soc.* **1996**, *118*, 11664.
- (32) Tessier-Youngs, C.; Beachley, O. T., Jr. *Inorg. Synth.* **1986**, *24*, 95.
- (33) Vidyaratne, I.; Scott, J.; Gambarotta, S.; Budzelaar, P. H. M.; Korobkov, I. *Inorg. Chem.* **2007**, *46*, 7040.
- (34) Blessing, R. *Acta Crystallogr.* **1995**, *A51*, 33.
- (35) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.
- (36) Sheldrick, G. M. Bruker AXS, Madison, WI, **2001**.
- (37) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.
- (38) a) Bhandari, G.; Kim, Y.; McFarland, J. M.; Rheingold, A. L.;

Theopold, K. H. *Organometallics* **1995**, *14*, 738.

b) MacAdams, L. A.; Buffone, G. P.; Incarvito, C. D.; Golen, J. A.; Rheingold, A. L.; Theopold, K. H. *Chem. Commun.* **2003**, 1164.

(39) Bart, S. C.; Chlopek, K.; Bill, E.; Bouwkamp, M. W.; Lobkovsky, E.; Neese, F.;

Wieghardt, K.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 13901.

(40) Knijnenburg, Q.; Gambarotta, S.; Budzelaar, P. H. M. *Dalton Trans.* **2006**, 5442.

(41) Scott, J.; Phull, H.; Gambarotta, S.; Korobkov, I. Manuscript in preparation.

(42) Bochmann, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1181.

(43) Kissin, Y. V.; Qian, C.; Xie, G.; Chen, Y. *J. Polym. Sci. A: Polym. Chem.* **2006**, *44*, 6159

***Chapter 3:* Dinitrogen Activation, Partial
Reduction, and Formation of Coordinated Imide
Promoted by a Chromium Diiminepyridine
Complex.**

(Published in *Inorg. Chem.* **2007**, 46, 7040)

Introduction

The continuing saga of dinitrogen activation¹ has steadily developed since the initial discovery of the ability of transition metals to form dinitrogen complexes. As a result of considerable research, the immobilized dinitrogen unit may be guided toward a few diversified stoichiometric transformations.² It is only in the past few years, however, that tremendous advances have been made toward understanding the elementary steps by which this exceedingly stable molecule is reduced, cleaved, and protonated.³ The ingenious design of a catalytic cycle capable of producing ammonia from dinitrogen under very mild conditions^{3a,b} can certainly be regarded as the most recent culmination of this chemistry.

Similar to the behaviour of the biologically occurring nitrogenase enzyme,⁴ the key to the success of the molybdenum based catalytic cycle relies on the possibility of separating the source of electrons and the source of protons through the judicious use of appropriate reagents. Another possible strategy, suggested by recent results in actinide chemistry,^{3d} is to enhance the radical activity of the reduced dinitrogen moiety bound to the metal center, thereby encouraging hydrogen atom extraction from the solvent. Today, dinitrogen activation is documented with almost all of the metals, but it is trivalent molybdenum^{1e,3a,b,5}, tantalum⁶ and niobium and divalent samarium⁷ that provide the largest variety of reduced species. In sharp contrast to the unique versatility of molybdenum, chromium appears to be one of the most reluctant elements to interact with dinitrogen. The only chromium-dinitrogen complexes reported so far are, in fact, less than a handful of Chatt-type zerovalent derivatives containing phosphine⁸ or arene ligands.⁹

In this chapter, we describe how further reduction of low valent chromium complexes of the diiminepyridine ligand reported in chapter two in the presence of nitrogen leads to a dinitrogen complex and subsequent cleavage of the N-N bond. The use of the diiminepyridine ligand system for this work was a key to these results. This particular ligand has attracted the attention of researchers for its ability to sustain an exceptional level of activity as an ethylene polymerization catalyst with late transition metals.¹⁰ The ability of this ligand to be directly involved in the organometallic chemistry

of the metal center has provided mechanistic insight into the variety of processes and transformations accompanying the polymerization.¹¹ Among the several features, there is the possibility of accommodating up to three electrons in the delocalized π system.¹² This, in turn, has allowed the formation of complexes that deceptively appear as low-valent but that are, in fact, comprised of a higher-valent metal coupled to a radical mono- or dianion.^{11,h,i,13} The electrons stored in the ligand-centered electron reservoir are still available for further chemistry, as is clearly shown by the recurrent dinitrogen activation by these systems.^{13d,e} This led us to investigate the possibility of going one step further by adding enough electrons to cleave the dinitrogen N-N bond. The use of chromium for this purpose was particularly challenging given its low tendency to form mono- or zerovalent species unless in the presence of highly stabilizing ligands such as cyclopentadienyl anions, carbon monoxide, or phosphines. Thus, chromium complexes of the diiminepyridine ligand 13h were good candidates for the formation of these “pseudoreduced” complexes, in which the metal actually rests in a higher, stable oxidation state and the electrons for reduction are available in the ligand.

Experimental Section

All preparations were performed under an inert atmosphere by using standard Schlenk techniques and a nitrogen atmosphere glovebox. $\text{CrCl}_2(\text{THF})_2$ was prepared following the standard procedure, and $\{2,6-[2,6-(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]_2(\text{C}_5\text{H}_3\text{N})\}\text{CrCl}_3$ 11c (**3.0**), $\{2,6-[2,6-(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]_2(\text{C}_5\text{H}_3\text{N})\}\text{CrCl}_2$ (**2.1**), 13h and $\{2,6-[2,6-(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]_2(\text{C}_5\text{H}_3\text{N})\}\text{CrCl}$ (**2.3**) 13h were prepared according to published procedures. IR spectra were recorded on Mattson 9000 and Nicolet 750-Magna FT-IR instruments from Nujol mulls prepared in a drybox. Samples for magnetic susceptibility measurements were weighed inside a drybox equipped with an analytical balance and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature and calculated following standard methods and applying corrections for underlying diamagnetism to the data. Elemental analyses were carried out with a Perkin-Elmer 2400 CHN analyzer. Data for X-ray crystal structure determinations were obtained with a Bruker diffractometer equipped

with a SMART CCD area detector. NMR spectra were recorded with a Varian AMX-500 spectrometer.

Preparation of $\{2[2,6(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]_6[2,6(i\text{-Pr})_2\text{PhNC}=\text{CH}_2](\text{C}_5\text{H}_3\text{N})\}\text{Cr}(\text{THF})$ (3.1)

A solution of **2.3** (1.138 g, 2.0 mmol) in THF (100 mL) was treated with a suspension of NaH (0.053 g, 2.2 mmol) in tetrahydrofuran (THF; 20 mL) under an argon atmosphere. The resulting green suspension was stirred for 7 days at room temperature, during which the color of the solution changed from green to dark brown. The solvent was evaporated in vacuo, and the dark-brown solid was redissolved in hexane (60 mL) and centrifuged. Dark-green crystals of **3.1** were isolated upon cooling of the resulting solution (0.967 g, 1.6 mmol, 80% yield). Anal. Calcd (found) for $\text{C}_{37}\text{H}_{50}\text{CrN}_3\text{O}$ (%): C, 73.48 (73.45); H, 8.33 (8.29); N, 6.95 (6.93). IR (Nujol mull, cm^{-1}): ν 2900 (s), 2854 (s), 1606 (m), 1574 (s), 1512 (s), 1464 (s), 1433 (s), 1402 (m), 1379 (s), 1357 (m), 1315 (m), 1300 (s), 1243 (s), 1221 (s), 1195 (m), 1174 (w), 1135 (w), 1091 (m), 1065 (m), 1052 (m), 1017 (m), 1003 (w), 978 (m), 925 (s), 899 (w), 871 (s), 859 (m), 824 (s), 804 (s), 774 (s), 755 (s), 738 (m), 725 (m), 690 (s) [$\mu_{\text{eff}} = 3.81\mu_{\text{B}}$].

Preparation of $\{[2,6\text{-}[2,6(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]_2(\text{C}_5\text{H}_3\text{N})]\text{Cr}(\text{THF})\}_2(\mu\text{-N}_2)\cdot\text{ether}$ (3.2)

Method A. A solution of **2.1** (1.31 g, 2.0 mmol) in THF (100 mL) was treated with NaH (0.100 g, 4.2 mmol) in THF (20 mL) or metallic sodium (4.1 mmol). The resulting purple mixture was stirred for 7 days at room temperature, during which the color of the solution changed from purple to dark green. The solvent was evaporated in vacuo, and the dark-green solid was redissolved in hexane (80 mL). Dark-green crystals of **3.2** were isolated upon cooling (0.255 g, 0.19 mmol, 19% yield). Suitable crystals for X-ray diffraction were grown from ether and were found to contain ether of crystallization (vide infra). Anal. Calcd (found) for $\text{C}_{78}\text{H}_{112}\text{Cr}_2\text{N}_8\text{O}_3$ (%): C, 71.31 (71.27); H, 8.59 (8.55); N, 8.53 (8.48). IR (Nujol mull, cm^{-1}): ν 2888 (s), 1907 (m), 1850 (m), 1599 (m), 1572 (m), 1540

(w), 1486 (w), 1463 (s), 1426 (s), 1377 (m), 1354 (m), 1338 (m), 1307 (m), 1279 (w), 1232 (m), 1194 (m), 1178 (m), 1155 (w), 1109 (m), 1094 (w), 1004 (w), 985 (w), 951 (w), 930 (w), 880 (s), 862 (m), 793 (m), 787 (m), 756 (s), 728 (s), 694 (w), 665 (w) [$\mu_{\text{eff}} = 5.72 \mu_{\text{B}}$].

Method B. A solution of **3.3** (1.138 g, 2.0 mmol) in THF (100 mL) was treated with either NaH (0.053 g, 2.2 mmol) in THF (20 mL) or metallic sodium (0.048 g, 2.1 mmol). The resulting green solution was stirred for 7 days at room temperature, during which the color of the solution changed from green to dark black-green. The solvent was evaporated in vacuo, and the dark-green solid was redissolved in hexane (80 mL). Dark-green crystals of **3.5** were obtained upon cooling (0.235 g, 0.179 mmol, 18% yield).

Preparation of $[\{2,6\text{-}[2,6\text{-}(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]_2 (\text{C}_5\text{H}_3\text{N})\}\text{Cr}(\text{THF})][\{2\text{-}[2,6\text{-}(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]\text{-}6\text{-}[2,6\text{-}(i\text{-Pr})_2\text{PhNC}=\text{CH}_2]\text{-}(\text{C}_5\text{H}_3\text{N})\}\text{Cr}(\text{THF})](\mu\text{-N}_2\text{H})(\mu\text{-Na})_2$ (3.3**)**

A solution of **3.2** (0.550 g, 0.42 mmol) was treated with NaH (0.024 g, 1.0 mmol) in toluene (15 mL) under a nitrogen atmosphere. The resulting mixture was stirred for 5 days at room temperature, during which time the color of the solution changed from dark green to dark brown. The excess of NaH was removed by centrifugation, and the resulting solution was evaporated to dryness. The solid residue was redissolved in toluene (25 mL). Dark-brown crystals of **3.3** were isolated at room temperature after standing for 1 week (0.167 g, 0.13 mmol, 31% yield). Anal. Calcd (found) for $\text{C}_{74}\text{H}_{102}\text{Cr}_2\text{N}_8\text{Na}_2\text{O}_2$ (%): C, 69.13 (68.92); H, 8.00 (8.11); N, 8.72 (8.66). IR (Nujol mull, cm^{-1}): ν . 3419 (s) {3374 (s) for 15[N]}, 2917 (s), 1907 (m), 1850 (m), 1599 (m), 1572 (m), 1540 (w), 1463 (s), 1426 (s), 1377 (s), 1354 (w), 1337 (w), 1306 (m), 1279 (m), 1232 (s), 1194 (m), 1337 (w), 1306 (m), 1279 (m), 1232 (s), 1194 (m), 1178 (m), 1155 (w), 1109 (m), 1094 (m), 1052 (w), 1029 (m), 1004 (w), 984 (m), 975 (m), 951 (w), 930 (w), 879 (s), 862 (s), 793 (m), 787 (m), 756 (s), 727 (s), 694 (m), 666 (w) [$\mu_{\text{eff}} = 1.92 \mu_{\text{B}}$].

Preparation of {2-[2,6-(*i*-Pr)₂PhN=C(CH₃)]-6-[2,6-(*i*-Pr)₂-PhNC=CH₂](C₅H₃N)}Cr(*i*-NH)][Na(THF)] (3.4)

Method A. A solution of **3.2** (1.138 g, 0.86 mmol) in THF (100 mL) was treated with a suspension of NaH (0.065 g, 2.7 mmol) in THF (15 mL). The resulting green solution was stirred for 7 days at room temperature, during which the color of the solution changed to dark brown. After centrifugation, the solvent was evaporated in vacuo and the dark-brown solid was redissolved in hexane (65 mL). Darkbrown crystals of **3.4** were isolated from a concentrated solution upon standing at room temperature for 10 days (0.141 g, 0.22 mmol, 13%). Anal. Calcd (found) for C₃₇H₅₂CrN₄NaO: C, 69.02 (68.88); H, 8.14 (8.25); N, 8.70(8.66). IR (Nujol mull, cm⁻¹): ν 3413 (m) {3366 (m) for 15[N]}, 2855 (s), 1617 (w), 1572 (s), 1512 (s), 1463 (s), 1402 (w), 1378 (m), 1355 (m), 1317 (w), 1261 (w), 1227 (m), 1195 (w), 1164 (w), 1149 (w), 1134 (w), 1092 (m), 1051 (m), 1016 (s), 973 (s), 932 (w), 871 (s), 803 (s), 761 (m), 750 (m), 724 (s), 695 (w), 665 (w), 634 (m).

Method B. A solution of **2.3** (0.750 g, 1.3 mmol) was treated with a suspension of NaH (0.206 g, 8.6 mmol) in THF (15 mL) under a nitrogen atmosphere, and the resulting mixture was stirred for 7 days at room temperature. The color of the solution changed from dark green to dark black-brown. Excess NaH was removed by centrifugation. After evaporation to dryness, the residue was redissolved in hexane (25 mL). Dark-brown crystals of **3.4** (0.276 g, 0.43 mmol, 33%) were isolated at room temperature after standing for 1 week.

Method C. A solution of **3.3** (0.530 g, 0.41 mmol) was treated with a suspension of NaH (0.042 g, 1.7 mmol) in THF (20 mL) under a nitrogen atmosphere, and the mixture was allowed to stir for 10 days at room temperature. The color of the solution changed from dark brown to dark brown. Excess NaH was removed by centrifugation and evaporated to dryness. The residue was redissolved in hexane (25 mL), and dark-brown crystals of **3.4** were isolated upon slow cooling at -38 °C (0.084 g, 0.13 mmol, 16% yield).

Degradation of 3.4 and Isolation of NH_4BPh_4

An analytically pure sample of **3.7** (0.200 g) was treated with a 9% $\text{HCl}/\text{H}_2\text{O}$ solution. After centrifugation of the solution and addition of NaBPh_4 , a white solid was collected, washed, identified by IR, NMR and MS spectra as NH_4BPh_4 (87%), and compared to those spectra of an analytically pure sample. The degradation test was also performed on the ^{15}N adduct of complex **3.7**. The IR spectrum displays the characteristic isotopic shift of a NH stretching band from 3218 to 3248 cm^{-1} . The MS spectrum also exhibits the ammonium ion peak at 19 m/z compared to the 18 m/z peak for the nonisotopically enriched sample. The ^{15}N NMR resonance was located at 140.1 ppm.

X-ray Crystallography

Suitable crystals were selected, mounted on a thin glass fiber with paraffin oil, and cooled to the data collection temperature. Data were collected on a Bruker AXS SMART 1K CCD diffractometer. The crystals consistently diffract very weakly, and the problem was particularly severe for complexes **3.3** and **3.4**, which collected only noise above $2\theta = 200$. Nonetheless, the data files gave structures sufficient to demonstrate the heavy atoms' connectivity. For all of the compounds, data collection was performed with three batch runs at $\varphi = 0.000$ (650 frames), at $\varphi = 120.000$ (650 frames), and at $\varphi = 240.000$ (650 frames). Initial unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied. The systematic absences and unit-cell parameters were consistent for the reported space groups. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2 . A cocrystallized solvent molecule in the structure of **3.2** was refined isotropically. All of the other non-hydrogen atoms in all of the structures were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the *SHELXTL 6.12* program library.

Complex **3.2** has one molecule of diethyl ether per two chromium atoms in the lattice, for which refinement gives the best result when refined with half-occupancy. Relevant crystal data and bond distances and angles are given in Tables 3.1 and 3.2, respectively.

Table 3.1. Crystal Data and Structure Analysis Results for **3.1 – 3.4**.

	3.1	3.2	3.3	3.4
Formula	C ₃₇ H ₅₀ CrN ₃ O	C ₃₉ H ₅₆ CrN ₄ O _{1.50}	C ₇₄ H ₁₀₂ Cr ₂ N ₈ Na ₂ O ₂	C ₃₇ H ₅₂ CrN ₄ NaO
FW	604.81	656.88	1287.63	644.82
space group	orthorhombic <i>P2(1)2(1)2(1)</i>	Monoclinic <i>C2/c</i>	monoclinic <i>P2/n</i>	monoclinic <i>P2(1)/c</i>
a (Å)	20.730(4)	25.143(3)	18.148(3)	12.024(3)
b (Å)	8.6418(16)	11.5634(14)	18.561(3)	16.623(5)
c (Å)	19.063(4)	30.241(4)	21.219(3)	18.556(5)
α (deg)	90	90	90	90
β (deg)	90	113.095(2)	103.198(2)	99.425(5)
γ (deg)	90	90	90	90
V (Å ³)	3415.0(11)	8087.7(17)	6958.6(16)	3658.8(17)
Z	4	8	4	4
radiation (Kα, Å)	0.71073	0.71073	0.71073	0.71073
T (K)	200(2)	213(2)	203(2)	208(2)
D _{calcd} (g cm ⁻³)	1.178	1.079	1.229	1.171
μ _{calcd} (mm ⁻¹)	0.366	0.316	0.375	0.357
F ₀₀₀	1304	2832	2760	1384
R, R _w ² a	0.0429, 0.1107	0.0674, 0.1757	0.0541, 0.1363	0.0764, 0.1653
GoF	1.054	1.086	1.054	1.045

$$^a R = \sum |F_o| - |F_c| / \sum |F|. R_w = [\sum (|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}.$$

Table 3.2. Selected Bond Distances (Å) and Angles (deg) for 3.1 – 3.4.

3.1	3.2	3.3	3.4
Cr1 - N1 = 2.020(3)	Cr1-N1 = 2.141(3)	Cr1-N1 = 2.054(4)	Cr1-N1 = 2.010(6)
Cr1-N2 = 1.945(3)	Cr1-N2 = 1.940(3)	Cr1-N2 = 1.953(4)	Cr1-N2 = 1.958(6)
Cr1-N3 = 2.019(3)	Cr1-N3 = 2.083(3)	Cr1-N3 = 2.086(4)	Cr1-N3 = 2.010(6)
Cr1-O1 = 2.084(2)	Cr1-N4 = 1.781(3)	Cr1-N7 = 1.770(4)	Cr1-N4 = 1.911(10)
N1-C14 = 1.379(4)	Cr1-O1 = 2.182(3)	Cr1-O1 = 2.124(3)	Na1-N4 = 2.157(10)
N3-C20 = 1.383(4)	N4-N4a = 1.241(6)	Cr2-N4 = 2.079(3)	Na1-O1 = 2.239(7)
C13-C14 = 1.425(5)	N1-C2 = 1.338(5)	Cr2-N5 = 1.944(4)	Na1-C22 = 2.962(8)
C20-C21 = 1.445(5)	N3-C8 = 1.366(5)	Cr2-N6 = 2.060(3)	Na1-C23 = 2.991(8)
C14-C15 = 1.436(5)	C1-C2 = 1.512(5)	Cr2-N8 = 1.765(4)	Na1-C24 = 3.021(8)
C19-C20 = 1.425(5)	C8-C9 = 1.505(6)	Cr2-O2 = 2.147(3)	Na1-C25 = 3.041(8)
N2-C15 = 1.361(4)	C2-C3 = 1.424(5)	N1-C2 = 1.400(6)	Na1-C26 = 2.989(8)
N2-C19 = 1.383(4)	C7-C8 = 1.406(5)	N3-C8 = 1.426(6)	Na1-C27 = 2.936(8)
N1-Cr1-N2 = 79.04(11)	N2-C3 = 1.372(5)	N2-C3 = 1.387(6)	Na1-C5A = 2.951(9)
N1-Cr1-N3 = 57.85(11)	N2-C7 = 1.404(5)	N2-C7 = 1.396(6)	Na1-C6A = 2.879(8)
N1-Cr1-O1 = 101.18(11)	N1-Cr1-N2 = 75.33(12)	C1-C2 = 1.465(6)	N3-C8 = 1.373(9)
N2-Cr1-N3 = 78.86(11)	N1-Cr1-N3 = 137.88(12)	C2-C3 = 1.405(7)	N2-C3 = 1.366(9)
N2-Cr1-O1 = 178.50(12)	N1-Cr1-N4 = 109.51(12)	C3-C4 = 1.415(7)	N2-C7 = 1.378(9)
N3-Cr1-O1 = 100.95(11)	N1-Cr1-O1 = 91.84(11)	C4-C5 = 1.352(7)	C1-C2 = 1.484(10)
	N2-Cr1-N3 = 76.61(12)	C5-C6 = 1.437(7)	C2-C3 = 1.408(10)
	N2-Cr1-N4 = 103.46(13)	C6-C7 = 1.470(7)	C7-C8 = 1.434(10)
	N2-Cr1-O1 = 151.88(12)	C7-C8 = 1.383(6)	C8-C9 = 1.452(10)
	N3-Cr1-N4 = 107.13(13)	C8-C9 = 1.470(7)	N1-Cr1-N2 = 78.1(3)
	N3-Cr1-O1 = 98.56(11)	N1-Cr1-N2 = 77.62(15)	N1-Cr1-N3 = 156.0(3)
	N4-Cr1-O1 = 104.41(12)	N1-Cr1-N3 = 138.31(15)	N1-Cr1-N4 = 102.6(3)
	Cr1-N4-N4a = 161.95(15)	N1-Cr1-N7 = 109.52(15)	N2-Cr1-N3 = 77.8(3)
		N1-Cr1-O1 = 95.04(14)	N2-Cr1-N4 = 178.9(4)

N2-Cr1-N3 = 77.93(15)	N3-Cr1-N4 = 101.4(3)
N2-Cr1-N7 = 101.55(15)	Cr1-N4-Na1 = 128.7(5)
N2-Cr1-O1 = 155.28(13)	
N3-Cr1-N7 = 108.12(15)	
N3-Cr1-O1 = 93.31(13)	
N7-Cr1-O1 = 103.15(14)	
Cr1-N7-N8 = 163.5(3)	
Cr2-N8-N7 = 159.7(3)	

Complex 3.1

Complex 3.1 is a simple monomeric species (Figure 3.1) featuring the chromium atom connected to the ligand [Cr1-N1 = 2.020(3) Å, Cr1-N2 = 1.945(3) Å, and Cr1-N3 = 2.019(3) Å] and a molecule of THF [Cr1-O1 = 2.084(2) Å] in a distorted squareplanar geometry [N1-Cr1-N2 = 79.04(11)°, N1-Cr1-N3 = 157.85(11)°, N1-Cr1-O1 = 101.18(11)°, N2-Cr1-N3 = 78.86(11)°, N2-Cr1-O1 = 178.50(12)°, and N3-Cr1-O1 = 100.95-(11)°]. The metal shows virtually no deviation from the plane identified by the four donor atoms. The bond distances formed by the methyl groups with the imine carbon atoms are shorter than expected for C-C single bonds [C13-C14 = 1.425(5) Å and C20-C21 = 1.445(5) Å]. This is indicative of deprotonation of one of the two methyl groups and which, by being disordered over the two equivalent positions, provide distances somewhat intermediate between the values expected for single and double bonds.

Complex 3.2

The structure consists of a symmetry-generated dimer with two identical {2,6-{2,6-(*i*-Pr)₂PhN=C(Me)}₂(C₅H₃N)}-Cr(THF) units connected by one bridging end-on-ligated dinitrogen unit (Figure 3.3). The coordination geometry around the metal center can best be described as distorted square-pyramidal ($\tau = 0.23$). The basal plane is comprised of the

three nitrogen atoms of the ligand system [Cr1-N1 = 2.141(3) Å, Cr1-N2 = 1.940(3) Å, and Cr1-N3 = 2.083(3) Å] and the coordinated THF oxygen atom [Cr1-O1 = 2.182(3) Å, N1-Cr1-N2 = 75.33(12)°, N1-Cr1-N3 = 137.88(12)°, N1-Cr1-O1 = 91.84(11)°, N2-Cr1-N3 = 76.61(12)°, N2-Cr1-O1 = 151.88(12)°, and N3-Cr1-O1 = 98.56(11)°]. The bridging dinitrogen unit is located on the apical position [Cr1-N4 = 1.781(3) Å, N4-Cr1-N1 = 109.51(12)°, N4-Cr1-N2 = 103.46(13)°, N4-Cr1-N3 = 107.13(13)°, and N4-Cr1-O1 = 104.41(12)°]. The N-N distance is longer than that in free dinitrogen [N4-N4a = 1.241(6) Å], and the geometry about the Cr₂N₂ unit deviates substantially from linearity [Cr1-N4-N4a = 161.95(15)°]. The long bonding distance formed by the two methyl groups with the imine carbon atoms [C1-C2 = 1.512(5) Å and C8-C9 = 1.505(6) Å] is consistent with the presence of C-C single bonds. However, the bond lengths of the imine functions have been lengthened with respect to the neutral ligand [N1-C2 = 1.338(5) Å and N3-C8 = 1.366(5) Å], which is also paralleled by a shortening in the C_{imine}-C_{ortho} bond distances [C2-C3 = 1.424(5) Å and C7-C8 = 1.406(5) Å] and a lengthening in the N_{pyr}-C_{ortho} bond distances [N2-C3 = 1.372(5) Å and N2-C7 = 1.404(5) Å].

Complex 3.3

The molecular structure of **3.3** is closely related to that of **3.2**, featuring a chromium dimer bridged by a dinitrogen unit (Figure 3.4). Each chromium center adopts a severely distorted trigonal-bipyramidal geometry in which the two imine nitrogen donor atoms of the ligand and the nitrogen atom of the dinitrogen residue are bound in the equatorial plane [Cr1-N1 = 2.054(4) Å, Cr1-N3 = 2.086(4) Å, Cr1-N7 = 1.770(4) Å, N1-Cr1-N3 = 138.31(15)°, N1-Cr1-N7 = 109.52(15)°, and N7-Cr1-N3 = 108.12(15)°]. The THF oxygen atom and pyridine nitrogen atom occupy the axial positions [Cr1-N2 = 1.953(4) Å, Cr1-O1 = 2.124(3) Å, N2-Cr1-O1 = 155.28(13)°, N1-Cr1-O1 = 95.04(14)°, N1-Cr1-N2 = 77.62(15)°, N2-Cr1-N3 = 77.93(15)°, N3-Cr1-O1 = 93.31(13)°, N7-Cr1-N2 = 101.55(15)°, and N7-Cr1-O1 = 103.15(14)°]. The Cr₂N₂ unit shows a folding comparable to that of **5** [Cr1-N7-N8 = 163.5(3)° and Cr2-N8-N7 = 159.7(3)°], and the N-N distance [N7-N8 = 1.288(5) Å] seems to be in agreement with the presence of a double bond, similar to that seen in complex **3.2**. The folding along the N-N vector could be the result

of the presence of hydrogen atoms on one or both of two nitrogen atoms, although the large Cr-N-N angles make this rather unlikely. The precise nature of the bridging dinitrogen unit will be discussed in more detail later on. Different from **3.2**, two sodium atoms are side-on-bonded to the dinitrogen unit [Na1-N7 = 2.618(4) Å and Na1-N8 = 2.478(4) Å], forming a puckered Na₂N₂ moiety. Each of the two sodium atoms is bonded to one imine nitrogen atom [Na1-N4 = 2.587(4) Å] as well as weakly π -bound to the pyridine ring of the opposite ligand. The coordination geometry of each sodium atom is completed by an agostic interaction with the methyl unit of one isopropyl group of one aromatic ring [Na1.....C54 = 3.079(6) Å]. The imine methyl groups show C-C distances [1.465(6), 1.470(7), and 1.486(6) Å with C45-C46 = 1.435(6) Å; average 1.464 Å] that are shorter than expected for C_{sp2}-C_{sp3} single bonds (usually around 1.50 Å, as found in **3.0**, **2.2**, **2.3**) but not short enough for the typical scenario of one deprotonated methyl group equally disordered over two positions (around 1.43 Å, as found in **3.0**). In this particular case, it suggests that a single deprotonation may have occurred in the dimer: one double bond disordered over four positions may well account for the observed C-C distances.

Complex 3.4

The structure of complex **3.4** (Figure 3.5) is comprised of a mononuclear square-planar chromium center, surrounded by the ligand system [Cr1-N1 = 2.010(6) Å, Cr1-N2 = 1.958(6) Å, and Cr1-N3 = 2.010(6) Å]. An NH or NH₂ group occupies the fourth coordination site [Cr1-N4 = 1.911(10) Å, N1-Cr1-N2 = 78.1(3)°, N1-Cr1-N3 = 156.0(3)°, N1-Cr1-N4 = 102.6(3)°, N2-Cr1-N3 = 77.8(3)°, N2-Cr1-N4 = 178.9(4)°, and N3-Cr1-N4 = 101.4(3)°], forming a bridge to a sodium atom [N4- Na1 = 2.157(10) Å]. In turn, the sodium cation carries one molecule of THF and is π -bound to one aryl ring of the ligand [Na1-O1 = 2.239(7) Å], assembling an infinite array via bonding to the meta and para carbon atoms of an identical unit [Na1-C5a = 2.951(9) Å and Na1-C6a = 2.879(8) Å]. The C_{methyl}-C_{imine} bonds are rather short for C-C single bonds and suggest that one of the two methyl groups might, in fact, have undergone deprotonation with consequent formation of a double bond. The other bond distance alterations are

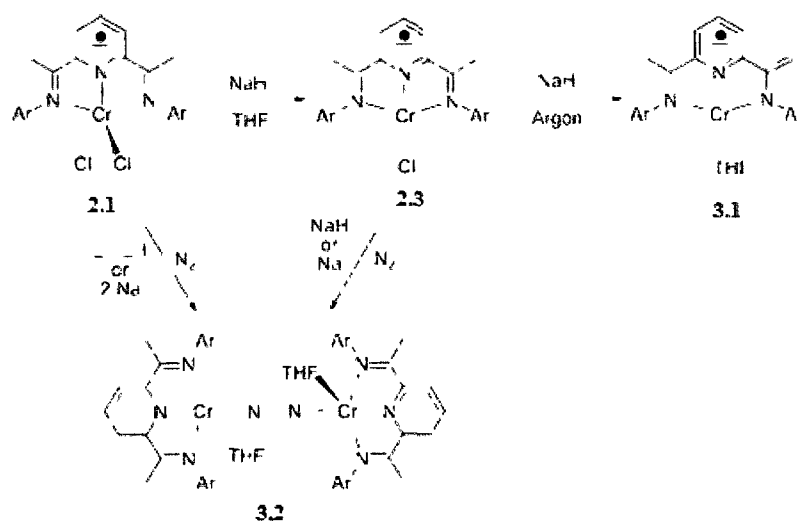
characteristic of reduction by two electrons [N1-C2 = 1.377(9) Å, N3-C8 = 1.373(9) Å, N2-C3 = 1.366(9) Å, N2-C7 = 1.378(9) Å, C2-C3 = 1.408(10) Å, and C7-C8 = 1.434(10) Å].

In calculations on mononuclear model systems, the 2,6-*i*-Pr)₂C₆H₃ groups were replaced by methyl groups and THF was replaced by Me₂O. Spin states up to $S = 5/2$ were considered for each species, and geometries were fully optimized for each individual spin state. The full system was then optimized, assuming the spin state that was lowest for the model system. Vibrational analyses were not feasible for these large open-shell systems. All calculations were carried out with the *Turbomole* program¹⁴ coupled to the PQS Baker optimizer.¹⁵ All calculations used the spin-unrestricted formalism; even for “ $S = 0$ ” systems, spin-unrestricted calculations gave significantly lower energies than spin-restricted calculations. Geometries were fully optimized at the b3-lyp level¹⁶ using the Turbomole SV(P) basis set^{14a,c} on all atoms. Orbital drawings were created using Molden.¹⁷

Results and Discussion

The divalent **2.2** is readily formed via a straightforward reaction of the neutral ligand with CrCl₂(THF)₂.^{13h} Its reduction with NaH in THF (Scheme 3.1) afforded the reduced species **2.3**, which forms a potent ethylene polymerization catalyst upon activation with monoamine oxidase.^{13h} In spite of the connectivity suggesting a rare case of the monovalent non-cyclopentadienylchromium complex, the fairly regular square-planar coordination geometry around the metal center strongly suggests that, similar to the cases of the recently reported aluminum and iron complexes,^{11i,13d,f,g} the complex contains a higher Valent metal center magnetically coupled to one or more ligand-centered unpaired electrons. This observation prompted further attempts to reduce both **2.2** and **2.3**.

Scheme 3.1



Treatment of **2.3** with NaH under argon (with careful exclusion of dinitrogen from the reaction medium) afforded a complex formulated as **3.1** (Scheme 3.1). The mononuclear structure (Figure 3.1) contains a formally Cr(I) atom surrounded by the monodeprotonated form of the ligand and one molecule of THF in an overall square-planar geometry. The formation of **3.1** arises from the deprotonation of one of the two methyl groups attached to the imine function, implying that, in the absence of dinitrogen, NaH acted as a base. The oxidation state of **3.1** is most likely the same as that in the starting complex **2.3**, as is strongly suggested by the similar square-planar coordination geometry and very comparable values of the magnetic moment. Although the magnetic values are not completely in agreement with the d^4 electronic configuration of divalent chromium, they can be reasonably explained in terms of a divalent chromium atom coupled to a ligand radical dianion.^{11h,13f}

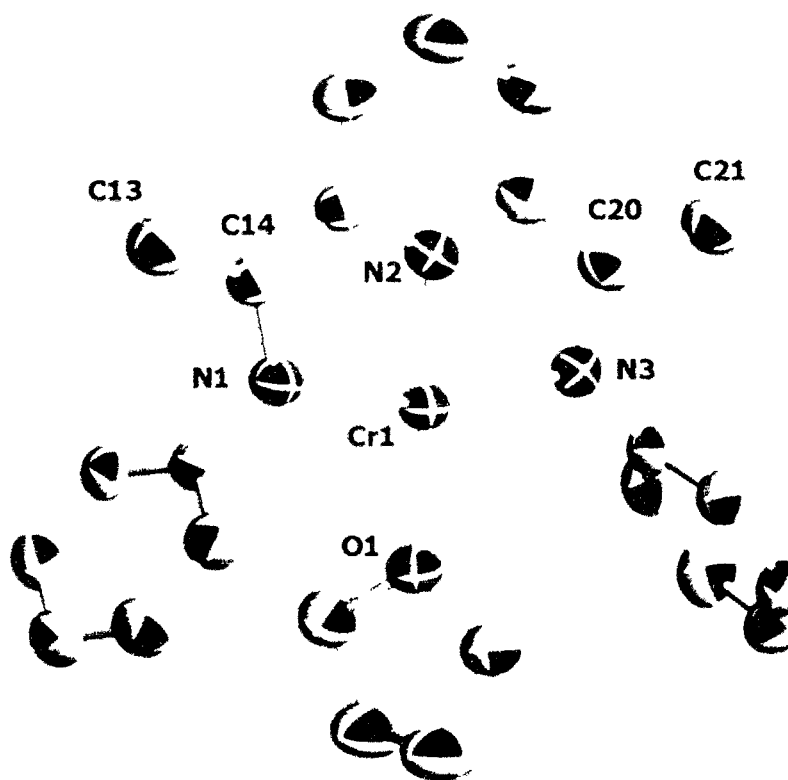


Figure 3.1. Thermal ellipsoid plot for **3.4** with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.

Electronic Structure of Mononuclear Chromium Complexes

Density functional theory calculations were performed for various spin states of simplified models of **3.0**, **2.2**, **2.3**, **3.1**. For the lowest-energy spin state, geometry optimizations were then performed for the complete molecule. Calculated geometrical parameters are collected and compared with experimental values in Table 3.3. The agreement was generally satisfactory, although calculated bond lengths to chromium are systematically long. The trivalent **3.0** prefers the expected high-spin ($S = 3/2$) ground state. It has an approximately octahedral metal environment, with the apical chloride atoms bent backward toward the pyridine ring. The calculated ligand C=N and C_{im}-C_{py}

distances are close to those of the free ligand and, as expected, indicate that there is no significant electron transfer to ligand π^* orbitals

Table 3.3 Calculated and Observed Bond Lengths for Mononuclear Chromium Complexes

Bond a	3.0		2.2		2.3		3.1	
	calcd	expb	calcd	expc	calcd	expb	calcd	exp
C-N	2.211	2.142	2.120	2.118	2.131	2.077	2.067	2.020
	2.026	1.991	1.931	1.993	1.964	1.934	1.974	1.945
C=N	1.292	1.301	1.318	1.296	1.323	1.321	1.377	1.381
C _{im} -C _{py}	1.495	1.468	1.452	1.484	1.450	1.438	1.457	1.431
C _{im} -“Me”	1.505	1.489	1.506	1.477	1.508	1.501	1.436	1.435
Cr-Cl/O	2.358	2.314	2.266	2.299	2.307	2.287	2.134	2.084
	2.265	2.282	2.269	2.416				

a Averaged where appropriate. b Reference 19. c Reference 13h.

Complex **2.2** prefers a triplet ($S = 1$) ground state by a small margin (ca. 0.5 kcal mol⁻¹ for the simplified model). This preference already indicates that the complex is *not* an ordinary Cr(II) complex (which would normally prefer a highspin $S = 2$ ground state).¹⁸ Rather, the orbital analysis of the triplet state shows occupied d_{xz} , d_{yz} , and d_{xy} orbitals in the R manifold but a mostly ligand π^* -type occupied orbital of β spin (of the same symmetry as d_{xz}). Thus, this complex is best described as having Cr(III) coupled to a ligand radical anion. In agreement with this description, it shows elongated C=N bonds and shortened C_{im}-C_{py} bonds.

Calculation

Interestingly, calculations indicate that complex **2.3** contains Cr(II) coupled to a ligand radical anion. Thus, whereas the reduction of the trivalent precursor to the divalent **2.2** is ligandcentered, further reduction to **2.3** is metal-centered. The R manifold of **2.3** contains occupied d_{xz} , d_{yz} , d_{xy} , and d_{z^2} orbitals, whereas a single occupied ligand π^* -like orbital is found in the β manifold.

The deprotonated complex **3.1** also features Cr(II) coupled to a ligand-centered unpaired electron mainly located in the intact imine-pyridine portion of the monodeprotonated ligand. In earlier work, we observed easy dimerization of similar monodeprotonated ligand complexes through coupling of the terminal methylene groups.^{11c,e} Dimerization might be made more difficult here by the presence of the additional unpaired electron on the ligand: the hypothetical dimer would contain two formally zerovalent chromium atoms.

The ligand C=N and $C_{im}-C_{py}$ distances can be used to estimate the amount of metal-to-ligand electron transfer.^{13b} Because of the small changes in the bond lengths involved, this requires either highly accurate X-ray data or the use of calculated distances (which suffer much less from random errors). Figure 3.2 shows calculated average distances for the above complexes (and for **3.4**, discussed later on), together with the “standard values” for transfer of zero to three electrons.¹³ⁱ The positions of complexes **3.0**, **2.2**, **2.3** in the graph are indeed consistent with the transfer of zero, one, and one electrons, respectively. Complexes **3.1** and **3.4b** do not follow the trend of the other points, which is to be expected because they contain a deprotonated ligand.

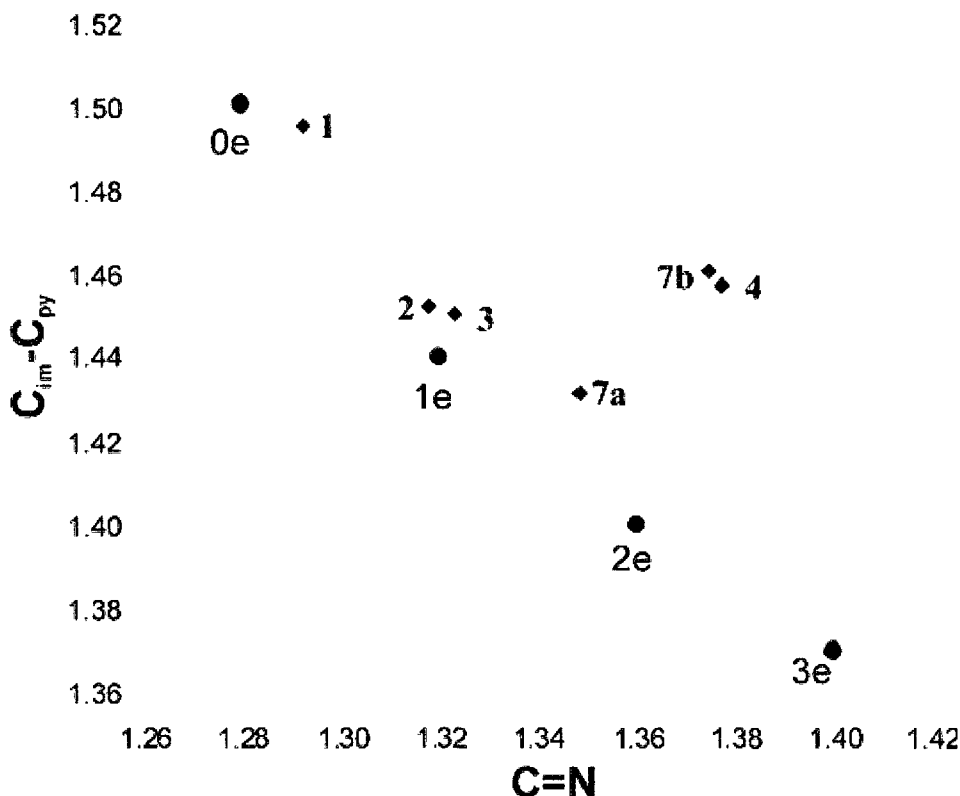


Figure 3.2. Calculated (♦) C=N and C_{im}-C_{py} distances for complexes **3.0**, **2.2**, **2.3** and **3.4a/3.4b**, compared to reference values (●) for the transfer of zero to three electrons.¹³ⁱ

Dinitrogen Activation

Complex **3.1** does not react with nitrogen. However, the reaction of both **2.2** and **2.3** with an appropriate amount of either metallic sodium or sodium hydride in THF and under a nitrogen atmosphere afforded the corresponding dinuclear dinitrogen complex **3.2**.

The connectivity of **3.2**, as established by an X-ray crystal structure (Figure 3.3), showed a dinuclear complex with the two square-pyramidal chromium atoms bridged by one endon- bonded dinitrogen unit and each surrounded by one ligand and one molecule of coordinated THF. The complex is basically isostructural with the vanadium analogue.^{13e} The N-N distance [N4-N4a) 1.241 Å] of the coordinated dinitrogen unit also compares well with that of the vanadium complex, possibly suggesting that the dinitrogen unit has undergone a two-electron reduction. Dinitrogen-bridged dichromium complexes

are rare, and the bridging bonding mode of dinitrogen between two chromium atoms has never been observed before.⁹ The partial reduction of dinitrogen suggests the

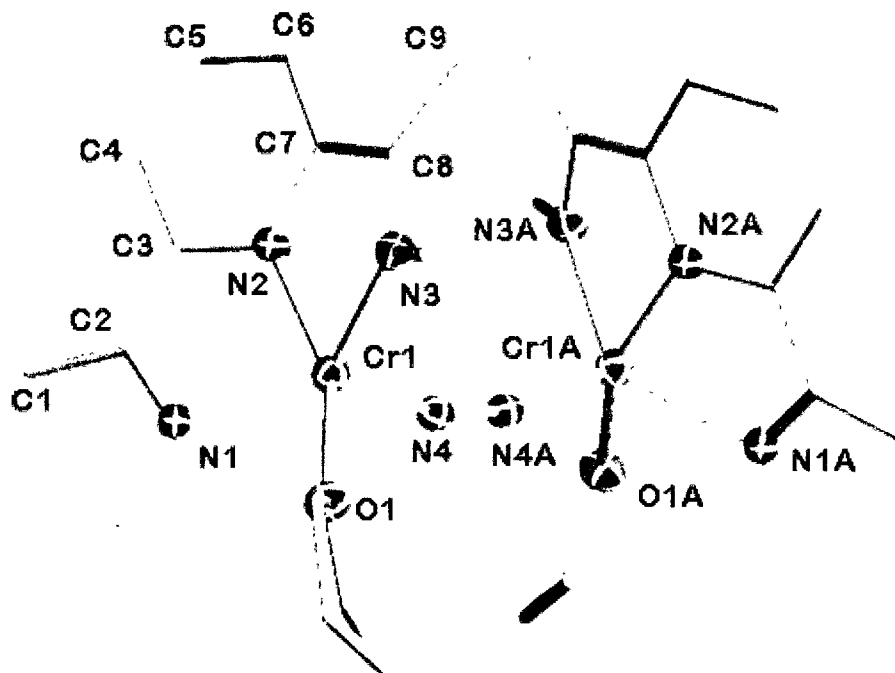


Figure 3.3. Thermal ellipsoid plot for **3.2** with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.

possibility of regarding the complex as bearing two divalent (or trivalent) chromium centers bound to monoanionic (or dianionic) ligands and bridged by an N_2^{2-} unit. Complex **3.2** is paramagnetic and displays a room temperature magnetic moment per molecule of $\mu_{\text{eff}} = 5.72 \mu_{\text{B}}$. This value is certainly lower than that expected for two high-spin Cr(II) d⁴ centers. On the other hand, the internal coupling between the metal center and the ligand radical anion, as is normally observed in the reduced species of this ligand system,^{11h,i} as well as the possible coupling between the two metal centers, may well result in a rather nondiagnostic value of the magnetic moment.

Regardless of how we consider the metal oxidation state in **3.2**, its formation can be easily rationalized in terms of reduction of the metal center followed by intramolecular reoxidation at the expense of both the coordinated dinitrogen unit and the ligand system.

The partial reduction of the dinitrogen unit in **3.2** is intriguing and suggests that further reduction of the dinitrogen moiety may be possible. Accordingly, the reaction of **3.2** with NaH afforded dark-brown paramagnetic crystals of a complex formulated as **3.3** on the basis of the X-ray crystal structure (Figure 3.4) and spectroscopic evidence. The yield, although low, was well reproducible. The dinuclear structure of the complex is surprisingly similar to that of **3.2**, with each chromium center surrounded by the ligand and a molecule of THF and the two chromium entities apparently bridged through

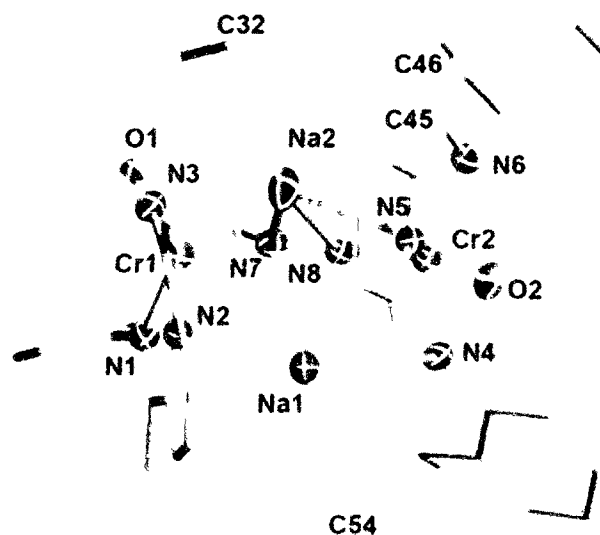


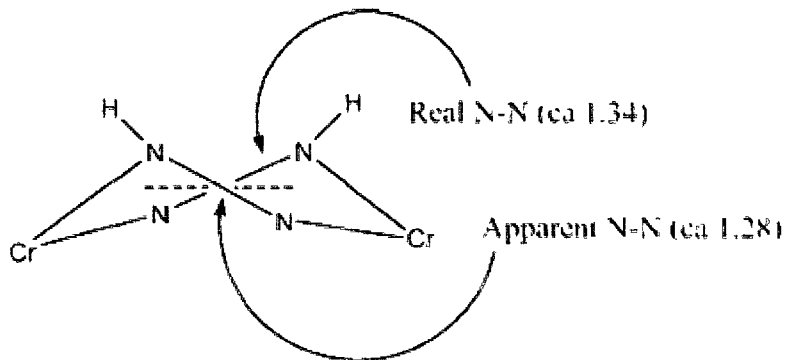
Figure 3.4. Thermal ellipsoid plot for **3.3** with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.

an end-on bonded dinitrogen moiety. Different from complex **3.2**, however, is the presence of two sodium atoms bonded to each side of the dinitrogen unit, forming a folded N_2Na_2 unit. In addition, each sodium atom is π -bound to one pyridine ring and forms an agostic contact with one of the four methylisopropyl groups of one aryl substituent. The severe puckering of the N_2Na_2 moiety and consequent pyramidalization of the nitrogen atom suggested that perhaps hydrogenation may have occurred. Accordingly, the IR spectrum of complex **3.3** did show one single medium/weak resonance at 3419 cm^{-1} that shifted to 3374 cm^{-1} in the sample prepared with $^{15}\text{N}_2$. This clearly indicates the presence of one N-H function. The room-temperature magnetic

moment is surprisingly low [$\mu_{\text{eff}} = 1.92 \mu_{\text{B}}$]. In spite of having been generated in THF and crystallized from toluene, the complex, once crystallized, shows no solubility in any solvent that it does not react with, thus regrettably preventing spectroscopic investigations in solution.

The formation of **3.3** from **3.2** implies from the formal point of view a two-electron reduction followed by one hydrogen atom transferred from one of the four imine methyl group to the dinitrogen moiety. Calculations on these structures could only be reconciled with the observed structure if it was assumed that the crystal shows disorder between Cr- NH=N-Cr and Cr-N=NH-Cr orientations of the N₂H bridge: an ordered bridge would be sharply angled at the NH moiety (ca 130°) and much closer to linear at the other nitrogen atom (Scheme 3.2). If the structure is indeed disordered, the observed N-N distance may not be meaningful. The large Cr-N-N angles appear to rule out the possibility of having a $\mu\text{-N}_2\text{H}_2$ unit in the structure.

Scheme 3.2



Electronic Structure of Dinuclear Chromium Complexes

In view of the uncertainties surrounding the formulation of **3.3**, we considered both N₂H bridged (**3.3a**: [$\{2,6\text{-}[2,6\text{-}(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)_2(\text{C}_5\text{H}_3\text{N})\}\text{Cr}(\text{THF})\}[\{2\text{-}[2,6\text{-}(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]\text{-}6\text{-}[2,6\text{-}(i\text{-Pr})_2\text{PhNC}=\text{CH}_2](\text{C}_5\text{H}_3\text{N})\}\text{Cr}](\mu\text{-N}_2\text{H})(\mu\text{-Na})_2$) and dinitrogen

bridged (3.3b: $\{ \{2,6-[2,6-(i\text{-Pr})_2\text{PhN}=\text{C}(\text{CH}_3)]_2(\text{C}_5\text{H}_3\text{N})\} \text{Cr}(\text{THF})_2(\mu\text{-N}_2)(\mu\text{-Na})_2 \}$) structures. Structure 3.3a, assumed above for complex 3.3, seems the most likely in view of the observation of an N-H stretch vibration in the IR spectrum. Structure 3.3b corresponds to simple two electron reduction of 3.2 and is of interest in itself even if it would not correspond to the actual structure of complex 3.3.

Constructing satisfactory theoretical descriptions of dinuclear complexes 3.2 and 3.3b turned out to be surprisingly difficult. Several spin states, differing mainly in the coupling between the electrons on different chromium atoms, are close in energy. It seems likely that the methods we are using (several functionals were tried) do not describe the balance between the donation to the highly delocalized ligand π^* system and to the rather compact dinitrogen π^* orbitals and the occupation of metal 3d orbitals very well.²⁰ In order to arrive at some sort of theoretical description, nonetheless, we constrained both Cr-N₂ bonds to their experimental (Xray) values.

For complex 3.2, this produces an electronic structure in which each chromium center is essentially Cr(III); each ligand has one π^* orbital *doubly* occupied and one 3d electron coupled to an electron in a dinitrogen π^* orbital; i.e., we have a doubly reduced dinitrogen molecule, isoelectronic with dioxygen. Other spin states show different couplings between the chromium centers and ligand π^* orbitals and also sometimes occupation of two different ligand π^* orbitals. In view of the problems mentioned above, we think that our results, in particular as regards coupling between chromium and ligand orbitals, should be treated with caution. However, a description as $[\text{L}_2\text{-Cr(III)(THF)}]_2(\text{N}_2^{2-})$ seems reasonable based on the results mentioned earlier for mononuclear complexes. The alternative $[\text{L-Cr(II)(THF)}]_2(\text{N}_2^{2-})$ description seems less likely because the Cr(II) centers in such a complex would have their d_{z^2} orbitals occupied and hence should not bind ligands in apical positions.²¹

For hypothetical structure 3.3b, the tendency to eliminate dinitrogen is strong. Calculations with Cr-N distances constrained to their experimental values produce an electronic structure that still is most easily described as containing two CrIII, each bound to a ligand trianion (one π^* orbital doubly and the other one singly occupied) and to N_2^{2-} . The role of the sodium atoms is just to provide electrons to the π^* systems of the

diiminepyridine ligands. Dissociation of dinitrogen allows rearrangement and occupation of the Cr d_z^2 orbitals, which (as for **3.2**) is the driving force for expulsion of dinitrogen.

Our preferred model **3.3a** does not dissociate in the calculation. The pronounced asymmetry of the complex makes unambiguous interpretation of the orbital occupation pattern difficult. The structure, like **3.2** and **3.3b**, appears to contain two Cr(III) centers, one bound to a ligand trianion monoradical (as in **3.3b**) and the other one to the monodeprotonated closed-shell ligand trianion. The bridging $N_a=N_bH$ fragment is effectively 1- and is nearly linear around N_a but sharply angled around N_b . This structure is well reconciled with the observed structure of **3.3** if we assume disorder in the N_2H bridge (and possibly also in the ligand deprotonation site), as explained above.

Cleavage of Dinitrogen

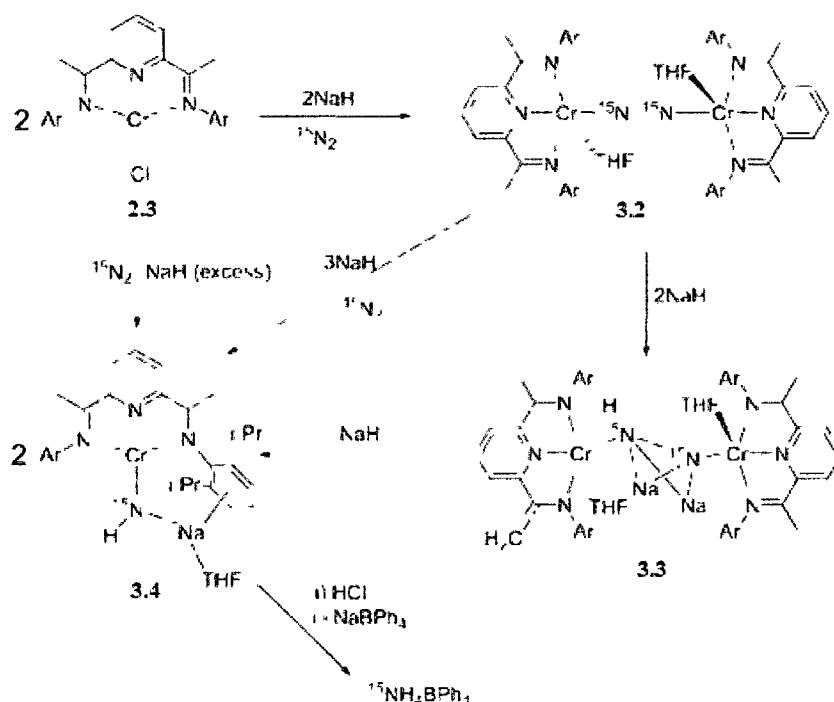
Further treatment of **3.3**, or more conveniently of either **3.2** or **2.3**, with NaH in appropriate amounts (Scheme 3.3) afforded a new paramagnetic [$\mu_{\text{eff}} = 3.60 \mu_B$] complex formulated as **3.4** on the basis of the X-ray crystal structure, spectroscopic data, and chemical degradation experiments. The yield was very low but always reproducible.

The structure revealed a chromium center in a squareplanar environment defined by the three donor atoms of the ligand system and a non-hydrogen light atom. This atom, in turn, bridges a sodium atom, π -bound to one of the aryl substituents (Figure 3.5). The thermal parameters of the bridging atom could be satisfactorily refined as either carbon or nitrogen. The hydrogen atom(s) at nitrogen could not be located, but the IR spectrum of **3.4** displays one sharp peak at 3413 cm^{-1} , in the area typical for NH stretching bands. Crystalline samples with identical cell parameters obtained by carrying out the same reaction under $^{15}\text{N}_2$ displayed an isotopic shift to 3366 cm^{-1} . In addition, chemical degradation with diluted HCl followed by precipitation with NaBPh_4 afforded analytically pure samples of $^{15}\text{NH}_4\text{BPh}_4$, therefore conclusively demonstrating that the bridging atom is nitrogen and its origin is dinitrogen gas.

The isotope enrichment demonstrates that the formation of **3.4** is the result of dinitrogen cleavage. The fact that **3.4** could be obtained from **2.3**, **3.2**, or **3.3** suggests that **3.2** and **3.3** may be regarded as intermediates in the formation of **3.4**, with **3.3** being the

immediate precursor. The square-planar geometry of the chromium center is very comparable to that of **2.3** and **3.1**, thus indicating that even in this case the metal center is present in the divalent state; i.e., reduction of **3.3** has taken place at nitrogen, not at the metal center.

Scheme 3.3



The low magnetic moment of [$\mu_{\text{eff}} = 3.60 \mu_{\text{B}}$] is not compatible with plain Cr(II) [expected to be in the range of $\mu_{\text{eff}} = 4.8 \mu_{\text{B}}$] but rather suggests that the complex contains high-spin Cr(III) coupled to a ligand-centered unpaired electron. There are two tautomeric formulations that together would account for the above observations (Scheme 3.4). The first is a complex containing a nondeprotonated ligand (as a radical anion) and a uninegative $\text{NHNa}(\text{THF})$ fragment. Electronically, this variation (**3.4a**) would be similar to complex **2.3**. As a second possibility, the complex may contain a monodeprotonated ligand (as a radical dianion) and a neutral $\text{NH}_2\text{Na}(\text{THF})$ fragment. Electronically, the

formulation **3.4b** would be similar to complex **3.4**. However, the fact that the IR spectrum shows only one slightly broad band for the N-H stretching possibly indicates that the structure **3.4a** is the dominant one in the tautomeric equilibrium.

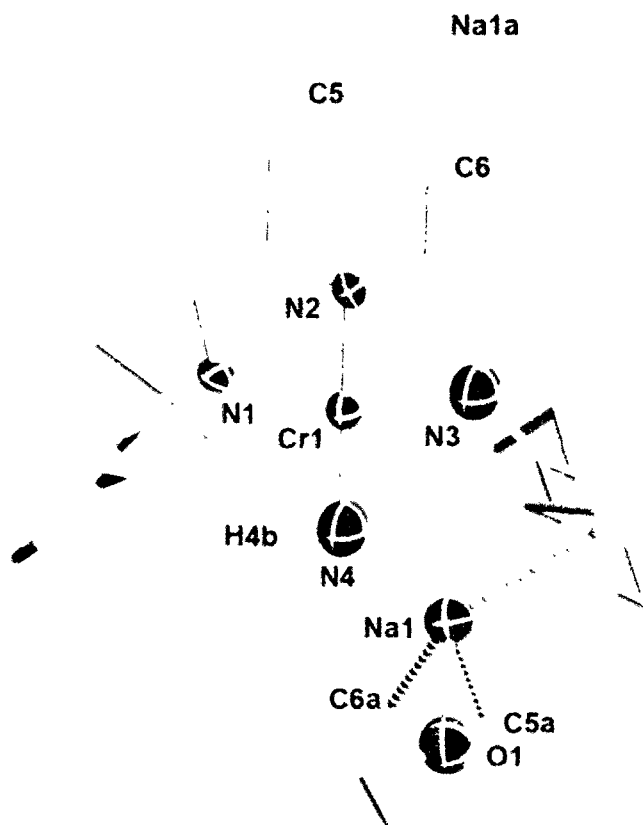
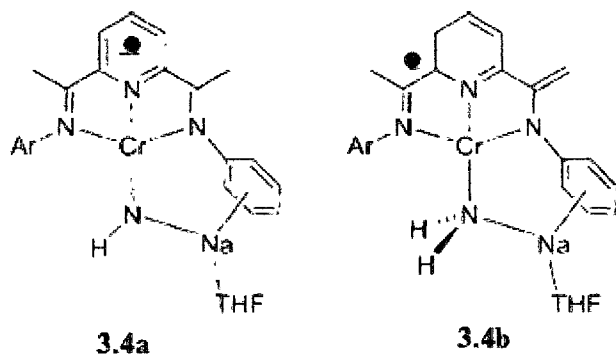


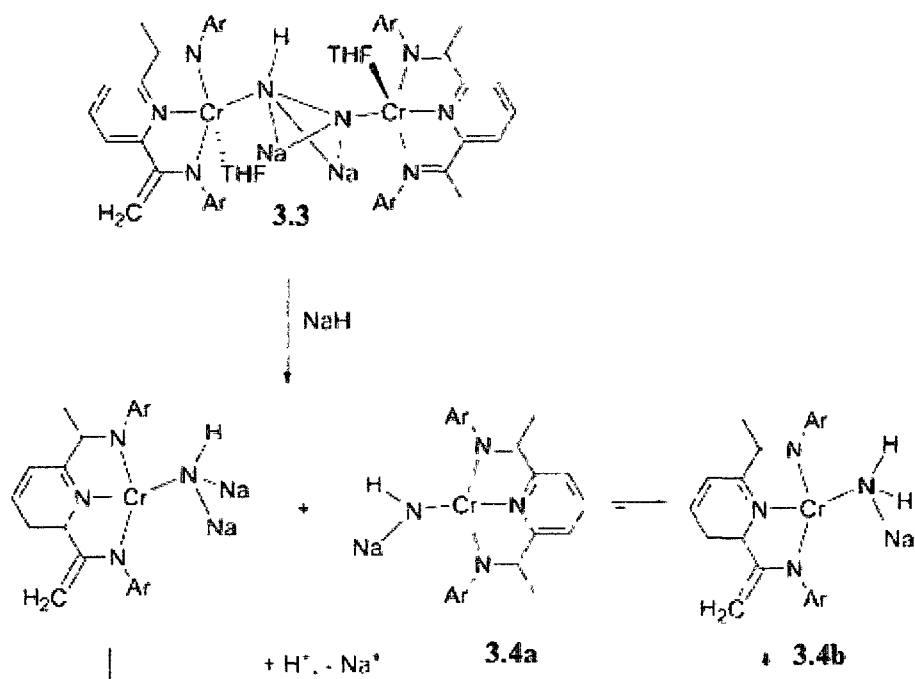
Figure 3.5. Thermal ellipsoid plot for **3.4** with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity

Scheme 3.4



A possible rationalization for the formation of 3.4 could start with 3.2 reacting with an additional 1 equiv of NaH and resulting in cleavage of the N-N bond, producing one monosodium amide and one disodium amide complex (Scheme 3.5). The latter is likely to be basic enough to deprotonate any solvent and form a monosodium amide.

Scheme 3.5



Conclusions

In this chapter, it has been reported the formation of a bridging chromium-dinitrogen complex, its partial reduction and hydrogenation, and eventual cleavage to an imide product. Given the unusual paucity of dinitrogen chemistry among chromium complexes, it seems plausible that the electron-storage capabilities of the diiminepyridine ligand play an important role in this sequence of reactions. The chemistry is complex, with several reactions occurring in parallel. Given that chromium seems to have no inclination for dinitrogen fixation/activation, these transformations, which have been otherwise observed only in molybdenum chemistry,^{3a,b,5} can only be ascribed to the remarkable ability of the diiminepyridine ligand to act as an electron reservoir in multistep reductive transformations.

Reference

- (1) a) MacLachlan, E. A.; Fryzuk, M. D. *Organometallics* **2006**, *25*, 1530.
b) Gambarotta, S. *J. Organomet. Chem.* **1995**, *500*, 117.
c) Gambarotta, S.; Scott, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 5289.
d) MacKay, B. A.; Fryzuk, M. D. *Chem. Rev.* **2004**, *104*, 385.
e) Hidai, M.; Mizobe, Y. *Chem. Rev.* **1995**, *95*, 1115.
f) Hidai, M. *Coord. Chem. Rev.* **1999**, *185-186*, 99. (g) Fryzuk, M. D.; Johnson, S. A. *Coord. Chem. Rev.* **2000**, *200-202*, 379.
- (2) Allen, A. D.; Senoff, C. V. *J. Chem. Soc., Chem. Commun.* **1965**, 621.
- (3) a) Yandulov, D. V.; Schrock, R. R. *Science* **2003**, *301*, 76.
b) Schrock, R. R. *Acc. Chem. Res.* **2005**, *38*, 955.
c) Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *Nature* **2004**, *427*, 527.
d) Korobkov, I.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem., Int. Ed.* **2003**, *42*, 4958.
- (4) a) Leigh, G. J. *Acc. Chem. Res.* **1992**, *25*, 177.
b) Howard, J. B.; Rees, D. C. *Chem. Rev.* **1996**, *96*, 2965.
c) Burgess, B. K.; Lowe, D. J. *Chem. Rev.* **1996**, *96*, 2983.
d) Burgess, B. K. *Chem. Rev.* **1990**, *90*, 1377.
- (5) a) Laplaza, C. E.; Cummins, C. C. *Science* **1995**, *268*, 861.
b) Laplaza, C. E.; Johnson, M. J. A.; Peters, J. C.; Odom, A. L.; Kim, E.; Cummins, C. C.; George, G. N.; Pickering, I. J. *J. Am. Chem. Soc.* **1996**, *118*, 8623.
c) Yandulov, D. V.; Schrock, R. R. *J. Am. Chem. Soc.* **2002**, *124*, 6252.
d) Mindiola, D. J.; Meyer, K.; Cherry, J.-P. F.; Baker, T. A.; Cummins, C. C. *Organometallics* **2000**, *19*, 1622.
e) Solari, E.; Da Silva, C.; Iacono, B.; Hesschenbrouck, J.; Rizzoli, C.; Scopelliti, R.; Floriani, C. *Angew. Chem., Int. Ed.* **2001**, *40*, 3907.
- (6) a) Fryzuk, M. D.; Johnson, S. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1998**, *120*, 11024. b) Fryzuk, M. D.; Johnson, S. A.; Patrick, B. O.; Albinati, A.; Mason, S. A.; Koetzle, T. F. *J. Am. Chem. Soc.* **2001**, *123*, 3960.
c) Fryzuk, M. D.; MacKay, B. A.; Johnson, S. A.; Patrick, B. O. *Angew. Chem., Int. Ed.* **2002**, *41*, 3709.

- (d) Fryzuk, M. D.; MacKay, B. A.; Patrick, B. O. *J. Am. Chem. Soc.* **2003**, *125*, 3234.
- (e) MacKay, B. A.; Patrick, B. O.; Fryzuk, M. D. *Organometallics* **2005**, *24*, 3836.
- (7) (a) Jubb, J.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 4477.
- (b) Dube', T.; Conoci, S.; Gambarotta, S.; Yap, G. P. A.; Vasapollo, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 3657.
- (c) Dube, T.; Ganesan, M.; Conoci, S.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2000**, *19*, 3716.
- (d) Guan, J.; Dube, T.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2000**, *19*, 4820.
- (8) a) Girolami, G. S.; Salt, J. E.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Am. Chem. Soc.* **1983**, *105*, 5954.
- b) Sellman, D.; Maisel, G. Z. *Naturforsch., B* **1972**, *27B*, 465.
- c) Karsch, H. H. *Angew. Chem., Int. Ed.* **1977**, *16*, 56. (d) Sobota, P.; Jezowski-Trzebiatowskq, B. *J. Organomet. Chem.* **1977**, *131*, 341.
- (9) a) Richards, R. L.; Chatt, J.; Fay, R. C. *J. Chem. Soc. A* **1971**, 702.
- b) Sellmann, D.; Brandl, A.; Endell, R. *J. Organomet. Chem.* **1975**, *90*, 309.
- c) Girolami, G. S.; Salt, J. E.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Am. Chem. Soc.* **1983**, *105*, 5954.
- d) Church, S. P.; Grevels, F. W.; Hermann, H.; Schaffner, K. *Inorg. Chem.* **1984**, *23*, 3830.
- e) Denholm, S.; Hunter, G.; Weakley, T. J. R. *J. Chem. Soc., Dalton Trans.* **1987**, 2789. (f) Zhang, Q.-F.; Chim, J. L. C.; Lai, W.; Wong, W.-T.; Leung, W.-H. *Inorg. Chem.* **2001**, *40*, 2470.
- (10) a) Small, B. L.; Brookhart, M.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049.
- b) Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 849.
- (11) a) Reardon, D.; Conan, F.; Gambarotta, S.; Yap, G.; Wang, Q. *J. Am. Chem. Soc.* **1999**, *121*, 9318.
- b) Reardon, D.; Aharonian, G.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2002**, *21*, 786.

- c) Sugiyama, H.; Aharonian, G.; Gambarotta, S.; Yap, G. P. A.; Budzelaar, P. H. M. *J. Am. Chem. Soc.* **2002**, *124*, 12268.
- d) Scott, J.; Gambarotta, S.; Korobkov, I.; Budzelaar, P. H. M. *J. Am. Chem. Soc.* **2005**, *127*, 13019.
- e) Scott, J.; Gambarotta, S.; Korobkov, I. *Can. J. Chem.* **2005**, *83*, 279. (f) Sugiyama, H.; Gambarotta, S.; Yap, G. P. A.; Wilson, D. R.; Thiele, S. K.-H. *Organometallics* **2004**, *23*, 5054.
- g) Bouwkamp, M. W.; Lobkovsky, E.; Chirik, P. J. *Inorg. Chem.* **2006**, *45*, 2.
- h) Sugiyama, H.; Korobkov, I.; Gambarotta, S.; Möller, A.; Budzelaar, P. H. M. *Inorg. Chem.* **2004**, *43*, 5771.
- i) Scott, J.; Gambarotta, S.; Korobkov, I.; Budzelaar, P. H. M. *Organometallics* **2005**, *24*, 6298.
- j) Bouwkamp, M. W.; Bart, S. C.; Hawrelak, E. J.; Trovitch, R. J.; Lobkovsky, E.; Chirik, P. J. *Chem. Commun.* **2005**, 3406.
- (12) Enright, D.; Gambarotta, S.; Yap, G. P. A.; Budzelaar, P. H. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3873.
- (13) a) de Bruin, B.; Bill, E.; Bothe, E.; Weyhermüller, T.; Wieghardt, K. *Inorg. Chem.* **2000**, *39*, 2936.
- b) Budzelaar, P. H. M.; de Bruin, B.; Gal, A. W.; Wieghardt, K.; van Lenthe, J. H. *Inorg. Chem.* **2001**, *40*, 4649.
- c) Knijnenburg, Q.; Hetterscheid, D.; Kooistra, T. M.; Budzelaar, P. H. M. *Eur. J. Inorg. Chem.* **2004**, 1204.
- d) Bart, S. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 13794.
- e) Vidyaratne, I.; Gambarotta, S.; Korobkov, I.; Budzelaar, P. H. M. *Inorg. Chem.* **2005**, *44*, 1187.
- f) Scott, J.; Gambarotta, S.; Korobkov, I.; Knijnenburg, Q.; de Bruin, B.; Budzelaar, P. H. M. *J. Am. Chem. Soc.* **2005**, *127*, 17204.
- g) Bart, S. C.; Chlopek, K.; Bill, E.; Bouwkamp, M. W.; Lobkovsky, E.; Neese, F.; Wieghardt, K.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 13901.
- h) Vidyaratne, I.; Scott, J.; Gambarotta, S.; Korobkov, I.; Duchateau, R. R. J. *Organometallics* **2007**, submitted for publication.

- i) Knijnenburg, Q.; Gambarotta, S.; Budzelaar, P. H. M. *Dalton Trans.* **2006**, 5442.
- (14) a) Ahlrichs, R.; et al. *Turbomole*, version 5; Theoretical Chemistry Group, University of Karlsruhe, Jan 2002.
- b) Treutler, O.; Ahlrichs, R. *J. Chem. Phys.* **1995**, *102*, 346-354.
- c) Schafer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571-2577.
- d) Schafer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829-5835.
- e) Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123-141.
- (15) a) *PQS*, version 2.4; Parallel Quantum Solutions: Fayetteville, AK, 2001 (the Baker optimizer is available separately from PQS upon request).
- b) Baker, J. *J. Comput. Chem.* **1986**, *7*, 385-395.
- (16) a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789.
- b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372-1377.
- c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652.
- d) All calculations were performed using the *Turbomole* functional "b3 lyp", which is not identical to the *Gaussian* "B3LYP" functional.
- (17) Schaftenaar, G.; Noordik, J. H. *J. Comput.-Aided Mol. Des.* **2000**, *14*, 123-134.
- (18) For example, see: (a) O'Connor, C. J. *Magnetochemistry Advances in Theory and Experimentation. Progress in Inorganic Chemistry*; John Wiley & Sons: New York, 1982; pp 203-283.
- b) Gambarotta, S. *Comments Inorg. Chem.* **1991**, *4*, 195.
- (19) Esteruelas, M. A.; Lopez, A. M.; Mendez, L.; Oliva'n, M.; Onate, E. *Organometallics* **2003**, *22*, 395.
- (20) The alternative possibility that the actual structure of **5** differs from the one we tried to model in having fewer or more hydrogen atoms cannot be entirely excluded at this stage.
- (21) In fact, upon elongation of the Cr-N₂ distance, the d_z² orbital becomes occupied, and this seems to cause dissociation of the dinitrogen molecule in the calculation.

Chapter 4: Dinitrogen Partial Reduction by
Formally Zero- and Divalent Vanadium
Complexes Supported by the Bis-iminopyridine
System.

(Published in *Inorganic Chemistry* **2005**, *44*, 1187)

Introduction

The ability of conjugated bis-imines to sustain high catalytic activity in olefin polymerization with a large variety of metals¹ has renewed the interest for this family of ligands which traditionally were confined to the domain of classical coordination chemistry.² Their remarkable versatility in terms of stabilization of highly reactive species³ may be ascribed to the capacity of these molecules to engage in redox processes with the metal center and to efficiently delocalize negative charge.⁴ The bis-iminopyridine ligand 2,6- $\{[2,6-(i\text{-Pr})_2\text{C}_6\text{H}_5]\text{N}=\text{C}(\text{CH}_3)\}_2(\text{C}_5\text{H}_3\text{N})$,⁵ in particular, can accept up to three electrons into the delocalized π -system to form a paramagnetic radical anion.⁶ This indicates that the occasional appearance of these complexes as low-valent species may be deceiving since in reality the metal might be in a higher oxidation state, one or more electrons being efficiently stored into the extended iminopyridine π -system.⁴ Nonetheless, depending on the extent of charge-transfer, the reducing power of the metal is not necessarily quenched. For example, highly reactive zero-valent Fe^3 and monovalent Co^7 complexes of this ligand system are sufficiently reactive to coordinate dinitrogen.

There are limitations though. It is now well-established that the bis-iminopyridine ligand may engage, particularly during alkylation processes, in a variety of transformations which span from alkylation at virtually any position of the pyridine ring,⁸ including the N atom,⁹ and of the imine functions,¹⁰ to deprotonation of one⁹ or both methyl imine substituents.¹¹ In both ligand-alkylation and ligand-deprotonation processes, the primary transformation undergone by the ligand system is to become either mono- or dianionic, thus providing accessibility to a new family of anionic ligands. Besides supporting new catalysts for olefin and diolefin polymerization,¹¹ these ligands may also store additional electron density in C-C bonds via dimerization reactions.^{4,8b} This redox dimerization may occur not only with the intervention of external reducing agents but also spontaneously and at the expense of the metal center. This was the case of a $\text{Co}(\text{II})$ species which was reduced by the anionic ligand to the monovalent state and became the precursor to dinitrogen fixation.¹²

These considerations prompted us to revisit the reactivity of the bis-iminopyridine complexes of vanadium which have already provided a potent ethylene polymerization catalyst but which also gave the first indication about how ligand alkylation may provide reduction pathways for the metal center.^{8a} A recurrent feature of di- and trivalent vanadium supported by N-donor based ligand systems (amides and amidinates) is the ability to form dinitrogen complexes¹³ which in two instances have provided the basis for further dinitrogen cleavage.¹⁴ We have therefore attempted the hydride-reduction of the vanadium center supported by both the neutral and dianionic forms of the bis-imine pyridine ligand system to probe the possibility to stabilize formal low oxidation states without quenching the reactivity of the metal center.

Experimental Section

All preparation were performed under an inert atmosphere by using standard schlenk type techniques and a glove box. $\text{VCl}_3(\text{THF})_3$,¹⁵ $2,6\text{-}\{2,6\text{-}(i\text{-Pr})_2\text{C}_6\text{H}_3\}\text{N}=\text{C}(\text{CH}_3)\}_2(\text{C}_5\text{H}_3\text{N})\}\text{VCl}_3$ ^{8a} and $\{[2,6\text{-}\{2,6\text{-}(i\text{-Pr})_2\text{C}_6\text{H}_3\}\text{N}=\text{C}(\text{CH}_2)\}_2\text{-}(\text{C}_5\text{H}_3\text{N})\}\text{Li}(\text{THF})\}\{\text{Li}(\text{THF})_4\}$ ¹⁷ were prepared according to published procedures. 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 Guoy balance (Johnson Matthey) at room temperature. Magnetic moments were calculated following standard method using Guoy balance and corrections for underlying diamagnetism were applied to the data. Elemental analyses were carried out with a Perkin Elmer 2400 CHN analyzer. Data for Xray crystal structure determinations were obtained with a Bruker diffractometer equipped with a SMART CCD area detector. NMR spectra were recorded with a Varian AMX-500 spectrometer.

Preparation of $[2,6\text{-}\{2,6\text{-}(i\text{-Pr})_2\text{C}_6\text{H}_3\}\text{N}=\text{C}(\text{CH}_3)\}_2(\text{C}_5\text{H}_3\text{N})\text{V}]_2(\mu\text{-N}_2)\cdot(\text{hexane})$ (4.1)

A solution of $\{2,6\text{-}\{2,6\text{-}(i\text{-Pr})_2\text{C}_6\text{H}_3\}\text{N}=\text{C}(\text{Me})\}_2(\text{C}_5\text{H}_3\text{N})\}\text{VCl}_3$ ^{8a} (1.31 g, 2.0 mmol) in THF (100 ml) was treated with a suspension of NaH (0.158 g, 6.6mmol) in THF (20 ml) The resulting cherry-red colored mixture was stirred for 4 days at room temperature

during which the color of solution changed from cherry-red to dark black/green. The solvent was evaporated in vacuo and the dark green solid was re-dissolve in hexane (80 ml). Dark black/green colored crystals of **(4.1)** were isolated upon cooling (0.855 g, 0.694mmol, 34.7 % yield) $\mu_{\text{eff}} = 4.97 \mu_{\text{B}}$

Preparation of {[2,6-(*i*-Pr)₂C₆H₃]N-C=CH₂]₂(C₅H₃N)]V(THF)}Cl·1.5Tol (**4.2**)

{[2,6-(*i*-Pr)₂C₆H₃]N-C=CH₂]₂(C₅H₃N)]Li(THF)}Li(THF)₄ (0.914g, 1.072mmol) was added to a solution of VCl₃(THF)₃ (0.400 g, 1.072 mmol) in THF (60 ml), and resulting mixture was stirred overnight at room temperature. The solvent was evaporated under reduced pressure to yield dark red solid, which was re dissolved in anhydrous toluene (40 ml). Dark red crystals of **4.2** were obtained after allowing the resulting solution to stand overnight at low temperature (-35°C) (0.766g, 0.986 mmol, yield = 92%) $\mu_{\text{eff}} = 2.92 \mu_{\text{B}}$.)

Preparation of [2,6-{[2,6-(*i*-Pr)₂C₆H₃]N-C=(CH₂)₂(C₅H₃N)]V]₂(μ -N₂)·(hexane) (**4.3**)

A freshly-cut fragment of metallic potassium (0.055g, 1.42 mmol) was added to a solution of **(4.2)** (1.000 g, 1.288 mmol) in THF (50 ml) under a nitrogen atmosphere and the resulting mixture was stirred for four hours at room temperature during which the color of the solution changed from dark red to dark greenish brown. Excess K and KCl were removed by centrifugation. After evaporation to dryness the residue was re-dissolved in hexane (100 ml). Dark green crystals of **(4.3)** were isolated at after standing at -38°C. (0.945 g, 0.767mmol, 59.6 % yield).

X-ray Crystallography

A suitable crystal was selected, mounted on a thin glass fiber using paraffin oil, and cooled to the data collection temperature. Data was collected on a Bruker AXS SMART 1K CCD diffractometer using 0.3° ω scans at 0°, 90°, 180°, and 270° in for ϕ the triclinic cells and 0°, 120°, and 240° in ϕ for the monoclinic cells. Initial unit-cell

parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.¹⁹ The diffraction data and unit cell parameters were consistent with the reported space group *C2/c* for complexes **4.1** and **4.3**. No symmetry higher than triclinic was observed, and the solution in the centrosymmetric space group yielded chemically reasonable and computationally stable results of refinement. The data for complex **4.2** were consistent with the space group *P*(1). All structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2 . All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. All scattering factors are contained in the SHELXTL 6.12 program library.²¹ Relevant crystal data and selected bond distances and angles are reported in Tables 4.1 and 4.2 respectively.

Table 4.1 Crystal Data and Structure Analysis Results for 4.1 – 4.3

	4.1	4.2	4.3
Formula	C ₄₀ H ₅₈ N ₄ O ₂ V	C _{47.50} H ₆₁ N ₃ ClO ₂ V	C ₄₀ H ₅₆ N ₄ O ₂ V
FW	661.87	776.38	658.86
Crystal system	Monoclinic	Triclinic	Monoclinic,
space group	C2/c	<i>P</i> (1)	C2/c
a (Å)	25.401(2)	10.872(3)	25.093(4)
b (Å)	11.6983(11)	13.618(5)	11.7898(18)
c (Å)	30.425(3)	15.139(6)	30.183(5)
α (deg)	90	77.14(4)	90
β (deg)	113.643(2)	86.54(4)	112.754(3)
γ (deg)	90	82.41(4)	90
V (Å ³)	8281.9(13)	2164.7(13)	8235(2)
Z	8	2	8
radiation (K α , Å)	0.71073	0.710 73	0.71073
T (K)	206(2)	213(2)	208(2)
D _{calcd} (g cm ⁻³)	1.131	1.191	1.086
μ_{calcd} (mm ⁻¹)	0.331	0.328	0.328
F ₀₀₀	3056	830	2903
R, R _w ^{2 a}	0.0658, 0.1420	0.0626, 0.1902	0.0634, 0.1568
GoF	1.038	1.096	1.004

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

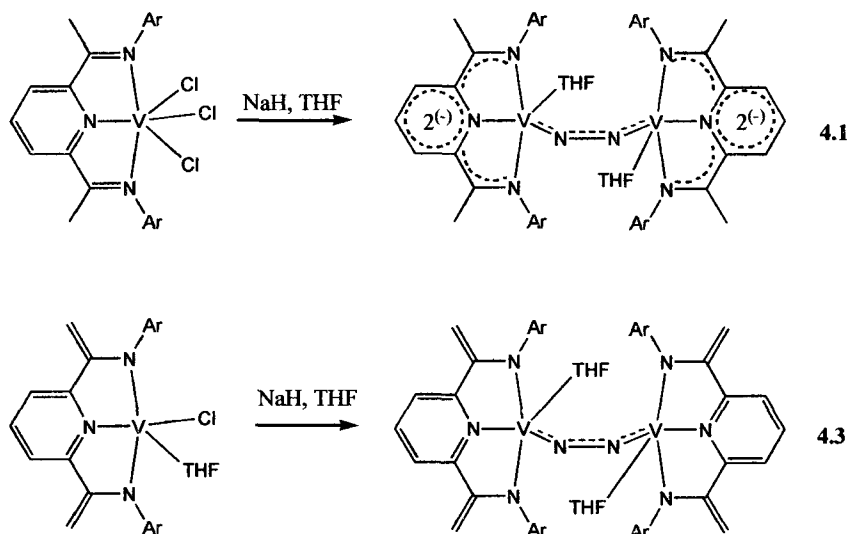
Table 4.2 Selected Bond Distances (Å) and Angles (deg) for **4.1- 4.3**

4.1	4.2	4.3
N4 - N4a = 1.259(6)	V - N3 = 1.948(7)	N4 - N4a = 1.242(5)
V1 - N4 = 1.777(3)	V - N1 = 1.967(7)	V1 - N4 = 1.777(2)
V1 - N1 = 2.141(3)	V - N2 = 2.024(6)	V1 - N1 = 2.024(3)
V1 - N2 = 1.931(3)	V - O = 2.138(6)	V1 - N2 = 2.029(3)
V1 - N3 = 2.084(3)	V - Cl = 2.300(7)	V1 - N3 = 2.049(2)
C1 - C2 = 1.500(6)	N3-V-N1 = 138.5(2)	C1 - C2 = 1.317(5)
C8 - C9 = 1.497(6)	N3-V-N2 = 78.0(3)	C8 - C9 = 1.350(4)
C2 - N1 = 1.341(5)	N1-V-N2 = 76.5(3)	C2 - N1 = 1.401(4)
C8 - N3 = 1.370(5)	N3-V-O = 100.0(3)	C8 - N3 = 1.387(4)
O1-V1-N1 = 92.44(12)	N1-V-O = 100.0(3)	O1-V1-N1 = 97.18(10)
O1-V1-N2 = 151.68(12)	N2-V-O = 170.66(16)	O1-V1-N2 = 157.55(10)
O1-V1-N3 = 97.97(12)	N3-V-Cl = 107.0(3)	O1-V1-N3 = 94.45(10)
O1-V1-N4 = 103.81(12)	N1-V-Cl = 107.5(3)	O1-V1-N4 = 103.38(10)
N1-V1-N2 = 75.24(13)	N2-V-Cl = 95.6(2)	N1-V1-N2 = 76.97(10)
N1-V1-N3 = 138.05(13)	O-V-Cl = 93.7(2)	N1-V1-N3 = 135.83(11)
N1-V1-N4 = 109.87(13)		N1-V1-N4 = 107.39(11)
N2-V1-N3 = 76.62(13)		N2-V1-N3 = 76.25(10)
N2-V1-N4 = 104.36(14)		N2-V1-N4 = 99.04(10)
N3-V1-N4 = 106.82(13)		

Results and Discussion

The reaction of the 2,6- $\{[2,6-(i\text{-Pr})_2\text{C}_6\text{H}_5]\text{N}=\text{C}(\text{CH}_3)\}_2(\text{C}_5\text{H}_3\text{N})\text{VCl}_3$ adduct^{8a} with an excess of NaH proceeded slowly at room temperature affording a dark-colored suspension from which dark crystals of the paramagnetic dinitrogen complex $[2,6-\{[2,6-(i\text{-Pr})_2\text{C}_6\text{H}_5]\text{N}=\text{C}(\text{CH}_3)\}_2(\text{C}_5\text{H}_3\text{N})\text{V}]_2(\mu\text{-N}_2)\cdot(\text{hexane})$ (**4.1**) were isolated in 35% yield (Scheme 4.1).

Scheme 4.1



Attempts to use other reductants, such as potassium, afforded intractable materials. The formation of **4.1** was accompanied by H_2 gas evolution which was recovered in significant yield (79% of the expected amount based on a presumed 100% conversion) by carrying the reaction in a sealed vessel connected to a Toepler pump.

The connectivity of **4.1** was yielded by an X-ray crystal structure (Figure 4.1) showing a dinuclear complex with the two vanadium atoms bridged by one end-on bonded dinitrogen unit and each surrounded by one ligand and one molecule of coordinated THF. The ligand system appears to have undergone no significant modification with respect to the starting trivalent complex.^{8a} The bond lengths and bond

angles are listed in the table. The C_{imine}-C_{Me} bonds are rather long and clearly are C-C single bonds.

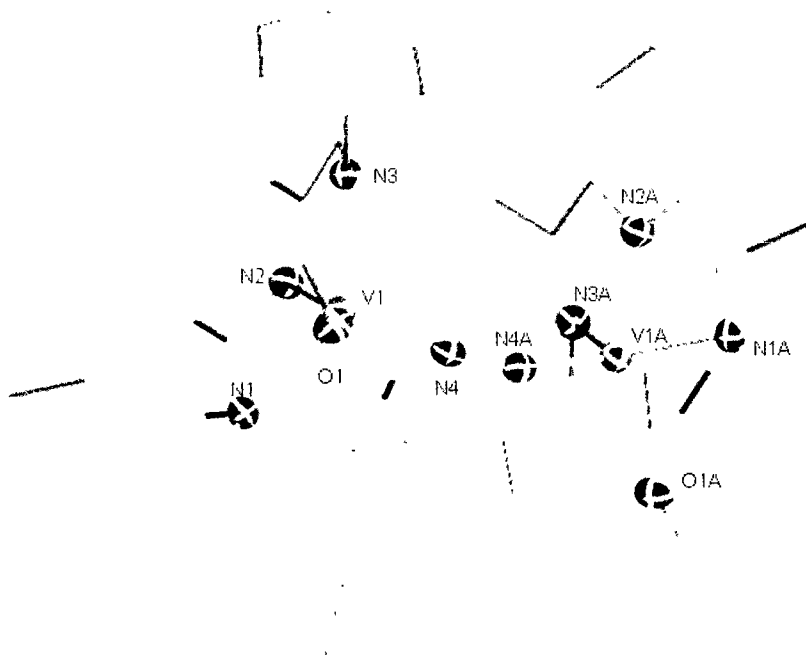


Figure 4.1 Thermal ellipsoid plot of 4.1 with 30% probability level.

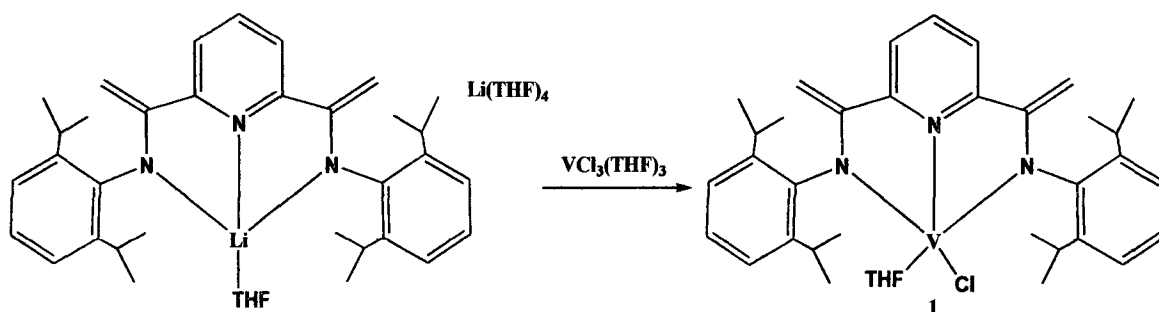
This rules out the possibility that the ligand might have been deprotonated by the strongly basic NaH. The V-N and N-N distances compare rather well with those of the other existing V(II) and V(III) dinitrogen complexes.¹⁷ The N-N bond is elongated relative to that of free N₂, indicating reduction to [N₂]²⁻. This alone would make each V atom monovalent. However, the C_{imine}=N_{imine} bonds are much longer than those in the free ligand or in its "innocent" complexes, while the C_{py}-C_{imine} bonds are shortened. The bond length changes indicate a transfer of more than 1.5 electrons from the metal to the ligand.¹⁸ Thus, the structure is best regarded as containing two V(III) atoms, bridged by an N₂²⁻ unit and each bearing a ligand dianion.

The structure does not show any distortion which may possibly be indicative of the presence of one or more hydrides. In addition, chemical degradation experiments

carried out with the Toepler pump did not yield any significant amount of H₂. The IR spectrum ruled out the possibility that the N atoms may have been protonated.

As mentioned above, the diminopyridine molecule 2,6-[[2,6-(*i*-Pr)₂C₆H₃]N=C(CH₃)₂]₂ (C₅H₃N) can be transformed into the corresponding dianion {[2,6-[[2,6-(*i*-Pr)₂C₆H₃]N-C=(CH₂)₂]₂(C₅H₃N)]²⁻ via simple treatment with 2 equiv of LiCH₂SiMe₃.⁴ Reaction of the dilithium salt of 2,6-[[2,6-(*i*-Pr)₂C₆H₃]N-C=CH₂]₂ (C₅H₃N) with VCl₃(THF)₃ in THF at room temperature afforded compound **4.2** in 80% yield (Scheme 4.2). Compound **4.2** was isolated as a dark red solid from toluene. Dark red crystals were obtained by freezing the toluene solution overnight. The magnetic moment calculated at room temperature is 2.93 μ_B clearly indicating the vanadium metal is in the +3 oxidation state.

Scheme 4.2



The connectivity of **4.2** was yielded by an X-ray crystal structure (Figure 4.2). The trivalent vanadium complex is surrounded by a ligand, a chlorine atom and a THF molecule. The selected bond distances, bond angles are given in the Table 4.1. The overall geometry around vanadium is distorted square pyramidal with the pyramidal position is occupied by a chlorine atom. The average bond distance of V-N is 1.98(7) Å. The V-Cl bond distance is 2.30 (7) Å. The C_{imine}-C_{Me} bonds are shorter than those of complex **4.1** and are clearly C-C double bonds with the average distance being 1.33 Å.⁵

Its treatment with K in THF resulted in a slow color change and yielded dark-colored crystals (60%) of the nearly diamagnetic dinitrogen complex $[\{[2,6\text{-}\{2,6\text{-}(i\text{-Pr})_2\text{C}_6\text{H}_3\}\text{N-C}(\text{CH}_2)\}_2(\text{C}_5\text{H}_3\text{N})]\text{V}]_2(\mu\text{-N}_2)\cdot(\text{hexane})$ (**4.3**) (Scheme 4.1).

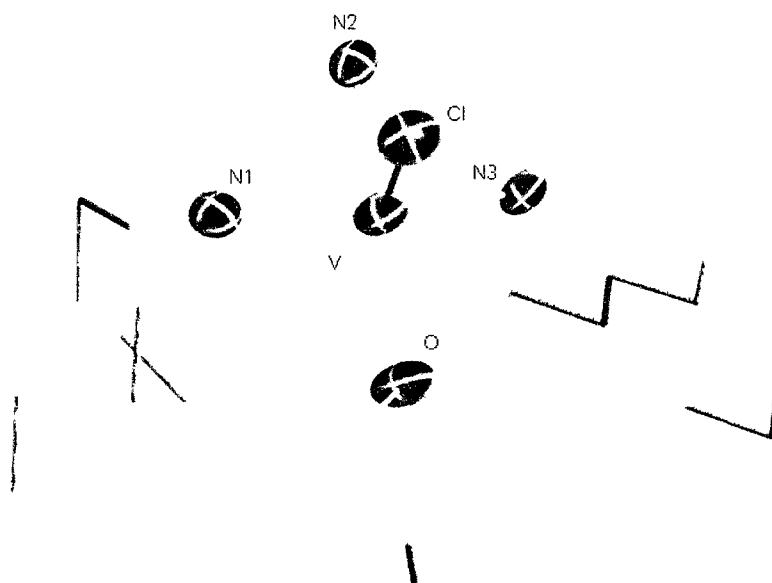


Figure 4.2 Thermal ellipsoid plot of **4.2** drawn at a 30% probability level

The crystal structure of **4.3** is very similar to that of **4.1**, and not surprisingly, the two species display almost identical crystallographic cell parameters (Figure 4.3). However, the former $\text{C}_{\text{imine}}\text{-C}_{\text{Me}}$ bonds are much shorter than those in **4.1** and are evidently double bonds (av. $\text{C}_{\text{imine}}\text{-CH}_2$ bond distance 1.334 Å). Thus, while in **4.1** a ligand dianion is formed through metal-to-ligand electron transfer, in **4.3** it has been

formed by deprotonation. The V-N distances seem to be unaffected by this change. Selected bond lengths and bond angles are listed in the table 4.1 and 4.2.

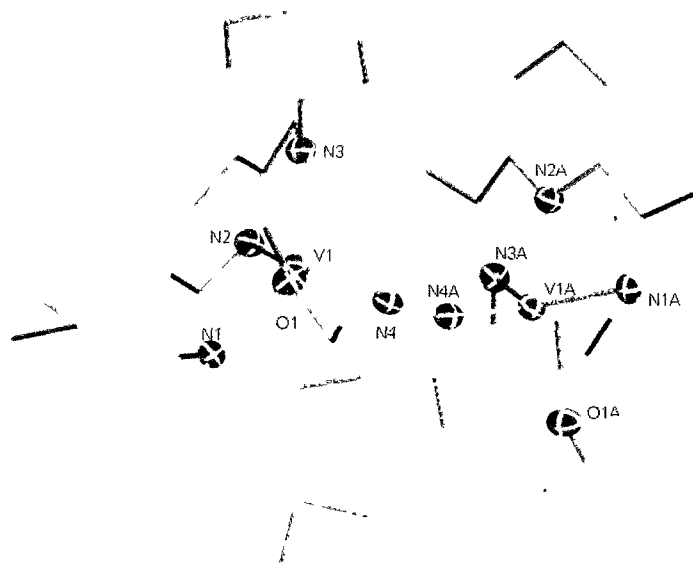


Figure 4.3 Thermal ellipsoid plot of **4.3** with 30% probability level.

The geometries of simplified models of complexes **4.1** and **4.3** (Me groups at N) were optimized using unrestricted DFT calculations.²⁰ For both complexes, spin "states" from $S = 0$ to 4 were considered. All $S = 2$ or higher states were found to be too high in energy to be relevant. The $S = 0$ state was calculated to be somewhat lower in energy than $S = 1$; the difference depends on the functional but is smaller for **4.1** (RI-bp86: 1.2 kcal/mol; b3-lyp: 7.4 kcal/mol) than for **4.3** (4.5 and 7.8 kcal/mol). The $S = 0$ "state" is heavily spin-contaminated. Therefore, although the absolute energies are probably not very meaningful, the general picture (singlet and triplet close, triplet relatively more stable for **4.1**) should be reliable. The experimental results suggest that we overestimate the stability of the singlet, possibly because of the use of a model ligand, and that for the real systems **4.1** has a triplet ground state, while **4.3** is actually a singlet.

The calculated geometries for $S = 0$ and $S = 1$ are very similar. Figure 4.4 compares the observed and calculated ($S = 1$ for **4.1**, $S = 0$ for **4.3**) geometries. The agreement is sufficient to give credibility to the computational results. The bonding picture that emerges for **4.1** is perhaps clearer if we start with two V^0 centres, each with the occupation $d_{xz}^2 d_{yz}^2 d_{xy}^2$ where each V centre has its own local axis system, with the z axis parallel to the V-N₂ bond and the x axis along V-N_{py}. The d_{yz} electrons (both α and β) backdonate into the N₂ π^* -orbitals, whereas the d_{xz} electrons are mostly transferred into ligand π^* orbitals (only *one* π^* -orbital of each ligand participates). The d_{xy} orbitals on the two V centres interact only weakly and the coupling between these two gives rise to the singlet and triplet states. For **4.3**, the ligand, N₂ π^* and metal d orbitals are strongly mixed and the analysis is not as clear. The highest occupied orbitals show backdonation from d_{xz} and d_{yz} to the N₂ π^* orbitals just like in **4.1**. The activation of N₂ is therefore not much different in the two complexes. However, there is now only one metal electron left to interact with the bis-iminopyridine π^* orbitals, and these π^* orbitals are higher in energy for the dianionic ligand in **4.3** than for the originally neutral ligand in **4.1**. Thus, the metal-ligand bonding in **4.3** is more concentrated in the iminate-V σ -bonds, as is evident from the longer V-N_{py} and shorter V-N_{imine} bonds and the smaller C-C/C-N distances of the pyridine ring in **4.3** as compared to **4.1**. The strong mixing in the orbitals just below the frontier orbitals may explain why the coupling between the remaining electrons on the two V centres is stronger than in **4.1** and results in a diamagnetic ground state. Partial thermal depopulation of the HOMO provides a reasonable explanation for the little residual paramagnetism observed at room temperature.

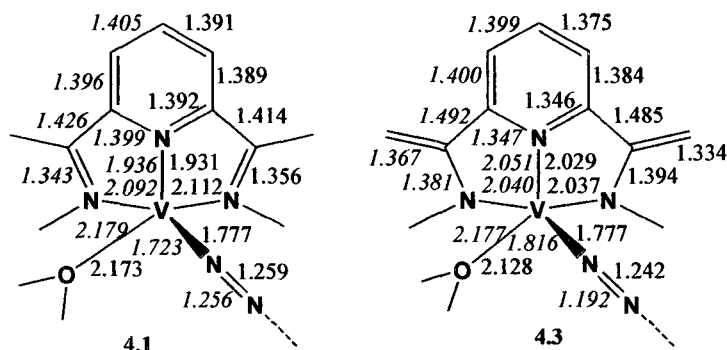


Figure 4.4 Observed and *calculated* bond lengths (Å) for complexes **4.1** ($S = 1$) and **4.3** ($S = 0$).

Conclusion

Reduction of the two trivalent 2,6- $\{[2,6-(i\text{-Pr})_2\text{C}_6\text{H}_5]\text{N}=\text{C}(\text{CH}_3)\}_2(\text{C}_5\text{H}_3\text{N})\text{VCl}_3$ and $\{[2,6-\{[2,6-(i\text{-Pr})_2\text{C}_6\text{H}_3]\text{N}-\text{C}(\text{CH}_2)\}_2(\text{C}_5\text{H}_3\text{N})]\text{VCl}(\text{THF})$ complexes with excess NaH and K respectively afforded two corresponding end-on dinitrogen-bridged complexes $[2,6-\{[2,6-(i\text{-Pr})_2\text{C}_6\text{H}_5]\text{N}=\text{C}(\text{CH}_3)\}_2(\text{C}_5\text{H}_3\text{N})\text{V}]_2(m\text{-N}_2) \cdot (\text{hexane})$ (**4.1**) and $\{[2,6-\{[2,6-(i\text{-Pr})_2\text{C}_6\text{H}_3]\text{N}-\text{C}(\text{CH}_2)\}_2(\text{C}_5\text{H}_3\text{N})]\text{V}\}_2(m\text{-N}_2) \cdot (\text{hexane})$ (**4.3**). These results confirm the versatility of the bis-iminatopyridine ligand for the stabilization of reduced species via extensive metal-to-ligand charge transfer. This implies that the occasional appearance of these complexes as low-valent can be deceiving. Nevertheless, although the actual metal oxidation state in the reduced species is likely to be higher, the formation of the vanadium dinitrogen complexes reported herein, and of the recently reported Fe dinitrogen complexes,³ gives a clear indication about the very high reactivity of the intermediates obtained during the reduction reactions of these derivatives. Therefore, since reduced species can be stabilized without quenching the reactivity of the metal center, this ligand system opens interesting perspectives for its use as an electron storage device.

References

- (1) a) Britovsek, G. J. P.; Bruce, M.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mastroianni, S.; McTavish, S. J.; Redshaw, C.; Solan, G. A.; Strömberg, S.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 8728.
 b) Britovsek, G. J. P.; Dorer, B. A.; Gibson, V. C.; Kimberley, B. S.; Solan, G. A. (BP Chemicals Limited) Patent WO 99/12981, 1999; *Chem Abstr.* **1999**, *130*, 252793.
 c) Britovsek, G. J. P.; Mastroianni, S.; Solan, G. A.; Baugh, S. P. D.; Redshaw, C.; Gibson, V. C.; White, A. J. P.; Williams, D. J.; Elsegood, M. R. J. *Chem. Eur. J.* **2000**, *6*, 2221.
 d) Bruce, M.; Gibson, V. C.; Redshaw, C.; Solan, G. A.; White, J. P. A.; Williams, D. J. *Chem. Commun.* **1998**, 2523.
 e) Small, B. L.; Brookhart, M. *Polymer Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1998**, *39*, 213.
 f) Small, B. L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 7143. (f) Dias, E. L.; Brookhart, M.; White, P. S. *Chem. Commun.* **2001**, 423.
 g) Bennett, A. M. A. (DuPont) Patent WO 98/27124, 1998; *Chem Abstr.* **1998**, *129*, 122973x. (h) Bennett, A. M. A. *CHEMTECH* **1999**, July, 24-28.
- (2) See for example: Gillard, R. D.; McCleverty, J. A. *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1984.
- (3) See for example: Bart, S. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 13794.
- (4) Sugiyama, H.; Korobkov, I.; Gambarotta, S.; Möller, A.; Budzelaar, P. H. M. *Inorg. Chem.* **2004**, *43*, 5771.
- (5) a) Gibson, V. C.; Kimberley, B. S.; White, A. P. J.; Williams, D. J.; Howard, P. J. *Chem. Soc., Chem. Commun.* **1998**, 313.
 b) Small, B. L.; Brookhart, M. S.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049.
 c) Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1998**, 849.

- (6) Enright, D.; Gambarotta, S.; Yap, G. P. A.; Budzelaar, P. H. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3873.
- (7) Gibson, V. C.; Humphries, M. J.; Tellmann, K. P.; Wass, D. F.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **2001**, 2252.
- (8) a) Reardon, D.; Conan, F.; Gambarotta, S.; Yap, G. P. A.; Wang, Q. *J. Am. Chem. Soc.* **1999**, *121*, 9318.
b) Sugiyama, H.; Aharonian, G.; Gambarotta, S.; Yap, G., P. A.; Budzelaar, P. H. M. *J. Am. Chem. Soc.* **2002**, *124*, 12268.
- (9) a) Korobkov, I.; Gambarotta, S.; Yap, G. P. A.; Budzelaar, P. H. M. *Organometallics* **2002**, *21*, 3088.
b) Clentsmith, G. K. B.; Gibson, V. C.; Hitchcock, P. B.; Kimberly, B. S.; Rees, C. W. *J. Chem. Soc., Chem. Commun.* **2002**, 1498.
- (10) Bruce, M.; Gibson, V. C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1998**, 2523.
- (11) Sugiyama, H.; Gambarotta, S.; Yap, G. P. A.; Wilson, D. R.; Thiele, S. K. H. *Organometallics* **2004**, *23*, 5054.
- (12) Scott, J.; Gambarotta, S.; Korobkov, I. *Can. J. Chem. (special issue)*, in press.
- (13) a) Hao, S.; Berno, P.; Minhas, R. K.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 7417.
b) Hao, S.; Berno, P.; Minhas, R. K.; Gambarotta, S. *Inorg. Chim. Acta* **1996**, *244*, 37. (c) Song, J. I.; Berno, P.; Gambarotta, S. **1994**, *116*, 6927.
- (14) a) Clentsmith, G. K. B.; Bates, V. M. E.; Hitchcock, P. B.; Cloke, G. F. N. *J. Am. Chem. Soc.* **1999**, *121*, 10444.
b) Berno, P.; Gambarotta, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 822.
- (15) Manzer, L.E. *Inorg. Synth.* **1982**, *21*, 138.
- (16) Johnson, L. K.; Killian, C. M.; Brookhardt, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 6414.
- (17) a) MacKay, B. A.; Fryzuk, M. D. *Chem. Rev.* **2004**, *104*, 385.
b) Shaver, M. P.; Fryzuk, M. D. *Adv. Synth. Catal.* **2003**, *345*, 1061.
c) Fryzuk, M. D. *Chem. Record.* **2003**, *3*, 2.
d) Fryzuk, M. D. *Mod. Coord. Chem.* **2002**, 187.

- e) Gambarotta, S. *Inorg. Chem. Highlights* **2002**, 285. Gambarotta, S. *J. Organomet. Chem* **1995**, 500, 117. Scott, J.; Gambarotta, S. *Angew. Chem., Int. Ed.* **2004**, 43, 5298.
- (18) a) Budzelaar, P. H. M.; De Bruin, B.; Gal, A. W.; Wieghardt, K.; Van Lenthe, J. H. *Inorg. Chem.* **2001**, 40, 4649.
- b) Kooistra, T. M.; Knijnenburg, Q.; Smits, J. M. M.; Horton, A. D.; Budzelaar, P. H. M.; Gal, A. W. *Angew. Chem., Int. Ed.* **2001**, 40, 4719.

Chapter 5: Isolation of a Self-Activating Ethylene

Trimerization Catalyst.

(Published in *Angew. Chem. Int. Ed.* **2009**, 48, 1)

Introduction

Among the several elements that produce interesting catalysts for ethylene polymerization, without doubt, chromium occupies a special position. The heterogeneous Phillips polymerization system based on chromium-impregnated silica¹ is still among the most widely used, inexpensive, and best-performing catalytic systems for the worldwide commercial production of high-density polyethylene. Related and no less important is the ability of the same element to provide catalysts for selective ethylene trimerization.² In fact, chromium accounts for more than 90% of all the existing ethylene oligomerization catalysts.^{2, 3} Even today, a pyrrole/ chromium/ AlR_3 catalyst is the only catalytic system commercially employed for the selective production of 1-hexene.³ Furthermore, the sole existing homogeneous catalytic system that predominantly forms 1-octene is also based on chromium.⁴

In a modeling study on the Chevron Phillips ethylene trimerization system, we recently reported the isolation of catalytically active chromium species acting as self-activating trimerization and polymerization catalysts.⁵ This study has allowed the metal oxidation state to be linked to the particular catalytic behaviour: monovalent chromium as responsible for selective trimerization, whilst polyethylene is produced by divalent chromium. With the aim of generalizing and further clarifying these findings, we have further investigated the chemistry of chromium with aluminatopyrrolyl anions.

Owing the ability of the pyrrolide ligand to stabilize a wide range of metal oxidation state via its coordinative flexibility,⁶ we expected these systems to be ideally suited for the isolation and study of the chromium catalysts resting states aiming at understanding both chromium polymerization and trimerization mechanistic path ways. Similar to Cp and its sterically bulky derivative (Cp^*)⁷, pyrrolides ligand also can adopt η^5 coordination modes leading to form sandwich type structures.⁸

By using a combination of tetramethylpyrrole, $\text{CrCl}_3(\text{THF})_3$, and AlMe_3 , we had obtained a chromocene-type complex $[\{\eta^{5-2,3,4,5}\text{-Me}_4\text{C}_4\text{N}(\text{AlClMe}_2)\}_2\text{Cr}]$ (**5.1**). This aluminatopyrrolyl chromium complex acts as an active homogeneous single-site, single component polymerization catalyst. Interestingly, when the reaction that afforded **5.1** was carried out with $\text{CrCl}_2(\text{THF})_2$ instead of the trivalent salt, a new species, $[\{\eta^{5-2,3,4,5}$

$\text{Me}_4\text{C}_4\text{N}(\text{AlClMe}_2)\text{Cr}\}_2(\mu\text{-Me})_2]$ (**5.3**), was isolated and it is a very good self-activating oligomerization catalyst instead.

Experimental Section

All operations were performed under an inert atmosphere by using standard Schlenk type techniques. $\text{CrCl}_3(\text{THF})_3$, $\text{CrCl}_2(\text{THF})_2$ and tetramethylpyrrol were prepared according to published procedures. Samples for magnetic susceptibility measurements at room temperature were pre-weighed inside a dry-box equipped with an analytical balance and flame sealed into calibrated 5 mm o.d. quartz tubes. Magnetic measurements were carried out using a Johnson Matthey magnetic balance. Background corrections for the sample holder were included in the magnetic calculations. Standard corrections for the underlying diamagnetism were applied to the data.⁹ Elemental analyses were carried out with a Perkin-Elmer 2400 CHN analyzer. Data for the X-ray crystal structure determinations were obtained with a Bruker diffractometer equipped with a Smart CCD area detector.

Preparation of [$\eta^5\text{-2,3,4,5-Me}_4\text{C}_4\text{N}(\text{AlClMe}_2)\}_2\text{Cr}]$ (**5.1**)

A solution of tetramethylpyrrole (0.233 g, 1.89 mmol) in toluene (15 mL) and a suspension of $\text{CrCl}_3(\text{THF})_3$ (0.400 g, 1.07 mmol) were combined after cooling to -35°C . The resulting mixture was stirred for 5 min and treated with neat AlMe_3 (0.615 g, 8.53 mmol). The color changed immediately from purple to green. The solution was allowed to warm slowly to room temperature, and was then stirred for an additional 4 h. The solvent was evaporated under reduced pressure to yield green solid, which was re-dissolved in anhydrous hexane (20 mL). Dark bluish-green crystals were obtained after allowing the resulting solution to stand for one week at -15°C (0.205 g, 0.43 mmol; yield 40%). $\mu_{\text{eff}} = 2.77 \mu_{\text{B}}$; elemental analysis (%) calcd for $\text{C}_{20}\text{H}_{36}\text{Al}_2\text{Cl}_2\text{CrN}_2$: C 49.90, H 7.54, N 5.82; found: C 49.87, H 7.52, N 5.79.

Preparation of $[\{\eta^5\text{-}2,3,4,5\text{-Me}_4\text{C}_4\text{N}(\text{AlMe}_2\text{Cl})\}\text{CrMe}(\mu\text{-NPh})_2\text{AlMe}_2][\text{Me}_3\text{Al}(\text{THF})]$ (5.2).

Method A: PhN=NPh (0.094 g, 0.52 mmol) was added to a solution of **1** (0.250 g, 0.52 mmol) in toluene (20 mL). The color of the mixture changed from red to brown during stirring for 4 h. The solvent was then removed in vacuo to yield a dark-brown solid, which was re-dissolved in freshly distilled hexane (15 mL). The solution was filtered to remove a small quantity of insoluble material. A dark brown amorphous compound was isolated after standing for one week at -35°C . Upon addition of THF (0.52 mmol), the solid redissolved, and dark reddish brown crystals of **5.2** separated at room temperature after 6 days (0.105 g, 0.20 mmol; yield 31%). $\mu_{\text{eff}} = 1.87 \mu_{\text{B}}$; elemental analysis (%) calcd for $\text{C}_{32}\text{H}_{54}\text{Al}_3\text{ClCrN}_3\text{O}$: C 57.78, H 8.18, N 6.32; found: C 57.66, H 8.15, N 6.29.

Method B: A solution of tetramethylpyrrole (0.291 g, 2.36 mmol) in toluene (20 mL) and a suspension of $\text{CrCl}_3(\text{THF})_3$ (0.500 g, 1.334 mmol) in toluene (25 mL) were cooled to -35°C prior to mixing. The combined mixture was stirred for 5 min, followed by the addition of neat AlMe_3 (0.769 g, 10.67 mmol). An immediate color change from purple to green was observed. The solution was allowed to warm slowly to room temperature, and was then stirred for an additional 4 h. The addition of PhN=NPh (0.243 g, 1.33 mmol) and further stirring overnight resulted in a color change from green to reddish-brown. The solvent was evaporated under reduced pressure and the resulting reddish-brown solid was dissolved in anhydrous hexane. A small amount of insoluble material was removed by centrifugation, and reddish-brown crystals of **5.2** were obtained upon standing at room temperature for 5 days (0.191 g, 0.37 mmol; yield 28%).

Preparation of [η^5 -2,3,4,5-Me₄C₄N(AlClMe₂)Cr]₂(μ -Me)₂] (5.3).

A solution of tetramethylpyrrole (0.9 g, 7.31 mmol) in toluene (5 mL) was combined with a suspension of CrCl₂(THF)₂ (0.97 g 3.63 mmol) in toluene (4 mL), stirred for 20 min, and cooled to - 30 °C. Neat AlMe₃ (1.05 g, 14.57 mmol) was pre-cooled to - 30 °C and added to the resulting mixture. The solution was allowed to warm slowly to room temperature, and was then stirred for additional 4 h. Then the suspension was centrifuged, and the solvent of the clear solution was removed under reduced pressure. The resulting dark oil was redissolved in anhydrous hexane (5 mL). Dark purple crystals were obtained after allowing the resulting solution to stand for 2 days at - 30 °C. (0.36 g, 0.65 mmol; yield 35%). ¹H NMR (500.177 MHz, [D₈]THF, 258C): δ = 36.4 (Dw1/2=700 Hz, 6H, m-MeA), 23.7 (Dw1/2= 700 Hz, 6H, m-MeB), 3.21 (Dw1/2=35 Hz, 6H, C₄NMe₂Me₂ A), 2.83 (Dw1/2=31 Hz, 6H, C₄NMe₂Me₂A), 2.49 (Dw1/2=23 Hz, 12H, C₄NMe₂Me₂ B), 1.77 (Dw1/2=22 Hz, 12H, C₄NMe₂Me₂ B), 1.57 (6H, C₄NMe₂Me₂ A, overlapped with resonance at 1.54 ppm), 1.54 (6H, C₄NMe₂Me₂ A, overlapped with resonance at 1.57 ppm), 0.33 (Dw1/2= 13 Hz, 9H, AlMe₃ A), 0.10 (12H, AlMe₂Cl B, overlapped with resonance at 0.05 ppm), 0.05 ppm (6H, AlMe₂Cl A, overlapped with resonance at 0.10 ppm). Elemental analysis (%) calcd for C_{22.42}H_{43.26}Al₂Cl_{1.58}Cr₂N₂ : C 48.53, H 7.86, N 5.05; found: C 48.77, H 7.89, N 5.01. Fractional stoichiometry is due to split Cl/Me occupation.

Polymerization / Oligomerization:

Samples were tested in a 200 mL high-pressure Büchi reactor containing a heating/cooling jacket. A pre-weighed amount of catalyst was dissolved in toluene (100 mL) under N₂ prior to loading the reaction vessel. Solutions were heated using a thermostatic bath and charged with ethylene; the pressure was maintained throughout the run. Polymerizations were quenched by addition of MeOH and HCl. The resulting polymer was isolated by filtration, sonicated with a solution of HCl, rinsed, and thoroughly dried prior to measuring the mass. Molecular weight and molecular weight distributions of the resulting polymers were determined by gel permeation chromatography on a PL-GPC210 equipped with a refractive index and a viscosity

detector and a 3 x PLgel 10 μ m Mixed-B column set at 135 $^{\circ}$ C using 1,2,4-trichlorobenzene as solvent. The molecular weight of the polyethylenes was referenced to polystyrene standards. Results of the oligomerization were assessed by NMR for activity and GC-MS for reaction mixture composition.

X-ray Cryatallography

The crystals were mounted on thin glass fiber using paraffin oil and cooled to the date collecting temperature. Data was collected on a Bruker AXS SMART 1K CCD diffractometer. Data for the compound **5.1**, **5.2** and **5.3** were collected with a sequence of 0.30 ω scans at 0, 120, and 2400 in ϕ . Initial unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.¹⁰ The diffraction data and unit cell parameters were consistent with the reported space group orthorhombic *Pbca* for complexes **5.1**, monoclinic *P2₁* for complex **5.2** and orthorhombic *Pna2₁* for complex **5.3**. No symmetry higher than triclinic was observed, and the solution in the centrosymmetric space group for compounds **5.1**, **5.2** and **5.3** yielded chemically reasonable and computationally stable results of refinement. All structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on *F*². All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. All scattering factors are contained in the SHELXTL 6.12¹¹ program library. Relevant crystal data and selected bond distances and angles are reported in Tables 5.1 and 5.2 respectively.

Table 5.1 Crystal Data and Structure Analysis Results for 5.1 – 5.3

	5.1	5.2	5.3
Formula	C ₂₀ H ₃₆ Al ₂ Cl ₂ CrN ₂	C ₃₂ H ₅₄ Al ₃ ClCrN ₃ O	C _{22 42} H _{43 26} Al ₂ C _{11 58} Cr ₂ N ₂
FW	481.37	665.17	554.86
space group	Orthorhombis, <i>Pbca</i>	Monoclinic, <i>P2</i> ₁	Orthorhombic, <i>Pna2</i> ₁
a (Å)	9.8897(11)	8.894(11)	21.213(10)
b (Å)	14.3759(15)	13.062(16)	9.226(4)
c (Å)	18.2210(19)	16.16(2)	15.055(7)
α (deg)	90	90	90
β (deg)	90	95.804(14)	90
γ (deg)	90	90	90
V (Å ³)	2590.5(5)	1868.4(4)	2960(2)
Z	4	2	4
radiation (Kα, Å)	0.71073	0.71073	0.71073
T (K)	200(2)	202(2)	202(2)
Dcalcd (g cm ⁻³)	1.234	1.183	1.241
μcalcd (mm ⁻¹)	0.787	1.183	1.245
F ₀₀₀	1016	710	1168
R, R _w 2 a	0.0470, 0.1228	0.0678, 0.1806	0.0433, 0.1188
GoF	1.068	1.025	1.039

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

Table 5.2 Selected Bond Distances (Å) and Angles (deg) for **5.1 - 5.3**

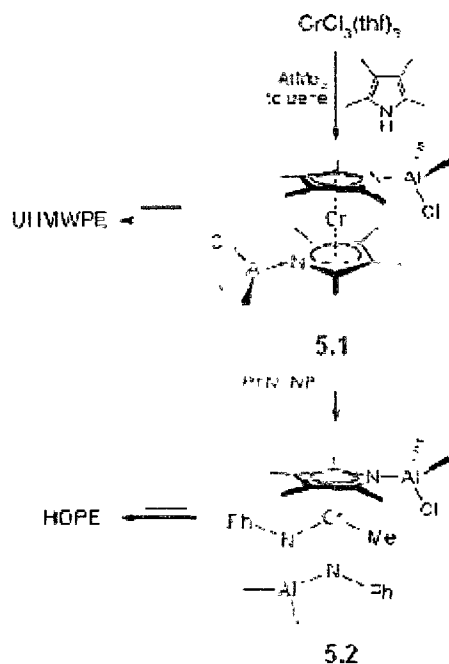
5.1	5.2	5.3
Cr1–N1 = 2.224(2)	Cr1–N1 = 2.284(5)	Cl1–Al1 = 2.187(3)
Cr1–C1 = 2.274(3)	Cr1–C1 = 2.326(5)	Cr–C1 = 2.181(5)
Cr1–C2 = 2.341(3)	Cr1–C2 = 2.388(5)	Cr1–C2 = 2.198(5)
Cr1–C3 = 2.312(3)	Cr1–C3 = 2.336(5)	Cr2–C1 = 2.172(4)
C1–C2 = 1.396(4)	Cr1–C4 = 2.246(5)	Cr2–C2 = 2.180(5)
C2–C3 = 1.425(5)	Cr–Cl1 = 2.074(6)	Cr1–C3 = 2.306(5)
C3–C4 = 1.396(4)	Cr1–N2 = 1.757(5)	Cr1–C4 = 2.341(5)
N1–Al1 = 1.993(2)	Cr1–N3 = 1.761(4)	Cr1–Cr2 = 2.274(1)
N3–V1–N2 = 83.50(10)	N2–Al2 = 1.966(5)	Cr1–C5 = 2.339(5)
N1–V1–N2 = 82.46(10)	N3–Al2 = 1.960(5)	Cr1–C6 = 2.317(4)
O1–V1–N2 =	N3–V1–O1 = 97.72(14)	Cr1–N1 = 2.350(4)
172.59(9)	N1–V1–N2 = 87.71(13)	Al1–N1 = 1.984(4)
N3–V1–Cl1 =	N3–V1–N2 = 89.13(13)	Cr1–Cl1 = 3.489(8)
119.98(8)	O1–V1–N2 = 169.51(13)	Cr2–Cl2 = 3.675(8)
N1–V1–Cl1 =		Cr1–centroid 1 = 2.003(5)
117.44(8)		Cr2–centroid = 1.992(5)
O1–V1–Cl1 = 87.24(7)		Cr2–Cr1–centroid1 = 152.9(3)
N2–V1–Cl1 = 99.85(7)		Cr1–Cr2–centroid2 = 152.9(3)

Results and Discussion

The reaction of $\text{CrCl}_3(\text{THF})_3$ with tetramethylpyrrole in toluene in the presence of AlMe_3 at low temperature afforded complex **5.1** in moderate yield (40%). (Scheme 5.1) Compound **5.1** was isolated as a dark green solid from toluene. Dark bluish green crystals were obtained by cooling an hexane solution for one week. Even though we have attempted the same reaction with simple pyrrole and its sterically bulky derivatives, we were unable to isolate relevant organometallic species in crystalline obtaining instead oily intractable materials.

The magnetic moment of **5.1** at room temperature [$2.77 \mu_B$] was as expected for the d^4 medium-spin electronic configuration of divalent chromium in an octahedral environment. The fact that a divalent species has been obtained from a trivalent starting material is not surprising given that reduction of trivalent chromium to the divalent state is commonly observed upon treatment with aluminum alkyl compounds.¹² The connectivity of **5.1** was yielded by an X-ray crystal structure (Figure 5.1) showing an homoleptic divalent chromium surrounded by two aluminato-pyrrolyl ligand. The selected bond distances and bond angles are given in Table 5.2. The overall geometry around chromium is likely to be distorted octahedral with two carbazoyl rings adopting the expected η^5 -coordination mode. It clearly shows that two parallel pyrrole rings symmetrically π bonded with Cr(II) centre. It is interesting to note the structural difference with the related complex [$\{(2,3,4,5\text{-C}_4\text{H}_4\text{N})\text{AlEt}_2\text{Cl}\}_2\text{Cr}$] ($\mu_{\text{eff}} = 4.78 \mu_{\text{BM}}$) in which the two rings are σ bonded bridging Al to the chromium centre.⁵

Scheme 5.1.



In **5.1** instead, each pyrrolyl nitrogen atom coordinates to one coplanar Me_2AlCl residue. As the result of the Cp-like donation to the metal centre, the ring C-C bond lengths have been elongated.

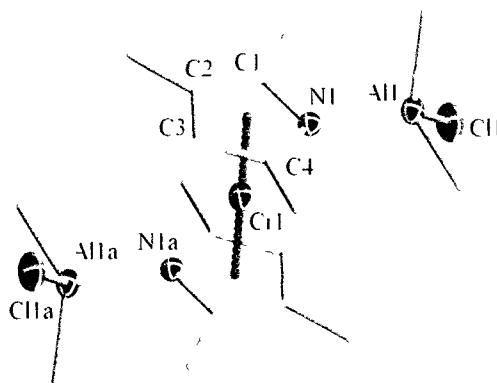


Figure 5.1. Thermal ellipsoid plot for **5.1** with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.

Complex **5.1** is thermally robust and does not decompose upon heating in toluene at 100°C for 12 hours. Unlike chromocene, which is catalytically inactive unless supported over silica,¹³ this aluminato-pyrrolate chromium complex acts as an active homogeneous single-site, single-component polymerization catalyst producing UHMWPE with very narrow polydispersity ($M_w = 2,650,000$; $PD = 1.7$, $T_m^1 = 145.7\text{ }^\circ\text{C}$, $T_m^2 = 139.0\text{ }^\circ\text{C}$, Table 5.3)

This system is reminiscent of a recently reported aluminatopyrrolyl-based vanadocene analogue.⁸ Complex **5.1** displays a somewhat higher catalytic activity and also produces UHMWPE. (Table 5.3) As in the vanadium case, questions arise about the catalytically active species formed during the self-activation process. Formation of a similar species has also been observed in the case of the vanadium analogue during the oxidation of the metal center. To study the possibility of alkyl transfer from aluminum to chromium in **5.1**, we deliberately oxidized the metal center by treatment with azobenzene. The reaction afforded a color change and deepening from the initial pale-turquoise to dark-brown, and yielded, after the addition of a small amount of THF, a pentavalent organochromium species $[\{\eta^5\text{-}2,3,4,5\text{-Me}_4\text{C}_4\text{N}(\text{AlMe}_2\text{Cl})\}\text{CrMe}(\mu\text{-NPh})_2\text{AlMe}_2][\text{Me}_3\text{Al}(\text{THF})]$ (**5.2**) (Scheme 5.1). The addition of a stoichiometric amount of THF after the reaction was only necessary to overcome the difficulties experienced for the crystallization of the complex. The structure of **5.2** (Figure 5.2) consists of the chromium atom π -bonded to one aluminatopyrrolide moiety $(\text{Me}_4\text{C}_4\text{N})\text{AlMe}_2\text{Cl}$ in a structure reminiscent of a piano-stool half-sandwich compound.

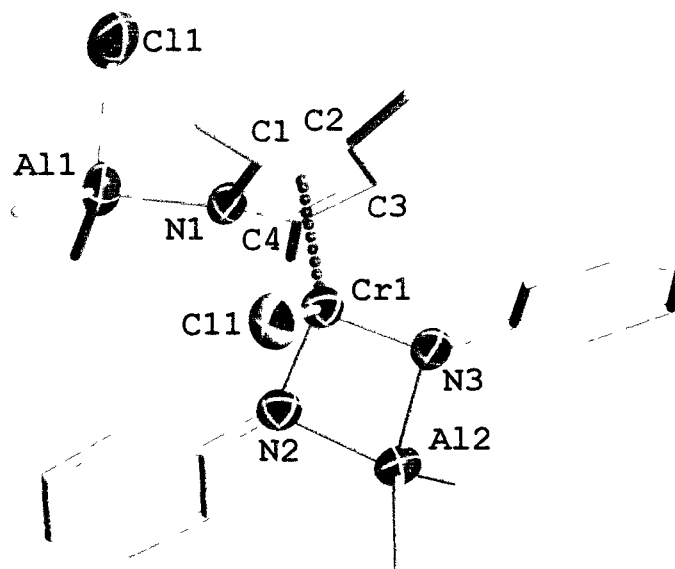


Figure 5.2. Thermal ellipsoid plot for **5.2** with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.

The four-electron cleavage of azobenzene during the formation of **5.2** is indeed accompanied by the anticipated aluminum-pyrrolyl dissociation and alkyl transfer. Complex **5.2** shows the paramagnetism expected for the d^1 electronic configuration of a monomeric chromium (v) complex ($\mu_{\text{eff}} = 1.87 \mu_{\text{BM}}$). The fact that the complex is pentavalent, and not hexavalent as (iy) might have been expected for the four-electron attack of the divalent metal center to azobenzene, is not completely surprising given the presence of reducing alkyl aluminum groups. The formation of **5.2** and alkyl transfer during the oxidative process is in agreement with the idea that a transient $\{[\eta^5\text{-}2,3,4,5\text{-Me}_4\text{C}_4\text{N}(\text{AlClMe}_2)]\text{CrMe}\}$ complex may be generated during the self-activation process of **5.1** in the presence of ethylene. Although complex **5.2** is very different from **5.1**, it is also a single-component catalyst. The catalytic activity was slightly higher than that of **5.1** under the best polymerization conditions. (Table 5.3) The molecular weight of the polymer is substantially lower than that formed by **5.1**. The polydispersity clearly reveals

the presence of a single-site catalyst ($M_w=850\,000$; $PDI=1.9$, $T_m^1=139.03\text{ }^{\circ}\text{C}$, $T_m^2=133.27\text{ }^{\circ}\text{C}$, Table 5.3)

Table 5.3 : Ethylene polymerization by **5.1** and **5.2**.

Cat #	MAO (eq)	P (bar)	T ($^{\circ}\text{C}$)	PE (g)	Activity (g/mol/h)	Tm1 ($^{\circ}\text{C}$)	Tm2 ($^{\circ}\text{C}$)	Mw (g/mol)	PDI (Mw/Mn)
1	0	41.37	110	8	8.5×10^5	145.7	139.0	2,650,000	1.7
2	0	41.37	80	11	1.1×10^6	139.03	133.27	850,000	1.9

Standard conditions: loading $10\text{ }\mu\text{mol}$ of complex; 100 mL of solvent, 1 h reaction time.

When the reaction that afforded **5.1** was carried out with $\text{CrCl}_2(\text{THF})_2$ the new species, $[\{\eta^5\text{-}2,3,4,5\text{-Me}_4\text{C}_4\text{N}(\text{AlClMe}_2)\text{Cr}\}_2(\mu\text{-Me})_2]$ (**5.3**), was isolated in crystalline form in a low, yet reproducible yield. (Scheme 5.2) The structure which closely resembles $[\{\eta^5(\text{Me}_5\text{C}_5)\text{Cr}-(\mu\text{-Me})\}_2]$,¹⁴ has a comparably short Cr - Cr distance of 2.274(1). (Figure 5.3) The positions of the chlorine atoms bonded to the two aluminum atoms have a partial occupancy by methyl groups (42%). The complex has the expected small residual paramagnetism [$\mu_{\text{eff}} = 0.85\text{ }\mu_{\text{BM}}$] for ligand-bridged dimers and does not thermally decompose at $100\text{ }^{\circ}\text{C}$ even after a few hours. The ^1H NMR spectrum showed rather broad resonances for the two bridging methyl groups. The partial methyl occupancy of the positions that contain chloride bonded to aluminum gives rise to multiple sets of resonances, with relative intensities of 0.42:0.58 for $[\{\eta^5\text{-}2,3,4,5\text{-Me}_4\text{C}_4\text{N}(\text{AlClMe}_2)\text{Cr}\}_2(\mu\text{-Me})_2]$ and $[\{\eta^5\text{-}2,3,4,5\text{-Me}_4\text{C}_4\text{N}(\text{AlClMe}_2)\text{Cr}\}_2(\mu\text{-Me})_2]$, respectively.

Scheme 5.2

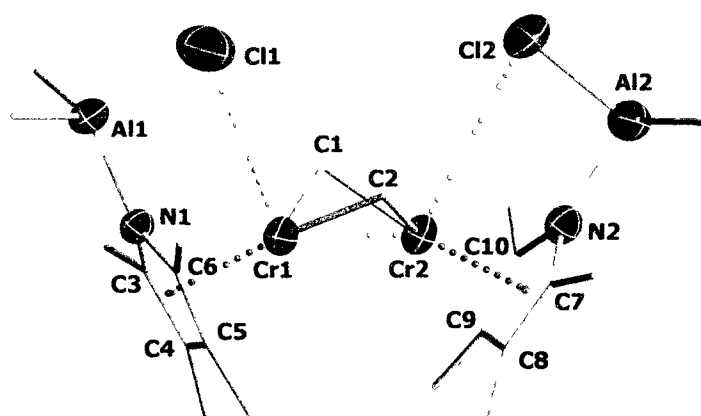
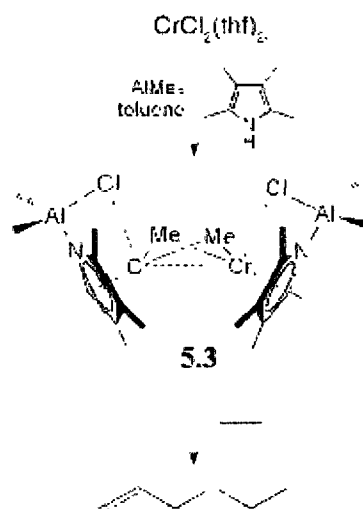


Figure 5.3. Thermal ellipsoid plot for **5.3** with ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.

Despite the close relationship with the species assumed to be generated during the self-activation of the polymerization catalyst **5.1**, complex **5.3** does not polymerize ethylene. In toluene, it is a moderately active self-activating oligomerization catalyst, producing a mixture of mainly 1-butene, 1-hexene, and 1-octene (Table 5.4, entry 1). However, when the reaction was performed with methylcyclohexane as solvent, 95% pure 1-hexene (Table 5.4, entry 5) was formed with very good activity (6.7×10^5 g/mol/h). A further improvement in both activity and selectivity was observed when Me_2AlCl was added to the catalytic mixture (Table 5.4, entries 2, 6). AlMe_3 , on the other hand, had a poisoning effect on the catalyst. Accordingly, an isostructural compound **5.3a** containing lesser amount of chlorine (0.35 instead of 1.58 per dimer), showed only marginal catalytic activity, confirming that the presence of chlorine is truly essential to catalytic activity. Species free of chlorine or with a definite stoichiometric ratio could not be properly characterized. Attempts to further activate **5.3** by treatment with $\text{B}(\text{F}_5\text{C}_5)_3$ resulted in no activity of any sort (Table 5.4, entry 4), which possibly indicates catalyst decomposition. In all the runs, only traces of polymer were observed.

Table 5.4. Ethylene oligomerization by 5.3.[a]

#	Solvent	Cocat.	PE (g)	Oligom. (g)	Activity (g/mole/h)	C4= %	C6= %	C8= %	C10= %	C12= %	C14= %	C16= %
1	toluene	-	Traces	4.2	1.4 x 10 ⁵	46	39	11	3	1	-	-
2	toluene	2.5 AlMe ₂ Cl	Traces	18.3	6.1 x 10 ⁵	33	52	11	3	1	-	-
3	toluene	2 TMP, * 3 AlMe ₂ Cl	Traces	9.0	3.0 x 10 ⁵	33	43	14	4	3	2	2
4	toluene	2 B(C ₆ F ₅) ₃	0.5	0.4	3.0 x 10 ⁴ **	24	44	18	14	-	-	-
5	Me-cyclohexane	-	Traces	20.2	6.7 x 10 ⁵	2	95	2	1	-	-	-
6	Me-cyclohexane	4AlMe ₂ Cl	Traces	36.7	1.2 x 10 ⁶	-	97.5	0.2	0.2	0.1	-	-

[a] Standard conditions: loading 30 mmol of complex, T=1050C, 100 mL of solvent, 36 bar of ethylene, 1 h reaction time. C_n=1-*n*-ene.

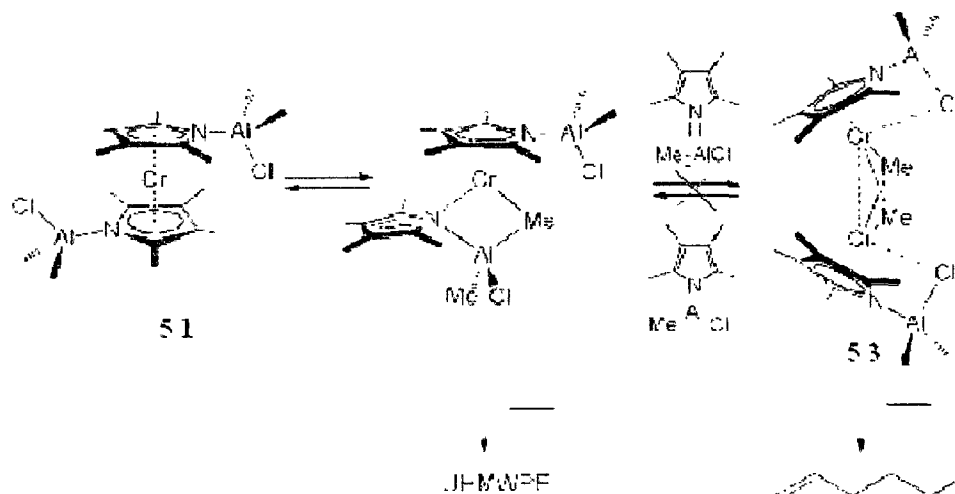
[b] Trace=less than 0.05 g of PE.

[c] TMP=tetramethylpyrrole.

[d] Based on PE+oligomers.

Catalytic tests of **5.3** carried out in the presence of deliberately added equivalent amount of tetramethylpyrrole and Me_2AlCl did not switch the catalytic selectivity towards polymerization (Table 5.4, entry 3), thus excluding the possibility that complex **5.1** and **5.3** might be connected in the catalytic cycles via an aluminum-pyrrole dissociation/association process (Scheme 5.3). Therefore, the two species are not interconvertible despite their close relationship, and they show distinctively different catalytic behavior. Complex **5.3** is, to the best of our knowledge, only the second example of a self-activating trimerization catalyst producing 1-hexene with high selectivity. Its catalytic activity is one order of magnitude higher than the recently reported chromium(I) carbazoyl.⁵

Scheme 5.3 Non-interconvertibility of complexes **5.1** and **5.3**



The catalytic behavior raises two main points. First, it seems to refute the possibility for “ $\{\eta^5\text{-}2,3,4,5\text{-Me}_4\text{C}_4\text{N}-(\text{AlClMe}_2)\text{CrMe}\}$ ” to be the catalytically active species in the self-activation of **5.1**. The two closely related species **5.1** and **5.3**, both bearing chromium in the divalent state, perform completely different catalytic processes. This might also indicate that, in the polymerization process promoted by **5.1**, both pyrrole rings possibly remain somehow connected to the chromium center. This is in line with the behavior of a closely related divalent carbazoyl derivative,⁵ which is also a self-

activating polymerization catalyst that produces UHMWPE. Second, the fact that **5.3** is an active self-activating selective trimerization catalyst and has the metal in the divalent state seems to contradict the recent findings that propose that only a chromium(I) aluminatopyrrolate complex should be capable of selective trimerization. On the other hand, it is certainly possible that complex **5.3** disproportionates in the presence of ethylene, generating the monovalent $\{\eta^5\text{-}2,3,4,5\text{-Me}_4\text{C}_4\text{N}(\text{AlClMe}_2)\text{Cr}\}$ and the corresponding trivalent $\{\eta^5\text{-}2,3,4,5\text{-Me}_4\text{C}_4\text{N}(\text{AlClMe}_2)\text{CrMe}_2\}$ species. In fact, the coordination of a catalytically active chromium(I) species to toluene to form the corresponding η^6 -arene complex is the only way to explain the spectacular poisoning effect of toluene, a feature never observed for divalent chromium.¹⁵ The beneficial effect of added chlorine on the catalytic activity by the addition of stoichiometric amount of Me_2AlCl is ascribed to further chlorine enrichment of the coordinated aluminum residues.

To support these ideas, we have evaluated the ΔG_{rxn} with the help of DFT calculations at the (PBE/TZVP) level for a few possible dimer dissociation scenarios (Table 5.5). Solvation effects (toluene versus cyclohexane) have also been taken into consideration. The calculations clearly indicated that the solvation effects are only minor, thus confirming that the toluene poisoning effect may indeed be due to the formation of a chromium–arene species. Among the several possibilities taken under consideration, both homolytic and heterolytic dissociation exhibited positive values of ΔG_{rxn} . The results were not different when the same dissociations were calculated in the presence of ethylene to form the corresponding olefin complexes.

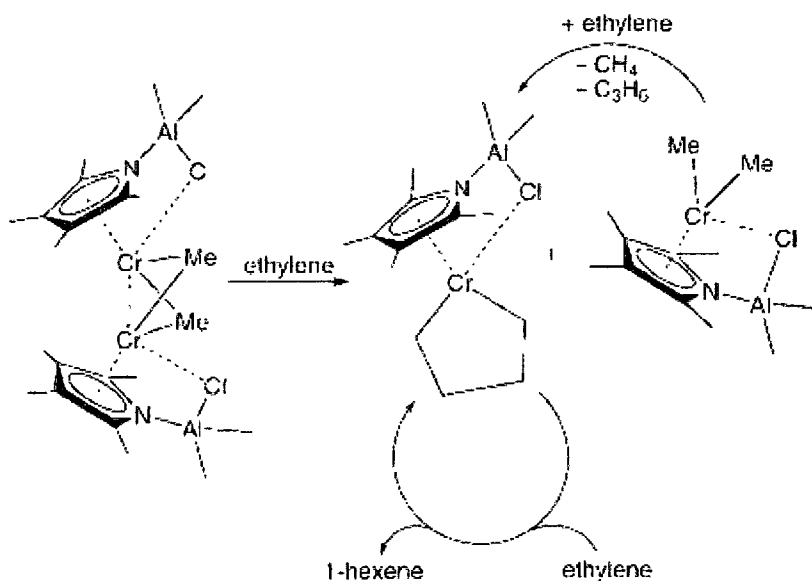
Table 5.5. Calculated thermodynamic parameters. [a]

	cyclohexane	cyclohexane	cyclohexane, Cl-free	toluene	toluene
Reaction	ΔG_{298K}	ΔG_{373K}	ΔG_{298K}	ΔG_{298K}	ΔG_{373K}
5.3 $\rightarrow$ 2 [CrIII(CH ₃)]	9.8	5.7	11.2	10.7	6.6
5.3 + 2C ₂ H ₄ $\rightarrow$ 2 [CrIII(CH ₃)(C ₂ H ₄)]	12.1	13.3	14.6	12.2	13.4
5.3 $\rightarrow$ [CrIII(CH ₃) ₂] + [CrII]	19.6	15.9	23.9	20.3	16.6
5.3 + C ₂ H ₄ $\rightarrow$ [CrIII(CH ₃) ₂] + [CrII(C ₂ H ₄)]	10.9	9.8	15.0	11.5	10.4
5.3 + 2C ₂ H ₄ $\rightarrow$ [CrIII(CH ₃) ₂] + [CrIII(C ₄ H ₈)]	-3.5	-0.8	0.7	-3.4	-0.7
5.3 + 3C ₂ H ₄ $\rightarrow$ [CrIII(CH ₃) ₂] + [CrIII(C ₄ H ₈)(C ₂ H ₄)]	11.2	16.4	11.9	10.8	16.0
[CrII] + C ₆ H ₆ $\rightarrow$ [CrII(C ₆ H ₆)]	-1.4	1.2	1.7	-3.0	-0.4

[a] Energies given in kcalmol⁻¹.

Remarkably, ΔG_{rxn} became negative only in the case where the intermediate chromium(I) species, as obtained from the heterolytic dissociation, is reoxidized by two molecules of ethylene to form a chromacyclopentane ring. (Scheme 5.4) Calculations predict that any one of the processes taken into consideration by using a chlorine-free compound (Me_3Al adducts) will only have more positive ΔG_{rxn} values (Table 5.5), which is also in agreement with the observed beneficial effect of chlorine feed on catalytic activity. Incidentally, these results explain the need for the use of dimethylaluminum chloride in the Chevron Phillips system, to which complex 5.3 is clearly closely related.

Scheme 5.4. Chromacyclopentane ring formed from an intermediate chromium(I) species.



Conclusion

In this chapter I have reported the preparation of a divalent chromium complex with a chromocene-type structural motif, which is a self-activating, single-site catalyst producing UHMWPE. A closely related species, with only one aluminatopyrrolyl ring and a dimeric structure, is instead an effective self-activating trimerization catalyst. The difference of catalytic behavior is explained by the fact that, in contrast to the “chromocene” type of complex, which maintains the divalent oxidation state, the dimeric complex disproportionates in the presence of ethylene to form a transient monovalent species.

Reference

- (1) Hogan, J. P.; Banks, R. L.; US Patent 2,835,721, 1958.
- (2) a) J. T. Dixon, Green, M.J.; Hess, F.M.; Morgan, D. H. *J. Chem. Organomet*, **2004**, 689, 3641.
- b) Carter, A.; Cohen, S. A.; Cooley, N. A.; Murphy, A.; Scutt, J.; Wass, D. F. *Chem. Commun.* **2002**, 858.
- c) McGuinness, D. S.; Wasserscheid, P.; Keim, W.; Hu, C.; Englert, U.; Dixon, J. T.; Grove, C. *Chem. Commun.* **2003**, 334.
- d) McGuinness, D. S.; Wasserscheid, P.; Keim, W.; Morgan, D. H.; Dixon, J. T.; Bollmann, A.; Maumela, H.; Hess, F. M.; Englert, U. *J. Am. Chem. Soc.* **2003**, 125, 5272.
- e) Morgan, D. H.; Schwikkard, S. L.; Dixon, J. T.; Nair, J. J.; Hunter, R. *Adv. Synth. Catal.* **2003**, 345, 939.
- f) Temple, C.; Jabri, A.; Crewdson, P.; Gambarotta, S. I.; Korobkov, R.; Duchateau, *Angew. Chem.* **2006**, 118, 7208; *Angew. Chem. Int. Ed.* **2006**, 45, 7050.
- g) Albahily, K.; Al-Baldawi, D.; Gambarotta, S.; Duchateau, R.; Ko, E.; Burchell, T. J.; *Organometallics* **2008**, 27, 5708.
- h) Agapie, T.; Day, M.W.; Henling, L. M.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **2006**, 25, 2733.
- i) Schofer, S. J.; Day, M.W.; Henling, L. M. Labinger, J. A.; Bercaw, J. E. *Organometallics* **2006**, 25, 2743.
- j) Agapie, T.; Schofer, S. J.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2004**, 126, 1304.
- k) Agapie, T.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2007**, 129, 14281.
- l) Zhang, J.; Braunstein, P.; Hor, A. *Organometallics* **2008**, 27, 4277.
- m) Khan, R. D.; Smith, D.; Mahon, M. F.; Prinz, M.; Mihan, S. *J. Organomet Chem.* **2003**, 683, 200.
- n) Blann, K.; Bolmann, A.; Dixon, J. T.; Hess, F.; Kilian, E.; Maumela, H.; Morgan, D. H.; Neveling, A.; Otto, S.; Overett, M.; *Chem. Commun.* **2005**, 620.
- o) Mimura, H.; Aoyama, T.; Yamamoto, T.; Oguri, M.; Koie, Y.; JP 09268133 (Tosoh Corporation), **1997**.

- p) Mahomed, H.; Bollmann, A.; Dixon, J. T.; Gokul, V.; Griesel, L.; Grove, C.; Hess, F.; Maumela, H.; Pepler, L.; *Appl. Catal. A* **2003**, 255, 355.
- q) Yoshida, T.; Yamamoto, T.; Okada, H.; Murakita, H.; US2002/ 0035029 (Tosoh Corporation), **2002**.
- (3) Reagan, W. K.; EP 0417477 (Phillips Petroleum Company), **1991**.
- (4) a) Bollmann, A.; Blann, K.; Dixon, J. T.; Hess, F. M.; Killian, E.; Maumela, H.; McGuinness, D. S.; Morgan, D. H.; Neveling, A.; Otto, S.; Overett, M.; Slawin, A. M. Z.; Wasserscheid, P.; Kuhlmann, D. S. *J. Am. Chem. Soc.* **2004**, 126, 14712.
- b) Overett, M. J.; Blann, K.; Bollmann, A.; Dixon, J. T.; Haasbroek, D.; Killian, E.; Maumela, H.; McGuinness, S.; Morgan, D. H. *J. Am. Chem. Soc.* **2005**, 127, 10723.
- (5) Jabri, A.; Mason, C. B.; Sim, Y.; Gambarotta, S.; Burchell, T. J.; Duchateau, R. *Angew. Chem.* **2008**, 120, 9863; *Angew. Chem. Int. Ed.* **2008**, 47, 9717.
- (6) a) Dixon, J.; Green, M.; Hess, F.; Morgan, D. *J. Organometallic chem.* **2004**, 689, 3641-3668.
- b) Nomura, K.; Sagara, A.; Imanishi, Y. *Macromolecules* **2002**, 35, 1583.
- c) Yamada, J.; Fujiki, M.; Nomura, K. *Organometallics*, **2005**, 24, 2248.
- (7) *Coordination Chemistry reviews*, Volumes 1-195 : Elsevier Pub. Co.: Amsterdam.
- (8) Jabri, A.; Korobkov, I.; Gambarotta, S.; Duchateau, R. *Angew. Chem.* **2007**, 119, 6231; *Angew. Chem. Int. Ed.* **2007**, 46, 6119.
- (9) Foese, G.; Gorter, C. J.; Smits, L. J. *Constantes Selectionnées Diamagnetisme, Relaxation Paramagnetique*; Mason: Paris, **1957**.
- (10) Blessing, R.; *Acta Crystallogr.* **1995**, A51, 33.
- (11) G. M. Sheldrick, Bruker AXS, Madison, WI, **2001**.
- (12) Jabri, A.; Temple, C.; Crewdson, P.; Gambarotta, S.; Korobkov, I.; Duchateau, R. *J. Am. Chem. Soc.* **2006**, 128, 9238.
- (13) a) Karol, F. J.; Johnson, R. N. *J. Pol. Sci. Pol. Chem. Ed.* **1975**, 13, 1607.
- b) Karapinka, G. L.; Patent U.S.; 3,709,853, **1973**.
- (14) Heintz, R. A.; Ostrander, R. L.; Rheingold, A. L.; Theopold, K. H. *J. Am. Chem. Soc.* **1994**, 116, 11387.
- (15) a) La Macchia, G.; Gagliardi, L.; Power, P. P.; Brynda, M. *J. Am. Chem. Soc.* **2008**, 130, 5104.

- b) Kreisel, K. A.; Yap, G. P. A.; Dmitrenko, O.; Landis, C. R.; Theopold, K. H. *J. Am. Chem. Soc.* **2007**, *129*, 14162.
- c) Tsai, Y.-C.; Wang, P.-Y.; Chen, S.-A.; Chen, J.-M. *J. Am. Chem. Soc.* **2007**, *129*, 8066.

***Chapter 6:* Dinitrogen Coordination and Cleavage
Promoted by Vanadium and Titanium Complexes of a
 σ,π,σ - Donor Ligand: Partial Hydrogenation, and
Silylation.**

(Published in *Angew. Chem. Int. Ed.* **2009**, 48, 7415 and *Inorg. Chem.* **2007**,
46, 8836)

Introduction

Since the initial discovery of the ability of transition metals to form dinitrogen complexes, the chemistry of dinitrogen has steadily developed in terms of activation,¹ transformation,² and reduction.^{1e,h,2a,e,f,3} Relying on the Haber-Bosch synthesis of ammonia from N₂ and H₂ under extreme conditions, mankind has managed to overcome the difficulties of this transformation,⁴ better known as one of the most significant discoveries of the twentieth century. The importance of discovering a catalytic process employing mild condition becomes obvious not only an energy conservation priority but also an intellectual challenge.

Although widely documented in the literature, fixation and activation of this exceedingly inert molecule remains a challenge given the high reactivity required by the metal precursors. Even more challenging is the complete cleavage of the very strong N-N triple bond (dissociation energy = 945 KJ/mol) requiring also six electrons in addition to the large amount of energy.⁵ Nature has devised a unique system for incorporation of N₂ into the biosphere, involving the catalytic reduction of N₂ by nitrogenase enzymes.⁶ Upon fixation of the dinitrogen moiety to the Fe-Mo-S core, a series of steps involves the transfer of 6 electrons from an electron pool towards the complete reduction of N-N triple bond and consequent cleavage.⁷ During each of these stages, protons are delivered to the reduced dinitrogen moiety. The major breakthrough in this direction has been achieved by Schrock *et al* few years ago with the design of a step by step catalytic cycle capable of producing ammonia from dinitrogen under mild conditions. Cobaltocene was used as source of electrons for the a molecule of dinitrogen coordinated to a molybdenum complex [HIPTN₃N]MoN₂, {[HIPTN₃N]³⁻ = [{3,5-(2,4,6-iPr₃C₆H₂)₂C₆H₃NCH₂CH₂}]₃N]³⁻}.^{1f,8} A pyridinium salt was used as source of protons. The beauty of this synthetic system relies on the stringent conceptual similarity with the very basics of the nitrogenase enzymes: separating the source of electrons and the source of protons.

Although fixation of dinitrogen has been observed with all metals, research has been mainly focused on strongly reducing low-valent early metals systems.^{1f,8-11} The early metal complexes became the most popular target for the studies due to the large volume of transformations including partial reduction followed by elemental

modifications or incorporation into ligand systems. These topics have been comprehensively reviewed in several recent reviews.¹² Furthermore, they are also capable of the series of steps through which the exceedingly stable N₂ may be cleaved and protonated. The cleavage to nitrides is also amply documented^{1g,h,l,2q,6} The hydrogenation can be obtained during either the partial or complete cleavage via three different processes. The first is the direct protonation of the nitride during the hydrolysis or protonolysis. The second is the direct reaction of reduced forms of coordinated dinitrogen with hydrogen gas and third is the attack by hydrides.

There is however another possibility. While attempting the synthesis of low-valent synthons of thorium (an element that has been reduced in only two instances),⁹ a Th-NH₂ unit was serendipitously obtained.¹⁰ Isotopic labeling studies clearly indicated that the nitrogen atom was derived from N₂ while the hydrogen atoms could in that case only be furnished by the solvent. In other words, by enhancing the radical behavior of an element that is hard to reduce, it was possible not only to cleave dinitrogen but also to enhance the radical behavior of reduced fragments affording extraction of hydrogen atoms from the solvent. Elements of the *f*-block series are versatile for this purpose since most of the reduction chemistry may be in fact explained in terms of enhanced radical behavior of transient reduced species.^{6g,11}

The use of ligand systems containing either non-coordinated or weakly-bonded π -systems has been recently shown to be a viable strategy for enhancing the radical behavior of transition metal complexes. In some instance, these ligands may act as electron storage units effectively promoting dinitrogen partial reduction,¹² cleavage, and even partial hydrogenation.^{6b} Following this strategy, we have designed a ligand system based on pyrrolide anions containing an additional hemilabile π -unit.^{6c} In fact, the pyrrolide anions are isoelectronic with the cyclopentadienyl anions and which have produced a number of dinitrogen complexes^{1c,d,e,h,m,l,p,13} including examples of dinitrogen reduction.^{1c,d,e,h,m,l,p}

The use of the so-called hemi-labile ligands provides another possibility. The definition applies to ligands acting as multi-dentate and which may strongly bind to a metal centre at one ligand site while at the same time having the ability to loosely coordinate to the metal from at least one other position on the ligand¹⁸. The propensity for

labile coordination to the metal from the second position allows for other substrates to access the metal coordination sphere. Ether moieties¹⁹ and sulfone²⁰ groups or molecular residues containing weakly bonding π -systems are prime examples of functional groups which can serve to generate hemi-labile ligand system.

Pyrrole based ligand systems and especially di- and cyclic tetrapyrroles have shown a particular versatility in enhancing and promoting the reactivity of metals towards dinitrogen fixation and activation. Their robustness towards strongly reducing metals is most likely at the basis of this useful behavior. However, ligand denticity also seems to be a rather critical factor given that simple monodentate pyrroles do not display any significant feature having so far yielded complexes with a large variety of metals where the σ -bonding mode is by far the most commonly adopted in spite of the close resemblance with the Cp anion. To the best of our knowledge no one single case of dinitrogen activation fixation has ever been reported with any metal while in combination with monodentate pyrrolide anion. On the other hand, the polypyrrolide ligand system almost invariably adopts the dual σ - and π -bonding mode in the process favoring the assembly of cluster structure capable of cooperative dinitrogen reduction. While in combination with pyrrolide based ligand system, the behavior of divalent vanadium has been so far disappointing having shown formation of unexciting σ -bonded complexes and no sign of possibility of reacting with dinitrogen.²⁰ Recently, a complex containing two π -bonded pyrrolide ring an overall vanadocene-type of structure has been obtained by using strong Lewis acids such as AlR_3 capable of locking the sp^2 orbital. However, no sign of dinitrogen activation has been detected in spite of the hemilability and dynamism of this particular species. Hence our design of the tripyrrolide 2,5-{2-[(C₆H₅)₂C]pyrrole}₂(N-Me-pyrrole) ligand system used in this work for targeting low-valent vanadium. The very empirical idea behind its design was to have a ligand with the two terminally positioned pyrrolide rings providing two σ -bonded anionic N atoms since in the chemistry of anionic amide complexes of vanadium have been shown capable of promoting dinitrogen fixation. The central pyrrolide ring instead was expected to provide the metal with a π -interaction which, as suggested by the chemistry of low-valent lanthanides, seems also beneficial to enhance and promote reactivity towards dinitrogen.

Among the diversified transformations promoted by complexes of vanadium and titanium, dinitrogen derivatives have traditionally provided the strongest motivation to justify synthetic effort towards developing the chemistry of the divalent state. The discovery of the presence of vanadium as key element in some of the nitrogenase enzymes is still posing challenging questions about the role of this element in the reduction of dinitrogen to ammonia. Today, a few cases of vanadium dinitrogen complexes have been discovered²⁴ as well as the possibility of forming vanadium nitrides via 6-electron reductive cleavage of the coordinated dinitrogen unit.^{1b,3j,4,22j,24b,26}

By reducing a trivalent Ti complex of the {2,5-[(C₄H₃N)CPh₂]₂[C₄H₂N(Me)]} dianion we have recently obtained a toluene mixed-valence complex with inverted sandwich structure and also olefin coordination.²⁷ We find puzzling that these clear signs of high reactivity were not accompanied by any apparent interaction with dinitrogen. By performing a reduction in an ethereal solvent such as DME instead of toluene and using a milder reducing agent, we have now obtained dinitrogen cleavage along with partial hydrogenation.

In this chapter, I also describe the synthesis and characterization of the V(II) and Ti(III) complexes of the tripyrrolide dinanion, the formation of the corresponding dinitrogen vanadium complex and further cleavage to a dinuclear linearly bonded mono-nitride species.

Experimental Section

All reactions were carried out under a dry nitrogen atmosphere unless otherwise stated. Solvents were dried using an aluminum oxide solvent purification system. VCl₃(THF)₃ and TiCl₃(THF)₃²⁷ and {2,5-[(C₄H₃N)CPh₂]₂[C₄H₂N(Me)]}TiCl¹⁸ was prepared via standard procedure. A solution of *n*-BuLi and benzophenone was purchased from Aldrich and used with no further purification. Reagent grade pyrrole was also purchased from Aldrich and used after distillation under reduced pressure (~50 Torr). Infrared spectra were recorded on an ABB Bomem FTIR instrument from Nujol mulls prepared in a dry box, except in the case of air-stable products. Samples for magnetic susceptibility were pre-weighed inside a drybox equipped with an analytical balance and

measured on a Johnson Matthey magnetic susceptibility balance. Elemental analysis was carried out with a Perkin-Elmer 2400 CHN analyzer. NMR data was collected on a Varian INOVA 500 spectrometer and referenced to SiMe₄. Data for X-ray crystal structure determination were obtained with a Bruker diffractometer equipped with a 1K Smart CCD area detector.

Preparation of 2, 5-[(C₆H₅)₂C(OH)]₂(N-Me-pyrrole)

A solution of *N*-Methylpyrrole (10.0 mL, 0.113 mol) in hexane (150 mL) was treated with neat TMEDA (51.0 mL, 0.338 mol) and then cooled to 0 °C in an ice bath. A solution of *n*-BuLi in hexane (0.338 mol) was added dropwise while stirring. The reaction mixture was warmed up to room temperature and refluxed for 4 h. The resulting off-white suspension was filtered and the solid portion was washed with hexane (3 x 50 mL), yielding a white product. The solid was dried under vacuum (1 h) and redissolved in THF (100 mL), and the resulting solution cooled to -20 °C. In a separate flask, 2.0 equiv of benzophenone (41.18 g, 0.226 mol) were dissolved in THF (100 mL) and cooled to -20 °C. The two solutions were then combined, resulting in the formation of a deep blue solution. This solution was then stirred for 12 h, after which time the solvent was removed under vacuum. Hexane (200 mL) was then added along with 4 equiv of water (8 mL, 0.452 mol), affording an off white suspension. This suspension was then filtered, and the solid washed with hexanes (4 x 50 mL). The product was extracted using several portions of CH₂Cl₂ (5 x 40 mL) and dried under vacuum, yielding the final product as an off-white solid. Yield 26.68 g (53.1%). Anal. Calcd (Found) for C₃₁H₂₇O₂N: C 83.57 (83.52); H 6.11 (6.05); N 3.14 (3.11). [M⁺] 445, found 445. ¹H NMR (CDCl₃, 500 MHz) δ 2.86 (br, 2H, OH), 3.13 (s, 3H, N-CH₃), 5.29 (s, 2H, central pyrrole) 7.27 (m, 20H, phenyl) ¹³C NMR (CDCl₃, 500 MHz) δ 35.00 (N-CH₃), 78.72 (C-OH), 110.06 (pyrrole), 126.90 (phenyl), δ 127.13 (phenyl), δ 127.74 (phenyl), δ 145.55 (ipsophenyl). IR (KBr pellet, cm⁻¹) ν 3484 s, br (OH); 3084, 3058, 3025, 2946 s; 1597, m; 1490, 1447, s; 1411, w; 1329, 1293, s; 1234, w; 1204, m; 1153, s; 1092, s; 1061, w; 1018, 1001, s; 924, 899, m; 867, m; 792, w; 755, 721, 701, s; 670 s; 628, 612, m; 559 w.

Preparation of 2,5-[(2-pyrrolyl) (C₆H₅)₂C]₂(MeNC₄H₂)(MeTPH₂)

Neat 2,5-[(C₆H₅)₂C(OH)]₂(N-Me-pyrrole) (15.00 g, 0.034 mol) was dissolved in hot (80 °C) pyrrole (60 mL). The addition of 6 drops of methanesulfonic acid resulted in the formation of a dark red suspension. After 72 h of stirring and heating, the suspension was cooled to room temperature. The solid was filtered and washed with cold methanol (3 x 30 mL), yielding the title compound as a white solid. The product was dried under vacuum and used without need for further purification (15.27 g, 0.021 mol, 63.4%). Anal. Calcd (Found) for C₃₉H₃₃N₃: C 86.15 (86.27), H 6.12 (6.17), N 7.73 (7.79). [M⁺] 543, found 543. ¹H NMR (CDCl₃, 500 MHz) δ 2.14 (s, 3H, N-CH₃), 5.46 (s, 2H, central pyrrole), 5.98 (m, 2H, pyrrole), 6.05 (m, 2H, pyrrole), 6.68 (m, 2H, pyrrole), 7.07 (m, 8H, phenyl), 7.13 (m, 4H, phenyl), 7.18 (m, 8H, phenyl), 7.69 (br s, 2H, N-H). ¹³C NMR (CDCl₃, 500 MHz) δ 34.80 (NCH₃), 56.19 (quaternary), 108.10 (pyrrole), 109.37 (pyrrole), 110.35 (pyrrole), 117.26 (phenyl), 126.73 (phenyl), 127.93 (phenyl), 129.66 (ipso-pyrrole), 139.06 (ipso-central pyrrole), 145.52 (ipso-phenyl). IR_{neat} (cm⁻¹): 3426, m; 3085, 3065, 3026, 2954, m; 1955, 1899, 1816, w; 1595, 1550, m; 1490, 1443, s; 1410, 1394, m; 1233, 1299, 1267, 1231, 1183 m; 1115, 1093, 1042, 1031, m; 1002, w; 962, 930, w; 903, 885, 847, m; 799, 761, 747, 722, 704, s; 622, w; 568, 548 s.

Preparation of [(MeTP)VCl(THF)].THF (6.1)

Solid MeTPH₂ (0.200 g, 0.368 mmol) was dissolved in 10 mL of THF and treated with KH (0.030 g, 0.754 mmol). After stirring for 4 h, VCl₃(THF)₃ (0.137 g, 0.368 mmol) was added to the solution, which turned brick-red. After stirring overnight, the solution was centrifuged to remove the small amount of insoluble material and layered with hexanes. After several days, dark red X-ray quality crystals of **6.1** were formed (0.123 g, 0.159 mmol, 43.3%). Anal. Calcd (Found) for C₄₇H₄₇ClN₃O₂V: C 73.09 (73.21); H 6.13 (6.17); N 5.44 (5.50). $\mu_{eff} = 2.85 \mu_B$.

Preparation of [(MeTPH₂)V(THF)].(C₇H₈)_{0.5} (**6.2**)

A dark red solution of **6.1** (0.410 g, 0.586 mmol) in THF (20 mL) was stirred with Na (0.015 g, 0.655 mmol) for about 4 h until all of the Na was consumed. The solvent was then removed under vacuum. The dry residue was redissolved in fresh THF (10 mL) and the suspension centrifuged to remove a small amount of insoluble material. Toluene (2 mL) was added to reduce the solubility, and the resulting dark brown mixture was cooled to -35 °C. Dark purple crystals of **6.2** suitable for X-ray diffraction were obtained (0.164 g, 0.231 mmol, 39.4%). Anal. Calcd (Found) for C_{46.50}H₄₃N₃OV: C 78.57 (78.21), H 6.10 (6.07), N 5.91 (5.60). $\mu_{\text{eff}} = 3.88 \mu_{\text{B}}$.

Preparation of [(MeTP)V(μ -N₂)].(C₇H₈)_{2.9} (**6.3**)

A solution of Me₃Al in toluene (0.300 mL, 2 M, 0.597 mmol) was added to a solution of complex **6.2** (0.425 g, 0.597 mmol) in the same solvent (15 mL) at -35 °C. The color of the mixture immediately changed from dark purple to dark black-brown. The resulting suspension was centrifuged, and the dark brown solution afforded dark brown crystals of **6.3** upon standing 2 days at -35 °C (0.688 g, 0.466 mmol, 78% yield). Anal. Calcd (Found) for C_{98.13}H₈₅N₈V₂: C 79.73 (79.66), H 5.80 (5.72), N 7.58 (7.44). $\mu_{\text{eff}} = 3.52 \mu_{\text{B}}$ (per vanadium atom). Addition of an equivalent amount of THF to a dark brown solution of **6.3** in toluene instantly turns the color to purple. Microcrystalline **6.2** can then be separated upon freezing (78%).

Preparation of [(MeTP)V]₂(μ -N)].(THF) (**6.4**)

A suspension of **6.3** (0.510 g, 0.345 mmol) in toluene (20 mL) was stirred at room temperature for 7 days in the presence of KC_{8.8} (0.010 g, 0.690 mmol). During this reaction, the color of the mixture gradually changed from purple to dark green. After 7 days of stirring, the dark green solution was centrifuged to remove a small amount of precipitate and concentrated to 12 mL. Dark green crystals of **6.4** were formed after standing at -35 °C for 3 days (0.120 g, 0.179 mmol, 52%). Anal. Calcd (Found) for C₈₆H₇₈N₇₀2V₂: C 76.88 (76.84), H 5.85 (5.81), N 7.30(7.27). $\mu_{\text{eff}} = 1.74 \mu_{\text{B}}$

Degradation of 6.4

An analytically pure sample of **6.4** (0.200 g) was treated with a 10% HCl/H₂O solution. After centrifugation of the solution and addition of NaBPh₄, a white solid was collected, washed, and identified by IR, NMR, and MS spectra as NH₄BPh₄ (43% isolated product) by comparison to the spectra of an analytically pure sample (Aldrich). The degradation test was also performed on the ¹⁵N adduct of complex **6.4**. The IR displays the characteristic isotopic shift of NH stretching band from 3218 to 3248 cm⁻¹. The MS spectrum also exhibits the ammonium ion peak at 19 *m/z* compared to the 18 *m/z* peak for the non-isotopically enriched sample. The ¹⁵N NMR resonance was located at 340.1 ppm (referenced to CH₃ ¹⁵NO₂).²⁸

Preparation of [Na(dme)₃]₄[{LNa}₂][(LTi)₂(μ-N)₂]·2dme (**6.5**)

A suspension of {2,5-[(C₄H₃N)CPh₂]₂[C₄H₂N(Me)]}TiCl (0.5 g, 0.95 mmol) with freshly prepared Na/Hg (0.035 g Na, 1.5 mmol, 3.4 g of Hg) in DME (7 mL) was stirred for 1 week at r.t. The color of the suspension slowly changed from the initial olive green to very dark green and finally back to olive green. The resulting mixture was centrifuged after Hg removal, and the supernatant was separated. A portion of THF (12-14 mL) was added to the residual solid in the centrifugation tube and the resulting suspension was vigorously shaken and then centrifuged again. The clear THF solution was separated, placed in a closed vial at r.t. and left undisturbed. Green crystals of **6.5** deposited after 2 weeks and which were separated by filtration, washed with DME (2 x 0.3 mL) and dried. Yield 0.36 g (0.23 mmol, 25%). Calculated (Found) for C₉₀H₉₄Na₈Ti₂O₆: C 71.88 (72.00), H 6.26 (6.20), N 7.45 (7.39). ¹H NMR (500.2 MHz, THF-d⁸, 25°C), δ_H (ppm) = 13.11 (Δω_{1/2} = 8.0 Hz, 1H, N-H), 7.38 (2H, *m*, C₄H₃N^A), 7.25, 7.20, 7.16, 7.14, 7.06, 7.00, 6.96 (40H, C₆H₅), 6.79 (2H, *m*, C₄H₃N^B), 5.98 (2H, *m*, C₄H₃N^A), 5.93 (2H, *m*, C₄H₃N^B), 5.91 (2H, *m*, C₄H₃N^B), 5.84 (2H, *m*, C₄H₃N^A), 5.77 (2H, *s*, C₄H₂NMe), 5.58 (2H, *s*, C₄H₂NMe), 3.43 (*s*, CH₂, DME), 3.27 (*s*, 6H, CH₃, DME), 2.19 (3H, *s*, MeNC₄H₂), 2.06 (3H, *s*, MeNC₄H₂). ¹³C¹H HMQC (ppm) = 131.5 (7.38, C₄H₃N^A), 129.0 (6.80), 128.2 (7.14), 125.5 - 123.0 (7.24 - 7.00), 122.8 (6.96), 116 (6.78) (phenyl carbons), 115.8 (5.77, C₄H₂NMe), 106.3 (5.93, C₄H₃N^B), 105.2 (5.98, C₄H₃N^A), 105.1

(5.91, $C_4H_3N^B$), 104.2 (5.84, $C_4H_3N^A$), 111.8 (5.58, C_4H_2NMe), 70.2 (3.43, DME), 56.3 (3.27, DME), 33.4 (2.19, $MeNC_4H_2$), 34.8 (2.06, $MeNC_4H_2$). ^{15}N -NMR (50.7 MHz, THF- d^8 , 25°C), δ_N (ppm) = 542.0 (Ti(μ -N)Ti), 132.2 (Ti(μ -NH)Ti). The assignment of NH group was confirmed by ^{15}N DEPT90 and ^{15}N - 1H HMQC spectroscopy with only the ^{15}N -NMR resonance at 132.2 ppm giving a cross peak with the proton resonance at 13.11 ppm. The coupling constant $J(^1H-^{15}N) = 67$ Hz was used for recording of ^{15}N - 1H HMQC 2-d spectrum. 1H NMR (500.2 MHz, C_6D_6 , r.t.), δ_H (ppm) = 13.12 (1H, $\Delta\omega_{1/2} = 5.7$ Hz, N-H), 8.00 (2H, *m*, $C_4H_3N^A$), 7.76 (*m*, 4H, C_6H_5), 7.45 - 6.95 (*m*, 36H, C_6H_5), 7.22 ($C_4H_3N^B$ overlapped with the C_6H_5 resonances, determined by cosy), 6.38 (2H, *m*, $C_4H_3N^B$), 6.34 (2H, *s*, C_4H_2NMe), 6.32 (2H, *m*, $C_4H_3N^A$), 6.15 (2H, *m*, $C_4H_3N^B$), 6.11 (2H, *m*, $C_4H_3N^A$), 6.05 (2H *s*, C_4H_2NMe), 3.30 (*s*, 4H, *s*, CH_2 , DME), 3.09 (*s*, 6H, *s*, CH_3 , DME), 2.10 (*s*, 3H, *s*, C_4H_2NMe), 2.06 (*s*, 3H, *s*, C_4H_2NMe). Solubility of **6.5** was less than 0.5 mg in 1 mL of C_6D_6 , precluding measurement of 1d ^{13}C NMR spectrum. ^{13}C 1H HMQC (ppm) = 132.7 (8.00, $C_4H_3N^A$), 131.0 (7.22, $C_4H_3N^B$), 130.4 (7.42, C_6H_5), 129.9 (7.24, C_6H_5), 129.2 (7.76, C_6H_5), 128.8 (7.30, C_6H_5), 128.6 (7.21, C_6H_5), 128.2 to 126.1 (7.11 to 6.96 overlapped C_6H_5), 119.5 (6.34 C_4H_2NMe), 116.1 (6.94 C_6H_5), 115.4 (6.05, C_4H_2NMe (1 or 2)), 109.6 (6.15, $C_4H_3N^B$), 109.4 (6.11, $C_4H_3N^A$), 107.9 (6.38, $C_4H_3N^B$), 107.5 (6.32, $C_4H_3N^A$), 71.9 (3.30, DME), 58.5 (3.09, DME), 38.6 (2.06, C_4H_2NMe), 37.8 (2.10, C_4H_2NMe). IR (KBr, cm^{-1} , Nujol mull): ν 3373 (*m*, N-H), 1595 (*m*), 1488 (*s*), 1422 (*s*), 1399(*w*), 1321 (*w*), 1281 (*m*), 1260 (*s*), 1244 (*m*), 1234 (*s*), 1205 (*w*), 1186 (*m*), 1170 (*s*), 1157 (*m*), 1139 (*vs*), 1123 (*s*), 1103 (*s*), 1082 (*vs*), 1059 (*s*), 1045 (*vs*), 1036 (*s*), 1001 (*m*), 983 (*m*), 967 (*s*), 931 (*w*), 917 (*w*), 901 (*m*), 958 (*s*), 840 (*m*), 789 (*vs*), 758 (*vs*), 743 (*vs*), 703 (*vs*), 683 (*s*), 655 (*s*), 645 (*m*), 626 (*s*), 614 (*sh*), 602 (*w*), 571 (*w*), 540 (*m*), 513 (*w*), 498 (*w*), 477 (*s*), 458 (*sh*), 431 (*s*), 418 (*sh*), 387 (*m*), 379 (*s*).

Degradation of **6.5**

Complex **6.5** (0.1 g, 67 μ mol) was placed in a vial, and treated with excess (1 mmol) of 1M solution of HCl in D_2O . The resulting suspension was heated (80-90 °C) for 10 minutes and finally filtered through a fine frit. The clear D_2O solution was transferred

to an NMR tube. ^{15}N -NMR (50.7 MHz, D_2O , 25°C), δ_{N} (ppm) = -359.0 (NH_4^+). Solid $[\text{}^{15}\text{NH}_4][\text{BPh}_4]$ deposited upon addition of a solution of $\text{Na}[\text{BPh}_4]$. The IR displays the characteristic isotopic shift of NH stretching band from 3218 to 3248 cm^{-1} . The MS spectrum also exhibits the ammonium ion peak at 19 m/z compared to the 18 m/z peak for the non-isotopically enriched sample.

Preparation of $[\text{Na}(\text{DME})_3]_4[\text{LNa}]_2[\text{LTi}(\text{N})_2\text{TiL}](\text{DME})_2$ (**6.6**)

A suspension of $\{2,5-[(\text{C}_4\text{H}_3\text{N})\text{CPh}_2]_2[\text{C}_4\text{H}_2\text{N}(\text{Me})]\}\text{TiCl}$ (1.0 g, 1.4 mmol) with freshly prepared Na/Hg (0.193 g Na, 8.34 mmol, 10.4 g of Hg) in DME (20 mL) was stirred for 1 week at r.t. The color of the suspension slowly changed from the initial olive green to very dark green and finally back to olive green. The resulting mixture was centrifuged after Hg removal, and the supernatant was separated. Concentration of the supernatant produced dark green oily liquid, and colorless crystals of $[\text{Na}(\text{DME})_3]_4[\text{LNa}]_2[\text{LTi}(\text{N})_2\text{TiL}](\text{DME})_2$ (**6.6**) deposited in 1 week from the centrifuged supernatant mixture. Further dilution of a supernatant solution by toluene caused formation of crystalline $[\text{Na}(\text{DME})_3]_2[\text{L}_2\text{Na}_2]$.¹⁶ The crude crystals of **6.6** were separated from the supernatant solution, cooled to -30°C , washed with cold (-30°C) toluene (3 x 0.2 mL) and gently dried when cold. Analytically pure samples were kept at low temperature in order to prevent loss of lattice solvent. Yield 0.25g, 0.08 mmol, 15 %. Calculated (Found) for $\text{C}_{220}\text{H}_{284}\text{N}_{14}\text{Na}_6\text{O}_{32}\text{Ti}_2$: C 68.22 (68.29), H 7.34 (7.39), N 5.06 (5.03).

Preparation of $[\text{Na}(\text{dme})_3]_2[\text{LTi}]_2(\mu\text{-N})_2$ (**6.7**)

An aliquot of complex **6.6** (0.3 g, 0.08 mmol) was suspended in THF (5 mL), vigorously shaken and then filtered. The solid on the filter was washed with THF (3 x 2 mL). The resulting pale yellow **6.7** was dried in vacuum (0.125 g, 0.07 mmol, 90%). Calculated (Found) for $\text{C}_{102}\text{H}_{114}\text{N}_8\text{Na}_2\text{O}_{12}\text{Ti}_2$: C 68.59 (68.53), H 6.44 (6.48), N 6.28 (6.24). Compound **6.7** is almost insoluble in THF thus preventing NMR characterization other than ^1H -NMR. ESI-MS (THF, assignment, rel. intensity): m/z : 1411 ($\{[\text{Na}(\text{DME})_2][\text{LTiNNTiL}]\}^+$, 2), 1397 ($\{[\text{Na}_2(\text{THF})_2][\text{LTiNNTiL}]\}^+$, 2), 1342

($\{[\text{Na}_2(\text{DME})][\text{LTi NNTiL}]\}^-$, 5), 1313 ($\{[\text{Na}_2(\text{DME})][\text{LTiNNTiL}]\}^- - \text{HCO}$, 2), 603 ($[\text{LTiNNTi L}]^{2-}$, 3), 542 ($[\text{LH}]^-$, 100). ^1H NMR (500.2 MHz, THF- d^8 , 25°C A = $[\text{LTi}(\text{N})_2\text{TiL}]^{2-}$, B = $[\text{LNa}]_2^{2-}$): δ_{H} (ppm) = 7.88 (4H, *m*, $\text{C}_4\text{H}_3\text{N}^{\text{A}}$), 7.53 – 6.96 (80H, C_6H_5), 6.73 (4H, *m*, $\text{C}_4\text{H}_3\text{N}^{\text{B}}$), 6.38 (4H, *m*, $\text{C}_4\text{H}_3\text{N}^{\text{A}}$), 6.29 (4H, *m*, $\text{C}_4\text{H}_2\text{NMe}^{\text{A}}$), 6.02 (4H, *m*, $\text{C}_4\text{H}_3\text{N}^{\text{B}}$), 5.97 (4H, *m*, $\text{C}_4\text{H}_3\text{N}^{\text{B}}$), 5.81 (4H, *m*, $\text{C}_4\text{H}_3\text{N}^{\text{A}}$), 5.17 (4H, *m*, $\text{C}_4\text{H}_2\text{NMe}^{\text{B}}$), 3.45 (56H, DME), 3.29 (84H, DME), 2.34 (6H, *s*, $\text{MeNC}_4\text{H}_2^{\text{B}}$), 2.20 (6H, *s*, $\text{MeNC}_4\text{H}_2^{\text{A}}$). IR (KBr, cm^{-1} , Nujol mull): 3158 (w), 3118 (m), 3107 (m), 3095 (m), 3082 (s), 3070 (s), 3066 (s), 3057 (s), 3046 (m), 3021 (s), 3014 (s), 2245 (m), 2190 (w), 2126 (w), 2113 (w), 2091 (w), 1971 (w), 1960 (w), 1903 (w), 1823 (w), 1776 (w), 1667 (w), 1597 (s), 1579 (m), 1560 (w), 1488 (s), 1463 (vs), 1413 (vs), 1269 (s), 1234 (s), 1186 (s), 1166 (s), 1157 (m), 1139 (vs), 1136 (vs), 1115 (m), 1100 (s), 1093 (m), 1081 (s), 1067 (w), 1048 (vs), 1043 (vs), 1035 (s), 1019 (m), 1002 (s), 998 (m), 992 (s), 987 (m), 975 (m), 963 (vs), 928 (s), 920 (s), 911 (sh), 903 (vs), 897 (s), 868 (m), 862 (s), 856 (m), 851 (s), 845 (w), 840 (w), 804 (vs), 789 (s), 769 (vs), 759 (vs), 753 (vs), 742 (vs), 732 (vs), 718 (s), 708 (vs), 701 (vs), 687 (vs), 659 (s), 647 (s), 641 (m), 619 (m), 611 (w), 603 (m), 530 (m), 517 (w), 504 (m), 479 (m), 434 (s), 418 (m), 413 (m), 408 (w), 394 (m), 382 (s).

Preparation of **LTiNSiMe₃** (6.8)

Compound **6.5** (0.36 g, 0.24 mmol) was suspended in THF (10 mL) and then Me_3SiCl (0.15 g, 1.37 mmol) added dropwise. The resulted mixture stirred overnight, then centrifuged to remove insoluble residue, clear solution was separated and all volatilities removed under dynamic vacuum. Then the toluene (1 mL) added to the residue. Clear toluene solution was kept 3 days at room temperature while yellow crystalline **6.8** deposited. Compound **6.8** was separated by filtration, washed with toluene (2 x 0.3 mL) and hexane (3 x 0.5 mL) and gently dried in vacuum. Yield 0.14 g 0.19 mmol, 40%. Calculated (Found) for $\text{C}_{46}\text{H}_{48}\text{N}_4\text{TiOSi}$: C 73.70 (73.80), H 6.41 (6.46), N 7.48 (7.42). ^1H NMR (500.2 MHz, C_6D_6 , r.t.), δ_{H} (ppm) = 7.84 (m, 2H, $\text{C}_4\text{H}_3\text{N}$), 7.26 (m, 4H, C_6H_5), 7.11 - 6.95 (m, 16H, C_6H_5), 6.63 (m, 2H, $\text{C}_4\text{H}_3\text{N}$), 6.60 (m, 2H, $\text{C}_4\text{H}_3\text{N}$), 6.03 (s, 2H, $\text{C}_4\text{H}_2\text{NMe}$), 3.54 (m, 4H, THF), 2.15 (s, 3H, $\text{C}_4\text{H}_2\text{NMe}$), 1.41 (m, 4H, THF), 0.18 (s, 9H,

SiMe₃). ¹³C¹H HMQC (ppm) = 130.3 (7.26, C₆H₅), 130.9 - 126.4 (7.11 - 6.95, C₆H₅), 126.5 (7.84, C₄H₃N), 109.9 (6.60, C₄H₃N), 108.5 (6.63, C₄H₃N), 108.5 (6.03, C₄H₂NMe), 67.7 (3.54, THF), 38.2 (2.15, C₄H₂NMe), 25.1 (1.41, THF), 2.3 (0.18, SiMe₃). ²⁹Si-NMR (99.33 MHz, C₆D₆, r.t.), δ_{Si} (ppm) = -17.12. ¹⁵N¹H HSQC (ppm) 136.8 (Ti=N-SiMe₃), -129.3 (C₄H₃N), -218.4 (C₄H₂NMe). IR (KBr, cm⁻¹, Nujol mull): 3134 (w), 3126 (w), 3100 (m), 3083 (m), 3060 (m), 3018 (sh), 1595 (m), 1580 (w), 1490 (s), 1444 (vs), 1432 (s), 1427 (s), 1322 (w), 1267 (m), 1242 (s), 1234 (m), 1227 (s), 1184 (m), 1160 (s), 1148 (s), 1133 (m), 1100 (vs), 1085 (m), 1069 (m), 1048 (m), 1003 (w), 985 (w), 958 (m), 919 (m), 908 (m), 898 (w), 885 (w), 843 (vs), 835 (vs), 827 (vs), 799 (m), 784 (m), 762 (vs), 747 (vs), 723 (vs), 707 (vs), 700 (vs), 686 (m), 684 (m), 667 (w), 656 (w), 651 (w), 638 (w), 630 (m), 623 (s), 612 (m), 606 (w), 569 (w), 543 (w), 516 (w), 498 (w), 481 (s), 459 (m), 404 (m), 383 (s).

X-ray Crystallography

A suitable crystal was selected, mounted on a thin glass fiber using paraffin oil, and cooled to the data collection temperature. Data was collected on a Bruker AXS SMART 1K CCD diffractometer using 0.3° ω scans at 0°, 90°, 180°, and 270° in φ for the triclinic cells and 0°, 120°, and 240° in φ for the monoclinic cells. Initial unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.³⁰ The diffraction data and unit-cell parameters were consistent with the reported space group *P*1 for complexes **6.2**, **6.4** and **6.6**. No symmetry higher than triclinic was observed, and the solution in the centrosymmetric space group yielded chemically reasonable and computationally stable results of refinement. The data for complex **6.1** and **6.5** were consistent with the space group *P*2₁/*c*, and *P*2₁/*n* respectively and those for **6.3** and **6.8** were consistent with *Cc* and *C*2/*c* respectively. All structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on *F*². All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. Structure **6.2** was treated with the Squeeze routine of PLATON²⁰ due to

two lattice toluene molecules which were disordered over four positions. All scattering factors are contained in the SHELXTL 6.12 program library.³¹ Relevant crystal data and selected bond distances and angles are reported in Tables 1, 2, 3 and 4 respectively.

Table 6.1 Crystal Data and Structure Analysis Results for **6.1 – 6.4**.

	6.1	6.2	6.3	6.4
Formula	C ₄₇ H ₄₇ ClN ₃ O ₂ V	C _{46.50} H ₄₃ N ₃ OV	C _{98.13} H ₈₅ N ₈ V ₂	C ₈₆ H ₇₈ N ₇ V ₂ O
FW	772.27	710.78	1478.12	
Crystal system	Monoclinic,	Triclinic	Monoclinic	Triclinic
Space group	<i>P2(1)/c</i>	<i>P-1</i>	<i>Cc</i>	<i>P-1</i>
a (Å)	13.551(4)	11.7083(18)	30.376(3)	11.872(5)
b (Å)	10.846(3)	13.427(2)	14.4526(16)	13.197(5)
c (Å)	26.981(8)	13.625(2)	24.201(3)	14.158(5)
α (deg)	90	93.545(3)	90	68.906(6)
β (deg)	100.833(5)	92.316(3)	126.7260(10)	86.868(6)
γ (deg)	90	113.775(3)	90	67.678(6)
V (Å ³)	3895(2)	1951.4(5)	8515.7(16)	1905.9(13)
Z	4	2	4	2
radiation (K α , Å)	0.71073	0.71073	0.71073	0.71073
T (K)	209(2)	213(2)	201(2)	208(2)
D_{calcd} (g cm ⁻³)	1.317	1.210	1.153	1.169
μ_{calcd} (mm ⁻¹)	0.367	0.292	0.270	0.296
F ₀₀₀	1624	748	3103	702
R, R _w ^{2 a}	0.0571, 0.1245	0.0605, 0.1535	0.0712, 0.1232	0.0937, 0.2228
GoF	1.002	1.054	1.040	1.027

$$^a R = \Sigma |F_o| - |F_c| / \Sigma |F|, R_w = [\Sigma (|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}.$$

Table 6.2 Crystal Data and Structure Analysis Results for 6.5 – 6.8.

	6.5	6.6	6.8
Formula	C ₄₅ H ₄₇ N ₄ Na _{0.50} O ₃ Ti	C ₂₂₀ H ₂₈₄ N ₁₄ Na ₆ O ₃₂ Ti ₂	C ₄₆ H ₄₈ N ₄ OSi Ti
FW	751.26	3870.35	748.87
Crystal system	Monoclinic	Triclinic	Monoclinic,
Space group	<i>P2(1)/n</i>	<i>P-1</i>	<i>C2/c</i>
a (Å)	13.50(4)	14.336(7)	22.3998(19)
b (Å)	17.07(5)	15.128(8)	17.0299(15)
c (Å)	18.27(5)	26.160(13)	21.015(2)
α (deg)	90	99.865(7)	90
β (deg)	97.79(5)	94.401(7)	105.401
γ (deg)	90	108.020(7)	90
V (Å ³)	4172(22)	5264(5)	7728.5(12)
Z	4	1	8
radiation (K α , Å)	0.71073	0.71073	0.71073
T (K)	203(2)	203(2)	100(2)
D _{calcd} (g cm ⁻³)	1.196	1.221	1.287
μ _{calcd} (mm ⁻¹)	0.253	0.160	0.294
F ₀₀₀	1586	2068	3168
R, R _w ^{2 a}	0.0672, 0.1702	0.0676, 0.1798	0.0664, 0.1570
GoF	1.018	1.040	1.032

$$^a R = \Sigma |Fo| - |Fc| / \Sigma |F|. R_w = [\Sigma (|Fo| - |Fc|)^2 / \Sigma w Fo^2]^{1/2}.$$

Table 6.3 Selected Bond Distances (Å) and Angles (deg) for 6.1- 6.4.

6.1	6.2	6.3	6.4
V1–N1 = 1.957(3)	V1–N1 = 2.067(4)	V1–N1 = 2.011(5)	V1–N1 = 2.020(7)
V1–N3 = 1.958(3)	V1–N3 = 2.075(4)	V1–N3 = 2.024(6)	V1–N3 = 2.001(7)
V1–O1 = 2.107(2)	V1–O1 = 2.115(3)	V1–centroid = 2.023(6)	V1–centroid = 2.040(7)
V1–N2 = 2.232(3)	V1–N2 = 2.193(3)	V1–N7 = 1.752(6)	V1–N4 = 1.7680(15)
V1–Cl1 = 2.2526(11)	V1–C6 = 2.293(4)	N7–N8 = 1.248(5)	N1 –V1–N3 = 103.2(2)
N3–V1–N1 = 122.35(11)	V1–C9 = 2.309(4)	N1 –V1–N3 = 100.1(2)	N1 –V1–N4 = 108.4(2)
N3 –V1–O1 = 94.87(10)	V1–C7 = 2.430(4)	N1 –V1–N7 = 106.3(2)	N3 –V1–N4 = 104.9(2)
N1 –V1–O1 = 92.40(10)	V1–C8 = 2.454(4)	N3 –V1–N7 = 105.7(2)	centroid–V1–N1 = 104.8(2)
N3 –V1–N2 = 83.50(10)	N1–V1–N3 = 106.68(14)	centroid–V1–N1 = 103.8(2)	centroid–V1–N3 = 103.9(2)
N1 –V1–N2 = 82.46(10)	N1–V1–O1 = 97.83(14)	centroid–V1–N3 = 105.02	centroid–V1–N4 = 129.1(2)
O1 –V1–N2 = 172.59(9)	N3–V1–O1 = 97.72(14)	centroid–V1–N7 = 131.7(2)	V1–N4–V1a = 180.0(2)
N3 –V1–Cl1 = 119.98(8)	N1–V1–N2 = 87.71(13)	V1–N7–N8 = 177.7(2)	
N1 –V1–Cl1 = 117.44(8)	N3–V1–N2 = 89.13(13)	N7–N8–V2 = 176.5(2)	
O1 –V1–Cl1 = 87.24(7)	O1–V1–N2 = 169.51(13)		
N2 –V1–Cl1 = 99.85(7)			

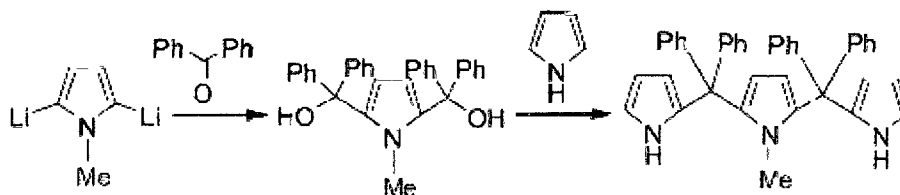
Table 6.4 Selected Bond Distances (Å) and Angles (deg) for **6.5- 6.8**.

6.5	6.6	6.8
Ti(1)–N(1) = 2.112(6)	Ti(1)–Ti(1A) = 2.642(2)	Ti(1)–N(1) = 2.043(4)
Ti(1)–N(3) = 2.118(6)	N(1)–N(1A) = 2.478(5)	Ti(1)–N(2) = 2.400(3)
Ti(1)–N(2) = 2.193(3)	Ti(1)–N(1) = 1.812(3)	Ti(1)–N(3) = 2.047(3)
Ti(1)–N(4) = 1.878(7)	Ti(1)–N(3) = 2.150(3)	Ti(1)–N(4) = 1.679(3)
Ti(1)–N(4A) = 1.837(6)	Ti(1)–N(2) = 2.157(3)	Si(1)–N(4) = 1.733(4)
Ti(1)–Ti(1A) = 2.786(6)	N(1)–Ti(1)–N(3) = 98.76(14)	N(4)–Ti(1)–N(1) = 108.14(15)
N(1)–Ti(1)–N(3) = 123.7(2)	N(1A)–Ti(1)–N(2) = 116.02(14)	N(4)–Ti(1)–N(3) = 110.69(15)
N(1)–Ti(1)–N(2) = 77.1(2)	N(1)–Ti(1)–N(2) = 99.21(13)	N(1)–Ti(1)–N(3) = 108.95(14)
N(3)–Ti(1)–N(2) = 76.9(2)	N(3)–Ti(1)–N(2) = 127.91(12)	Ti(1)–N(4)–Si(1) = 165.5(2)
N(4A)–Ti(1)–N(4) = 82.8(2)		
N(4)–Ti(1)–N(1) = 117.49(17)		
N(4A)–Ti(1)–N(3) = 96.5(2)		
N(4)–Ti(1)–N(3) = 118.3(2)		
N(4A)–Ti(1)–N(1) = 97.2(2)		
N(4A)–Ti(1)–N(2) = 166.22(16)		
N(4)–Ti(1)–N(2) = 110.95(18)		
N(4A)–Ti(1)–Ti(1A) = 41.96(15)		
N(4)–Ti(1)–Ti(1A) = 40.86(17)		
N(1)–Ti(1)–Ti(1A) = 113.17(18)		
N(3)–Ti(1)–Ti(1A) = 113.24(18)		
N(2)–Ti(1)–Ti(1A) = 151.81(9)		
Ti(1A)–N(4)–Ti(1) = 97.2(2)		

Results and Discussion

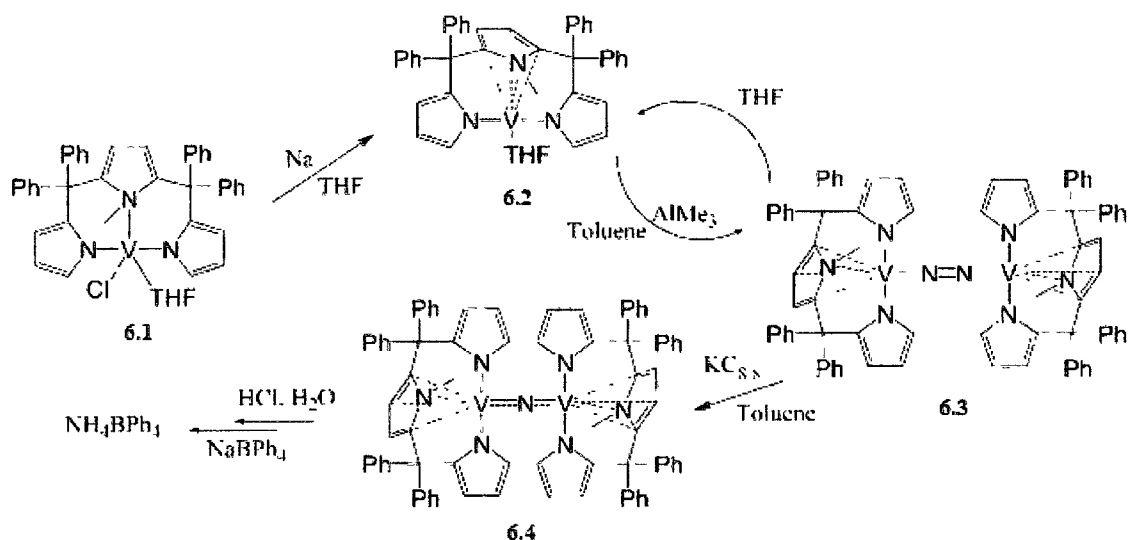
In order to prepare the tripyrrole ligand MeTPH₂, the classical direct condensation between pyrrole and carbonyl derivatives cannot be used, as it tends to lead to either dipyrrole or porphyrinogen-type structures with only small amounts of tripyrrole being produced.³² Thus, its synthesis (Scheme 6.1) was obtained via double lithiation of the two 1-methyl pyrrole R-positions³³ followed by the subsequent addition of benzophenone and quenching. In a second step, the resulting diol 2,5-[(C₆H₅)₂C(OH)]₂(N-Me-pyrrole) was condensed with neat pyrrole, acting as both a solvent and reagent, affording MeTPH₂ in good yield (83%) of analytically pure solid. Deprotonation of the two terminal pyrroles and formation of the corresponding dipotassium salt MeTPK₂ was conveniently carried out in situ via standard treatment with KH in THF.

Scheme 6.1



Reaction of TripyrrK₂ with VCl₃(THF)₃ in THF formed dark-red crystals of the corresponding [(Tripyrr)VCl(THF)]·THF (**6.1**) in moderate yield (39%) (Scheme 6.2).

Scheme 6.2



The connectivity has been confirmed by an X-ray crystal structure. The only unexpected feature in the structure (Figure 6.1) is that the central N-methylated ring does not adopt the expected η^5 -coordination mode, but formed instead a direct V-N σ - bond via quaternization of the nitrogen atom. The geometry around the metal center can be described in terms of distorted trigonal bipyramidal geometry with the apical positions occupied by the N atom of the N-methylated central ring [V1–N2 = 2.232(3) Å] and the oxygen atom of one coordinated THF [V1–O1 = 2.107(2) Å]. The equatorial plane is comprised of two σ - bound pyrrolides N atoms [V1–N1 = 1.957(3) Å and V1–N3 = 1.958(3) Å] and the chloride [V1–Cl1 = 2.2526(11) Å]. The axial vector deviates a little from the linearity [N2–V1–O1 = 172.59(9) $^\circ$], and a minor distortion is present in the equatorial plane [Cl1–V1–N3 = 119.98(8) $^\circ$, Cl–V1–N1 = 117.44(8) $^\circ$, N1–V1–N3 = 122.35(11) $^\circ$].

The magnetic moment was as expected for the high-spin d^2 electronic configuration of mononuclear trivalent vanadium.

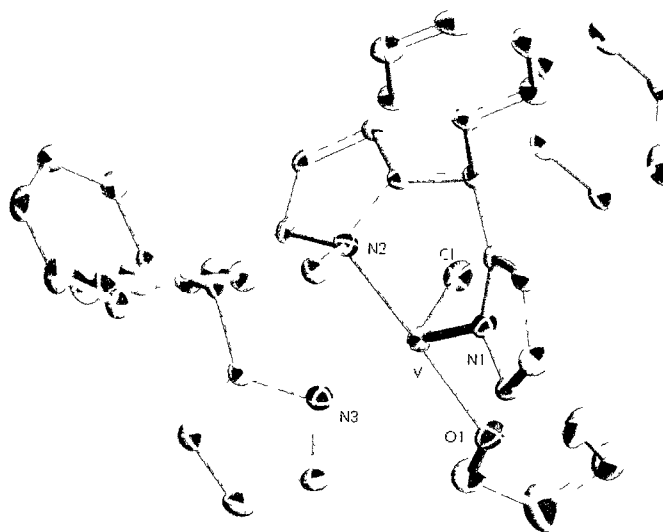


Figure 6.1 Thermal ellipsoid plot of **6.1** with ellipsoids drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

When complex **6.1** was reacted with metallic sodium in THF, a new species was isolated as dark purple crystals in moderate yield (Scheme 6.2). The divalent $[(\text{MeTP})\text{V}(\text{THF})] \cdot (\text{C}_7\text{H}_8)_{0.5}$ (**6.2**) was determined by an X-ray structure. (Figure 6.2) The N-methylated ring adopted a sort of skewed η^5 -bonding mode not perfectly centered over the V atom [V-centroid = 2.010(4) Å, V(1)-N(2) = 2.193(3) Å, V(1)-C(7) = 2.293(4) Å]. Overall, the coordination geometry of the metal center can be described as distorted pseudo-tetrahedral [$\text{N1-V1-N3} = 106.68(14)^\circ$, $\text{N1-V1-O1} = 97.83(14)^\circ$, $\text{N1-V1-centroid} = 107.59^\circ$] and is comprised by the centroid of the η^5 -bound ring, the two N atoms of the two σ -bonded pyrrolides rings [V1-N1 = 2.067(4) Å and V1-N3 = 2.075(4) Å] and the O atom of one coordinated molecule of THF [V1-O1 = 2.115(3) Å].

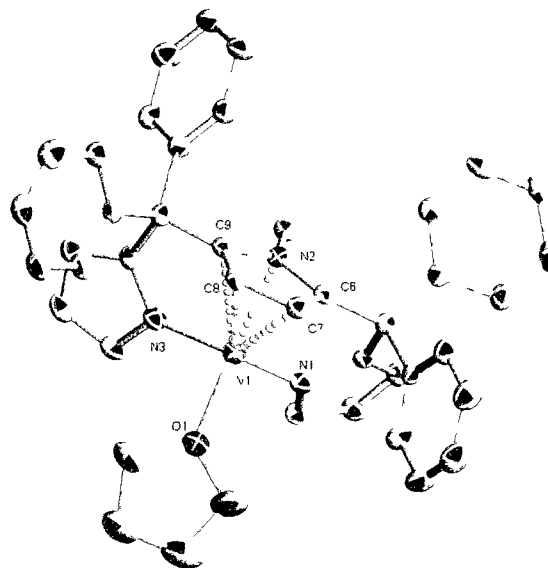


Figure 6.2 Thermal ellipsoid plot of **6.2** with ellipsoids drawn at 50% probability.
Hydrogen atoms have been omitted for clarity.

The lack of dinitrogen fixation in this complex containing divalent vanadium can certainly be ascribed to the coordination of one THF molecule. The exchange of THF for a weakly ligated N_2 was previously observed in the chemistry of divalent vanadium amidinates.^{22h} Thus, when the coordinated molecule of THF was extracted by a strong Lewis acid such as $AlMe_3$, coordination of dinitrogen was obtained with formation of the dinuclear dinitrogen-bridged complex $[(MeTP)V(\mu-N_2)]_2 \cdot (C_7H_8)_2 \cdot 9$ (**6.3**), which crystallized from toluene in moderate yield (Figure 6.3).

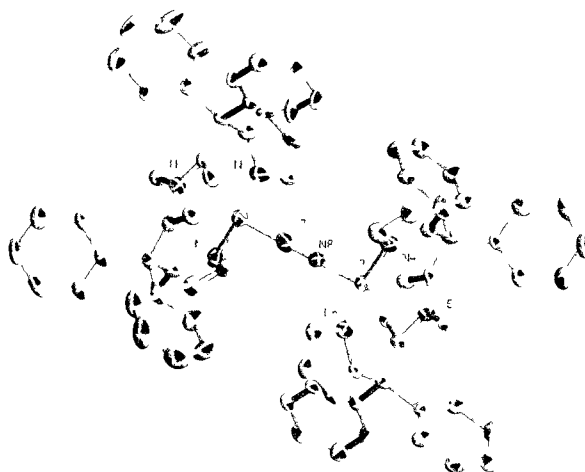


Figure 6.3 Thermal ellipsoid plot of **6.3** with ellipsoids drawn at 50% probability.

Hydrogen atoms have been omitted for clarity.

The structure shows the complex as formed by two metal centers, each surrounded by one tripyrrolide ligand system, and bridged by one dinitrogen unit in an almost linear V-N-N-V array [$\text{V1-N7-N8} = 177.7(2)^\circ$, $\text{N7-N8-V2} = 176.5(2)^\circ$]. Similar to complex **6.2**, each V centre is in a pseudo-tetrahedral coordination geometry comprised of the η^5 -bound ring [$\text{V1-centroid} = 2.023(6)\text{\AA}$], the two pyrrolides [$\text{V1-N1} = 2.011(5)\text{\AA}$, $\text{V1-N3} = 2.024(6)\text{\AA}$, $\text{V1-N7} = 1.752(6)\text{\AA}$, $\text{N1-V1-N3} = 100.1(2)^\circ$, $\text{N1-V1-N7} = 106.3(2)^\circ$, $\text{N1-V1-centroid} = 103.8(2)^\circ$] and one N atom of the bridging N_2 unit. The elongated di-nitrogen bond [$\text{N7-N8} = 1.248(5)\text{\AA}$ vs. $1.0968\text{\AA}$ for free N_2] and short V-N₂ distance [$1.752(6)\text{\AA}$] along with the near linear arrangement of the V1-N₂-V2 atoms [$\text{V1-N7-N8} = 177.7(2)^\circ$, $\text{N7-N8-V2} = 176.5(2)^\circ$] would tend to indicate significant double bond character and thus a $2e^-$ reduction. However, similar to the cases of other di-nitrogen bridged vanadium complexes³⁶ the magnetic moment ($\mu_{\text{eff}} = 3.52\mu_B$) indicates that the extent of reduction is rather minimal and the metal center is predominantly in the divalent state.

Further reduction of **6.3** in toluene in the presence of $\text{KC}_{8.8}$ afforded the nitride bridged complex $[(\text{Tripyr})\text{V}]_2(\mu\text{-N})\cdot(\text{THF})$ (**6.4**) which was crystallized from THF in moderate yield (Fig. 6.4). As in the previous cases the N-Me pyrrole ring is interacting with the metal centre in the η^5 bonding mode [$\text{V1-centroid} = 2.040(7) \text{ \AA}$]. Each V centre assumes a slightly distorted tetrahedral coordination geometry comprised of the η^5 ring, the two pyrrolides and the bridging nitride [$\text{V1-N1} = 2.020(7) \text{ \AA}$, $\text{V1-N2} = 2.001(7) \text{ \AA}$, $\text{V1-N4} = 1.7680(15) \text{ \AA}$, $\text{N1-V1-N3} = 103.2(2)^\circ$, $\text{N1-V1-N4} = 108.4(2)^\circ$, $\text{N1-V1-centroid} = 103.8(2)^\circ$]. The short V–N bond length and perfectly linear arrangement of the V–N–V bond [$180.0(2)^\circ$] are strong indicators of multiple bond character between the nitride and the metal centres.

In order to unambiguously identify the bridging atom as a nitride, a degradation experiment was performed by treating complex **6.4** with a diluted HCl solution. The resulting solution was treated with NaBPh_4 affording a white precipitated of NH_4BPh_4 in good yield. The solid was analyzed via electron-spray mass spectrometry and by comparison with an analytically pure sample. Finally, when the preparation of **6.3** and its further reduction were carried out under $^{15}\text{N}_2$ atmosphere, a sample of $^{15}\text{NH}_4\text{BPh}_4$ was obtained which showed the expected pattern in the mass spectrum. This conclusively demonstrated that not only the bridging atom as nitrogen but also that its origin is from the atmospheric dinitrogen. The room temperature magnetic moment [$\mu_{\text{eff}} = 1.74 \mu_B$] was in agreement for the nitride-bridged mixed-valent V(III) – V(IV) dimer with one unpaired electron configuration.

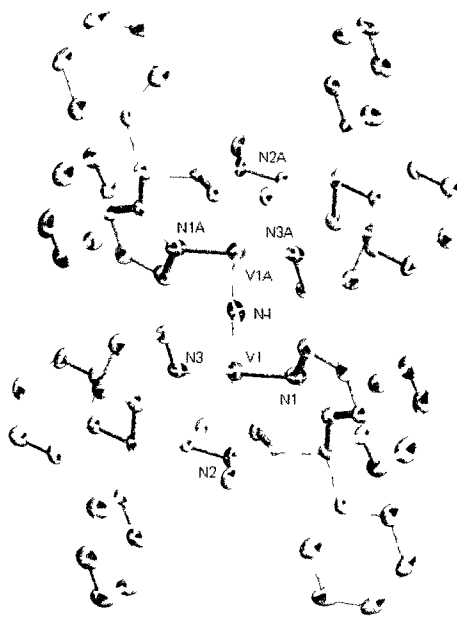
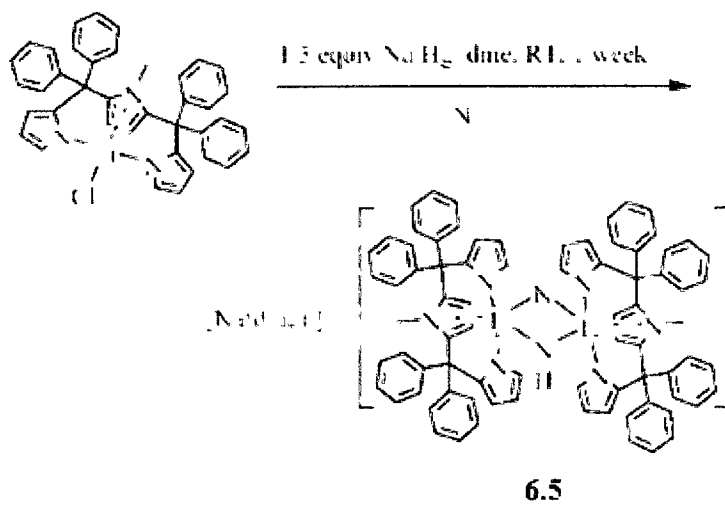


Figure 6.4 Thermal ellipsoid plot of 6.4 with ellipsoids drawn at 50% probability.

Hydrogen atoms have been omitted for clarity.

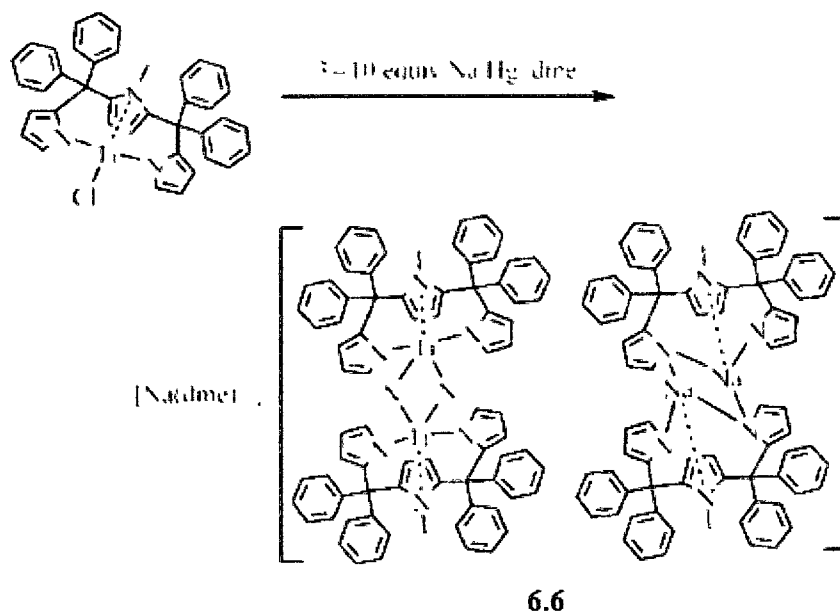
Scheme 6.3



The reduction of the trivalent LTiCl ($\text{L} = 2,5\text{-}[(\text{C}_6\text{H}_5)_2\text{C}(\text{C}_6\text{H}_5)_2]_2[\text{C}_6\text{H}_4\text{N}(\text{Me})]$) complex³² with the relatively mild reductant Na/Hg (1.5 equiv) in DME afforded a dark-green solution. Crystallization yielded the dinuclear and diamagnetic $[\text{Na}(\text{DME})_3][(\text{LTi})_2(\mu\text{-NH})(\mu\text{-N})]$ (**6.5**) as pale-green crystals (Scheme 6.3). The yield of the isolated product were improved up to 25% if crystallization was carried out in THF after evaporation of DME. Surprisingly, identical reaction in THF afforded intractable materials from where only $[\text{Na}(\text{DME})_3]_2[\text{L}_2\text{Na}_2]$ was isolated in crystalline form.³⁴

By doubling the amount of Na/Hg or even using larger excess, the diamagnetic complex $\{[\text{Na}(\text{DME})_3]_4[\text{L}_2\text{Na}_2][(\text{LTi})_2(\mu\text{-N})_2]\} \cdot (\text{DME})_2$ (**6.6**) was obtained. (Scheme 6.4) Attempts to solubilize **6.6** in THF or DME for NMR characterization gave deposition of the insoluble $[\text{Na}(\text{DME})_3]_2[(\text{LTi})_2(\mu\text{-N})_2]$ (**6.7**), while $[\text{Na}(\text{DME})_3]_2[\text{L}_2\text{Na}_2]$ was retained in solution and subsequently crystallized.³⁴

Scheme 6.4



The connectivities of **6.5** and **6.6** were yielded by X-ray crystal structures (Figures 6.5 and 6.6). Complex **6.5** shows the mono-anionic dimetallic unit as consisting of two

identical [LTi] moieties bridged by one nitride and one NH units forming a planar Ti_2N_2 core. Identification of the two bridging atoms as nitrogen was initially suggested by the successful refinement of the crystallographic thermal parameters and analytical data. The identification of these bridging atoms as well as of the presence of one hydrogen atom was confirmed by NMR, IR, mass spectrometry and chemical degradation including of the ^{15}N -labelled derivative. Complex **6.5** is diamagnetic as expected for the proposed tetravalent titanium formulation. ^1H -NMR, ^{13}C -NMR spectra showed the two expected sets of resonances for two magnetically non-equivalent ligands. One resonance, integrating for only one hydrogen atom per dimeric unit at 13.11 ppm, was not coupled to any carbon atoms thus giving the first indication about the presence of an N-H function. To conclusively prove the formulation, identical preparation was carried out under $^{15}\text{N}_2$ atmosphere. A crystalline product obtained in this manner, with identical cell parameters as **6.5**, was subjected to chemical degradation with HCl followed by precipitation with NaBPh_4 to confirm, with the formation of $^{15}\text{NH}_4\text{BPh}_4$, both the identity of the bridging atoms as nitrogen and their origin from atmospheric dinitrogen. Furthermore, the NMR spectra of the isotopically labelled compound were identical to **6.5**, except for the NH resonance at 13.11 ppm which showed the doublet expected for the coupling with the ^{15}N nucleus [$J(^{15}\text{N}-^1\text{H}) = 67 \text{ Hz}$]. In turn, the ^{15}N -NMR spectrum showed two distinct resonances at 542.0 for Ti ($\mu\text{-N}$)Ti and 132.2 ppm Ti ($\mu\text{-NH}$)Ti respectively. The second resonance was particularly broad and could not be resolved into the expected doublet. It was confirmed to be coupled to the corresponding H atom at 13.11 ppm in the ^{15}N DEPT90 and ^1H - ^{15}N HMQC spectra. The N-H stretch was also visible in the IR spectrum at 3373 cm^{-1} shifted to 3337 cm^{-1} in the isotopically labelled sample.

The structure of **6.6** showed instead two separate dianionic [$\{\text{L}_2\text{Na}_2\} \}^{2-}$ and [$\{(\text{LTi})(\mu\text{-N})\}_2 \}^{2-}$ moieties counterbalanced by four DME-solvated sodium cations. The Ti...Ti distances are substantially different in the two complexes [$2.786(6) \text{ \AA}$ and $2.642(2) \text{ \AA}$ for **6.5** and **6.6** respectively]. A smaller and yet visible difference may be also observed among the Ti-N distances [$1.837(6)$ and $1.878(7) \text{ \AA}$ in **6.5** and $1.812(3)$ for **6.6**.] These distances compare well with those of $\text{Ti}-(\mu\text{-NR})_2\text{-Ti}$ (ranging from 1.830 to $1.997 \text{ \AA}$, $\text{R} = \text{Me}, t\text{-Bu}, \text{SiMe}_3, \text{Ph}, \text{etc.}$),³⁵ and are shorter than in cluster complexes containing the $[\text{Ti}-(\mu\text{-NH})\text{-Ti}]$ bond [$1.94(2) - 1.97(1) \text{ \AA}$]³⁶ and bridging nitride [$1.958(5) - 2.193(4) \text{ \AA}$].³⁷

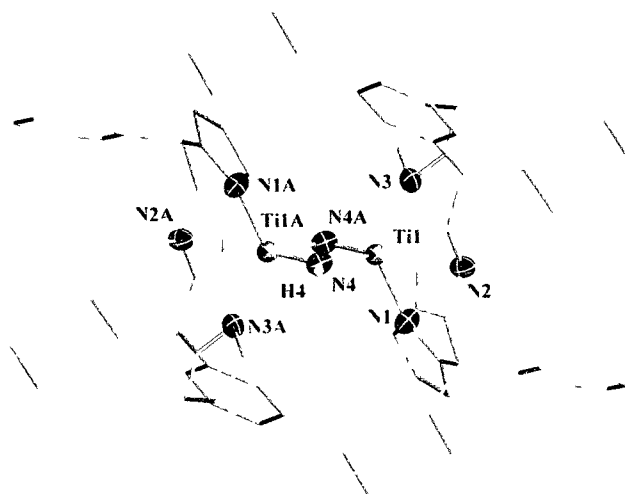


Figure 6.5 Thermal ellipsoid plot of anion of **6.5** with selected ellipsoids drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

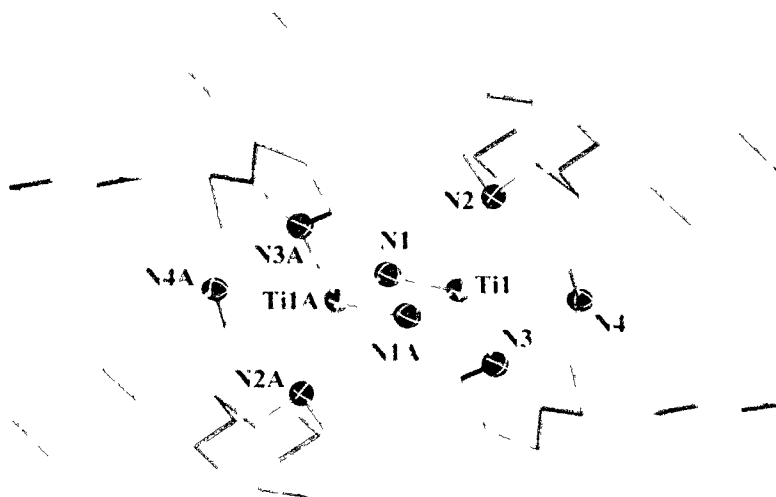
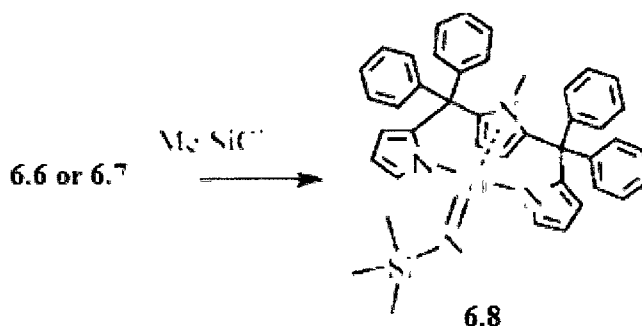


Figure 6.6 Thermal ellipsoid plot of **6.6** with selected ellipsoids drawn at 50% probability. Four $[\text{Na}(\text{DME})_3]$ cations and two LNa anions and hydrogen atoms have been omitted for clarity

Complex **6.6** decomposes upon solubilization with deposition of **6.7** thus preventing NMR characterization. Satisfactory elemental analysis data and ESI-MS were obtained in agreement with the proposed formulation. In addition, chemical degradation of a ^{15}N -riched sample, carried out as in the case of **6.5** with HCl followed by precipitation with NaBPh_4 , gave $^{15}\text{NH}_4\text{BPh}_4$. In turn this confirmed the identity and the origin of the bridging nitrides from gaseous nitrogen even in this case. The IR spectrum confirmed the absence of NH functions as it was also indicated by the diamagnetism of this compound. Complex **6.7** instead is sparingly soluble in THF and a meaningful ^1H -NMR spectrum could be obtained only upon partial removal of $[\text{L}_2\text{Na}_2][\text{Na}(\text{DME})_3]_2$. Suitable crystals of **6.7** could not be grown. Compounds **6.5** and **6.7**²⁹ are unreactive with MeI at room temperature but readily react with Me_3SiCl in THF forming NaCl and a yellow solution. Crystallization from toluene afforded yellow crystalline LTiNSiMe_3 (**6.8**) (Scheme 6.5).

Scheme 6.5.



The connectivity of **6.8** was yielded by an X-ray crystal structure (Figure 6.7) showing the presence of a bent TiNSiMe_3 imido moiety. The Ti – N bond length [1.697(3) Å] is in the expected range,^{38,39} The proton NMR spectrum of **6.8** is in agreement with the established structure (Figure 6.7) showing the ligand and SiMe_3 group resonances in the normal positions. The ^{29}Si -NMR gives a resonance at 17.12 ppm 179

while the $^{15}\text{N} - ^1\text{H}$ HSQC NMR spectrum clearly shows the coupling of the Me_3Si methyl groups to a ^{15}N resonance at 136.8 ppm.

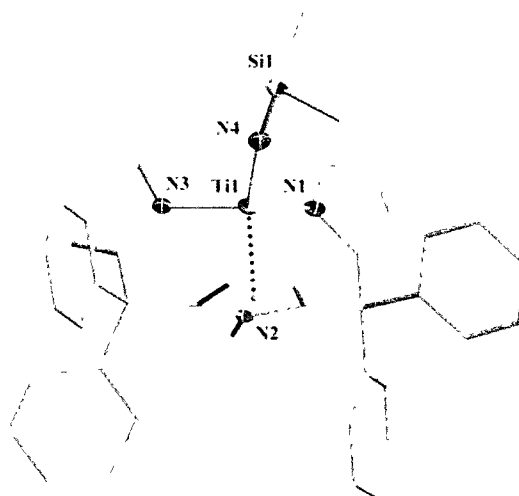


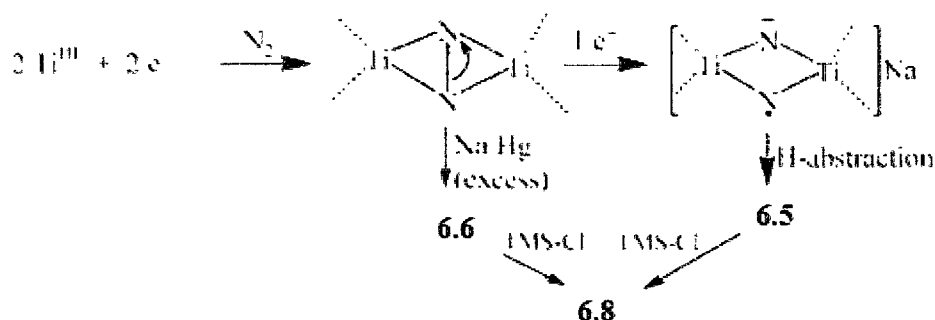
Figure 6.7 Thermal ellipsoid plot of **6.8** with selected ellipsoids drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

The reactions forming **6.5** and **6.6** must be carried out exclusively in DME since identical reactions in THF led to intractable mixtures from which only LNa_2 ³⁴ could be isolated. The formation of **6.5** required a careful control of the Ti/Na stoichiometric ratio.

The oxidation of the two starting trivalent Ti centers, in combination with two additional electrons provided by the Na/Hg reductant, would initially lead to a neutral tetravalent side-on hydrazido complex on the line of the reactive species isolated by Chirik,^{1d} Fryzuk^{1c} and Sita^{2f} with group 4 elements (Scheme 6.6). For **6.5** to be formed, one would have to assume that a simple one-electron attack on such intermediate may cleave the residual N-N single bond generating one nitride (hence the necessity for the Na counteraction) and one nitrogen radical. Since ethers are known to be attacked by radicals

or by species with radical-type of behavior affording a variety of fragmentation patterns,⁴⁰ it is conceivable that simple hydrogen atom abstraction may readily form the final compound.

Scheme 6.6



However, it is also possible that the hydrogen atom has been provided by the ligand system of another molecule at the expense of the reaction yield. While a similar process has been observed during the reduction of Th,³⁷ the origin of the proton from the solvent cannot be conclusively substantiated by isotope labeling experiment given the stringent solvent requirement of the reaction. The formation of **6.6** is a more straightforward process. It is the typical six-electron reduction with two electrons provided by the two trivalent Ti atoms and the rest from Na/Hg. This transformation however has only one precedent in the chemistry of Ti^{4b} where the reactive intermediate bis-nitrides moieties further reacted with the donor atoms of the ligand. Possible involvement of nitride was also claimed in the reduction of titanocene forming ammonia.⁴¹ The cocrystallization with LNa_2 observed in **6.6** seems to indicate the presence even in DME of a degradation pattern similar to that occurring more extensively during reactions in THF.

The silylation of the nitride of **6.6** and **6.7** is rather straightforward proceeding with elimination of NaCl and LNa_2 (for **6.6**). In the case of **6.5**, it is tempting to suggest

that a $\text{LTiCl}(\text{NHSiMe}_3)$ compound may be the byproduct of this transformation but, at this stage, we could not find conclusive evidence for it. Formation of imide species from dinitrogen has been observed only in the partial silylation of a Ta nitride derivative^{2e} performed by PhSiH_3 and in the $\text{Mo}=\text{NH}$ unit as detected in the Schrock's catalytic cycle.⁵

Conclusion

The tripyrrolide ligand system showed some unanticipated flexibility in the π - bonding. While the trivalent complex prefers to adopt a σ -type of bonding with the simple N atom, the softer divalent species, (both as THF or as N_2 complexes) display the expected π -bonding mode. While we find no sign of reversibility in the coordination of N_2 in **6.3** further reduction indicated that it is possible to cleave the coordinated N_2 unit into nitride anion. However, rather than forming two bridging nitrides as previously reported in two instances in the chemistry of vanadium dinitrogen, for the first time a simple linearly bonded nitride has been obtained via reduction of dinitrogen. It have been also here reported that five-electron reduction of dinitrogen may lead to nitride species provided of radical behavior capable of abstracting hydrogen atom from the reaction environment. Six-electron reduction affords instead a standard bis-nitride complex. The nucleophilic behavior of the nitride has enabled functionalization to a monomeric imido function.

Reference

- (1) a) Fryzuk, M. D. *Acc. Chem. Res.*, **2009**, *42*, 127.
b) Schrock, R. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 5512.
c) Ohki, Y.; Fryzuk, M. D. *Angew. Chem., Int. Ed.* **2007**, *46*, 3180.
d) Chirik, P. J. *Dalton Trans.* **2007**, 16.
e) MacLachlan, E. A.; Fryzuk, M. D. *Organometallics* **2006**, *25*, 1530.
f) Schrock, R. R. *Acc. Chem. Res.* **2005**, *38*, 955.
g) Shaver, M. P.; Fryzuk, M. D. *Adv. Synth. & Catalysis* **2003**, *345*, 1061.
h) MacKay, B. A.; Fryzuk, M. D. *Chem. Rev.* **2004**, *104*, 385.
i) Fryzuk, M. D. *Chem. Record* **2003**, *3*, 2.
j) Schrock, R. R. *Chem. Comm.* **2003**, *19*, 2389.
k) Fryzuk, M. D. *Modern Coordination Chemistry* **2002**, 187.
l) Fryzuk, M. D.; Johnson, S. A. *Coord. Chem. Rev.* **2000**, *200*, 379.
m) Hidai, M.; Mizobe, Y. *Chem. Rev.* **1995**, *95*, 1115.
n) Hidai, M. *Coord. Chem. Rev.* **1999**, *185-186*, 99.
o) Peters, J. C.; Mehn, M. P.; *Bio-organometallic Approaches to Nitrogen Fixation Chemistry. In Activation of Small Molecules*, W. B. Tolman, ed.; Wiley-VCH: Weinheim, **2006**, 81.
p) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589.
q) Hidai, M.; Mizobe Y.; *Metal Ions in Biological Systems* **2002**, *39*, 121.
r) Gambarotta, S.; Scott, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 5298.
s) Hidai, M.; Mizobe, Y. *Pure Appl. Chem.* **2001**, *73*, 261.
t) Fryzuk, M. D.; *Nature* **2004**, *427*, 498.
(2) a) Pun, D.; Bradley, C. A.; Lobkovsky, E.; Keresztes, I.; Chirik, P. J. *J. Am. Chem.*

Soc. **2008**, *130*, 14046.

, W. H.; Chirik; P. J. *J. Am. Chem. Soc.* **2004**, *126*, 14326.

b) Tanaka, H.; Mori, H.; Seino, H.; Hidai, M.; Mizobe, Y.; Yoshizawa, K. *J. Am. Chem. Soc.* **2008**, *130*, 9037.

c) Knobloch, D. J.; Toomey, H. E.; Chirik, P. J. *J. Am. Chem. Soc.* **2008**, *130*, 4248.

d) Yuki, M.; Miyake, Y.; Nishibayashi, Y. *Organometallics* **2008**, *27*, 3947.

e) Hirotsu, M.; Fontaine, P. P.; Zavalij, P. Y.; Sita, L. R. *J. Am. Chem. Soc.* **2007**, *129*, 12690.

f) Hirotsu, M.; Fontaine, P. P.; Epshteyn, A.; Zavalij, P. Y.; Sita, L. R. *J. Am. Chem. Soc.* **2007**, *129*, 9284.

g) MacLachlan, E. A.; Hess, F. M.; Patrick, B. O.; Fryzuk, M. D. *J. Am. Chem. Soc.* **2007**, *129*, 10895.

h) Bart, S. C.; Bowman, A. C.; Lobkovsky, E.; Chirik, P. J.; Paul, J. *J. Am. Chem. Soc.* **2007**, *129*, 7212.

i) Bernskoetter, W. H.; Lobkovsky, E.; Chirik, P. J. *Angew. Chem., Int. Ed.* **2007**, *46*, 2858-2861.

j) MacKay, B. A.; Munha, R. F.; Fryzuk, M. D. *J. Am. Chem. Soc.* **2006**, *128*, 9472.

k) Bernskoetter, W. H.; Lobkovsky, E.; Chirik, P. J. *Angew. Chem., Int. Ed.* **2007**, *46*, 2858.

l) Studt, F.; Tucek, F. *Angew. Chem., Int. Ed.* **2005**, *44*, 5639.

m) Studt, F.; MacKay, B. A.; Johnson, S. A.; Patrick, B. O.; Fryzuk, M. D.; Tucek, F.; *Chem. Eur. J.* **2005**, *11*, 604.

n) Bernskoetter, W. H.; Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2005**, *127*, 7901.

- o) Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *Nature* **2004**, 427, 527.
- p) Pool, J. A.; Bernskoetter, M. D.; MacKay, B. A.; Patrick, B. O. *J. Am. Chem. Soc.* **2003**, 125, 3234.
- (3) a) Pun, D.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2008**, 130, 6047.
- b) Hanna, T. E.; Bernskoetter, W. H.; Bouwkamp, M. W.; Lobkovsky, E.; Chirik, P. *J. Organometallics* **2007**, 26, 2431.
- c) Dubé, T.; Ganesan, M.; Conoci, S.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2000**, 19, 3716.
- d) Dube, T.; Conoci, S.; Gambarotta, S.; Yap, G. P. A.; Vasapollo, G. *Angew. Chem., Int. Ed.* **1999**, 38, 3657.
- e) Bérubé, C. D.; Yazdanbakhsh, M.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2003**, 22, 3742.
- f) Campazzi, E.; Solari, E.; Floriani, C.; Scopelliti, R. *Chem. Comm.* **1998**, 2603.
- g) Jubb J.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, 116, 4477.
- (4) a) Ertl, G. *Catalytic Ammonia Synthesis Ed.* Jennings, J. R., plenum, New york, 1991.
- b) Schlogl, R. *Angew. Chem. Int. Ed.* **2003**, 42, 2004.
- (5) In *CRC Handbook of Chemistry and physics 73 rd Ed*, Ed. In Chief: Lide, D. R., CRS Press, **1992**.
- (6) a) Leigh, G. J. *Acc. Chem. Res.* **1992**, 25, 177.
- b) Howard, J. B.; Rees, D. C. *Chem. Rev.* **1996**, 96, 2965.
- c) Burgess, B. K.; Lowe, D. J. *Chem. Rev.* **1996**, 96, 2983.
- d) Burgess, B. K.; *Chem. Rev.* **1990**, 90, 1377.
- (7) a) Seefeldt, L. C.; Dance, I. G.; Dean, D. R.; *Biochemistry* **2004**, 43, 1401.
- b) Seefeldt, L. C.; Dean, D. R.; *Acc. Chem. Res.* **1997**, 30, 260.

- (8) a) Yandulov, D. V.; Schrock, R. R. *Inorg. Chem.* **2005**, *44*, 1103.
b) Yandulov, D. V.; Schrock, R. R. *Science* **2003**, *301*, 76.
c) Morello, L.; Ferreira, M. J.; Patrick, B. O.; Fryzuk, M. D. *Inorg. Chem.* **2008**, *47*, 1319.
- (9) a) Korobkov, I.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem.* **2003**, *115*, 838, *Angew. Chem. Int. Ed.* **2003**, *42*, 814.
b) Korobkov, I.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem.* **2003**, *115*, 5108; *Angew. Chem. Int. Ed.* **2003**, *42*, 4958.
- (10) a) Kozak, C. M.; Mountford, P. *Ang. Chem. Int. Ed.* **2004**, *43*, 1186.
b) Fryzuk, M. D.; Love, J. B.; Rettig, S. J.; Young, V. G. *Science* **1997**, *275*, 1445.
c) Basch, H.; Musaev, D. G.; Morokuma, K.; Fryzuk, M. D.; Love, J. B.; Seidel, W. W.; Albinati, A.; Koetzle, T. F.; Klooster, W. T.; Mason, S. A.; Eckert, J. *J. Am. Chem. Soc.* **1999**, *121*, 523.
d) Fryzuk, M. D.; Johnson, A. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1998**, *120*, 11024.
e) Fryzuk, M. D.; Johnson, S. A.; Patrick, B. O.; Albinati, A.; Mason, S. A.; Koetzle, T. F. *J. Am. Chem. Soc.* **2001**, *123*, 3960.
- (11) a) Curley, J. J.; Cook, T. R.; Reece, S. Y.; Miller, P.; Cummins, C. C.; *J. Am. Chem. Soc.* **2008**, *130*, 9394.
b) Vidyaratne, I.; Scott, J.; Gambarotta, S.; Budzelaar, P. H. M.; *Inorg. Chem.* **2007**, *46*, 7040.
c) Figueroa, J. S.; Cummins, C. C.; *Dalton Trans.* **2006**, 2161.
d) Studt, F.; Lamarche, V. M. E.; Clentsmith, G. K. B.; Cloke, F. G. N.; Tucek, F. *Dalton Trans.* **2005**, 1052.
e) Fryzuk, M. D.; Kozak, C. M.; Bowdridge, M. R.; Patrick, B. O.; Rettig, S. J. *J. Am.*

Chem. Soc. **2002**, *124*, 8389.

f) Korobkov, I.; Gambarotta, S.; Yap, G. P. A.; *Angew. Chem.* **2002**, *114*, ; *Angew. Chem. Int. Ed.* **2002**, *41*, 3433.

g) Solari, E.; Da Silva, C.; Iacono, B.; Hesschenbrouck, J.; Rizzoli, C.; Scopelliti, R.; Floriani, C. *Angew. Chem.* **2001**, *113*, 4025 ; *Angew. Chem. Int. Ed.* **2001**, *40*, 3907.

h) Caselli, A.; Solari, E.; Scopelliti, R.; Floriani, C.; Re, N.; Rizzoli, C.; Chiesi-Villa, A. *J. Am. Chem. Soc.* **2000**, *122*, 3652.

i) Laplaza, C. E.; Cummins, C. C. *Science* **1995**, *268*, 861.

(12) a) Avenier, P.; Taoufik, M.; Lesage, A.; Solans-Monfort, X.; Baudouin, A.; Mallmann, A. de.; Veyre, L.; Basset, J. M.; Eisenstein, O.; Emsley, L.; Quadrelli, E. *A. Science* **2007**, *317*, 1056.

b) Li, J.; Li, S.; *Angew. Chem.* **2008**, *120*, 8160; *Angew. Chem. Int. Ed.* **2008**, *47*, 8040.

c) Smith, J. M.; Lachicotte, R. J.; Holland, P. L. *J. Am. Chem. Soc.* **2003**, *125*, 15752.

d) Fryzuk, M. D.; Johnson, S. A.; Patrick, B. O.; Albinati, A.; Mason, S. A.; Koetzle, T. F. *J. Am. Chem. Soc.* **2001**, *123*, 3960.

e) Akagi, F.; Matsuo, T.; Kawaguchi, H. *Angew. Chem.* **2007**, *119*, 8934; *Angew. Chem. Int. Ed.* **2007**, *46*, 8778.

f) Wolf, J. M. de; Blaauw, R.; Meetsma, A.; Teuben, J. H.; Gyepes, R.; Varga, V.; Mach, K.; Veldman, N.; Spek, A. L. *Organometallics* **1996**, *15*, 4977.

g) Chirik, P. J.; Henling, L. M.; Bercaw, J. E. *Organometallics* **2001**, *20*, 534.

(13) a) Parry, J. S.; Cloke, G. F. N.; Cole, S. J.; Hursthouse, M. B. *J. Am. Chem. Soc.* **1999**, *121*, 6867.

b) Kanellakopulos, B.; Dornberger, E.; Baumgaertner, F. *Inorg. Nucl. Chem. Lett.*

- 1974, 10, 155.
- c) Blake, P. C.; Lappert, M. F.; Atwood, J. L.; Zhang, H. *J. Chem. Soc. Chem. Commun.* **1986**, 15, 1148.
- d) Spirlet, M. R.; Rebizant, J.; Goffart, J. *Acta Crystallogr. Sect. B* **1982**, 38, 2400.
- (14a) Roussel, P.; Scott, P. *J. Am. Chem. Soc.* **1998**, 120, 1070.
- b) Mindiola, D. J.; Tsai, Y. C.; Hara, R.; Chen, Q.; Meyer, K.; Cummins, C. C. *Chem. Commun.* **2001**, 125.
- c) Cloke, F. G. N.; Hitchcock, P. B. *J. Am. Chem. Soc.* **2002**, 124, 9352.
- d) Evans, W. J.; Kozimor, S. A.; Ziller, J. W. *J. Am. Chem. Soc.* **2003**, 125, 14264.
- e) Korobkov, I.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem.* **2002**, 114, 3583; *Angew. Chem. Int. Ed.* **2002**, 41, 3433.
- f) Castro-Rodriguez, I.; Nakai, H.; Gantzel, P.; Zakharov, L. N.; Rheingold, A. L.; Meyer, K. *J. Am. Chem. Soc.* **2003**, 125, 15734.
- g) Summerscales, O. T.; Cloke, G. F. N.; Hitchcock, P. B.; Green, J. C.; Hazari, N. *Science* **2006**, 311, 829.
- h) Castro-Rodriguez, I.; Nakai, H.; Zakharov, L. N.; Rheingold, A. L.; Meyer, K. *Science* **2004**, 305, 1757.
- i) Diaconescu, P. L.; Arnold, P. L.; Baker, T. A.; Mindiola, D. J.; Cummins, C. C. *J. Am. Chem. Soc.* **2000**, 122, 6108.
- j) Evans, W. J.; Kozimor, S. A.; Ziller, J. W.; Kaltsoyannis, N. *J. Am. Chem. Soc.* **2004**, 126, 14533.
- (15) Vidyaratne, I.; Scott, J.; Gambarotta, S.; Budzelaar, P.; *Inorg. Chem.* **2008**, 47, 896.
- (16) Grills, D. C.; Huang, K. W.; Muckerman, J. T.; Fujita, E. *Coord. Chem. Rev.* **2006**, 250, 1681.

- (17) Saito, C. S.; Weinberger, D. A.; Mirkin, C. A. *Prog. Inorg. Chem.* **1999**, *48*, 233.
- (18) Nikiforov, G. B.; Crewdson, P.; Gambarotta, S.; Korobkov, I.; Budzelaar, P. H. M. *Organometallics* **2007**, *26*, 48.
- (19) (a) Ganesan, M.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 766.
- (20) Edema, J. J. H.; Gambarotta, S.; Meetsma, A.; Spek, A. L.; Veldman, N. *Inorg. Chem.* **1991**, *30*, 2062.
- (21) Jabri, A.; Korobkov, I.; Gambarotta, S.; Duchateau R. *Angew. Chem.* **2007**, *119*, 6231; *Angew. Chem. Int. Ed.* **2007**, *46*, 6119.
- (22)a) Edema, J. J. H.; Meetsma, A.; Gambarotta, S. *J. Am. Chem. Soc.* **1989**, *111*, 6878.
- b) Plass, W.; Verkade, J. G. *J. Am. Chem. Soc.* **1992**, *114*, 2275.
- c) Rehder, D.; Woitha, C.; Pribsch, W.; Gailus, H. *J. Chem. Soc., Chem. Commun.* **1992**, 364.
- d) Ferguson, R.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 396.
- e) Buijink, J. K. F.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 2004.
- f) Berno, P.; Hao, S.; Minhas, R.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 7417.
- g) Song, J. I.; Berno, P.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 6927.
- h) Desmangles, N.; Jenkins, H.; Rupp, K. B.; Gambarotta, S. *Inorg. Chim. Acta* **1996**, *250*, 1.
- i) Ferguson, R.; Solari, E.; Floriani, C.; Osella, D.; Ravera, M.; Re, N.; Chiesi Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1997**, *119*, 10104.
- j) Clentsmith, G. K. B.; Bates, V. M. E.; Hitchcock, P. B.; Cloke, F. G. N. *J. Am. Chem. Soc.* **1999**, *121*, 10444.

- k) Shaver, M. P.; Thomson, R. K.; Patrick, B. O.; Fryzuk, M. D. *Can. J. Chem.* **2003**, *81*, 1431.
- l) Vidyaratne, I.; Gambarotta, S.; Korobkov, I.; Budzelaar, P. H. M. *Inorg. Chem.* **2005**, *44*, 1187.
- m) Smythe, N. C.; Schrock, R. R.; Muller, P.; Weare, W. W. *Inorg. Chem.* **2006**, *45*, 9197.
- (23)a) Jubb, J.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 4477.
- b) Dube, T.; Conoci, S.; Gambarotta, S.; Yap, G. P. A.; Vasapollo, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 3657.
- c) Guan, J.; Dube, T.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2000**, *19*, 4820.
- d) Dube, T.; Ganesan, M.; Conoci, S.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2000**, *19*, 3716.
- e) Korobkov, I.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 3433.
- (24)a) Denisov, N. T.; Efimov, O. N.; Shuvalova, N. I.; Shilova, A. K.; Shilov, A. E. *Zh. Fiz. Khim.* **1970**, *44*, 2694; C.A. 1971, 74, 35950.
- b) Shilov, A. E.; Denisov, D. N.; Efimov, O. M.; Shuvalov, N. F.; Shuvalova, N. I.; Shilova, A. E. *Nature (London)* **1971**, *231*, 460.
- c) Zones, S. I.; Vickery, T. M.; Palmer, J. G.; Schrauzer, G. N. *J. Am. Chem. Soc.* **1976**, *98*, 1289.
- d) Zones, S. I.; Palmer, M. R.; Palmer, J. G.; Doemeny, J. G.; Schrauzer, G. N. *J. Am. Chem. Soc.* **1978**, *100*, 2113.
- e) Luneva, N. P.; Nikonova, L. A.; Shilov, A. E. *Kinet. Katal.* **1980**, *21*, 1041.

- f) Schrauzer, G. N.; Palmer, M. R. *J. Am. Chem. Soc.* **1981**, *103*, 2659.
- g) Schrauzer, G. N.; Strampach, N.; Hughes, L. A. *Inorg. Chem.* **1982**, *21*, 2184.
- (25)a) Bishop, P. E.; Jarlenski, D. M. L.; Hetherington, D. R. *J. Bacteriol.* **1982**, *150*, 1244.
- b) Robson, R. L.; Eady, R. R.; Richardson, T. H.; Miller, R. W.; Hawkins, M.; Postgate, J. R. *Nature (London)* **1986**, *332*, 388.
- c) Hales, B. J.; Case, E. E.; Morningstar, J. E.; Dzeda, M. F.; Mauterer, L. A. *Biochemistry* **1986**, *25*, 7251.
- d) Arber, J. M.; Dobson, B. R.; Eady, R. R.; Stevens, P.; Hasnain, S. S.; Garner, C. D.; Smith, B. E. *Nature (London)* **1986**, *325*, 372.
- e) Eady, R. R. *Chem. Rev.* **1996**, *96*, 3013.
- f) Rehder, D. *Coord. Chem. Rev.* **1999**, *182*, 297.
- g) Smith, B. E. *Adv. Inorg. Chem.* **1999**, *47*, 159.
- h) Eady, R. R. *Coord. Chem. Rev.* **2003**, *237*, 23.
- i) Janas, Z.; Sobota, P. *Coord. Chem. Rev.* **2005**, *249*, 2144.
- (26)a) Berno, P.; Gambarotta, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 822.
- b) Abernethy, C. D.; Bottomley, F.; Decken, A.; Cameron, T. S. *Organometallics* **1996**, *15*, 1758.
- c) Bates, V. M. E.; Clentsmith, G. K. B.; Cloke, F. G. N.; Green, J. C.; Jenkin, H. D. *Chem. Commun.* **2000**, 927.
- d) Studt, F.; Lamarche, V. M. E.; Clentsmith, G. K. B.; Cloke, F. G. N.; Tuczek, F. *Dalton Trans.* **2005**, 1052.
- (27) Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 138.
- (28) Emsleay, J. W.; Feeney, J.; Sutcliffe, L. H. *High resolution NMR Spectroscopy*;

Pergamon Press: Elmsford, NY, 1966; Vol. 2, p 1034.

(29) Compound 6.8 may also be obtained from 6.7 using a similar experimental procedure.

(30) Blessing, R. *Acta Crystallogr.* **1995**, *A51*, 33.

(31) Sheldrick, G. M. Bruker AXS, Madison, WI, 2001.

(32) a) Taniguchi, S.; Hasegawa, H.; Nishimura, M.; Takahashi, M. *Synlett* **1999**, *1*, 73.

b) Ka, J.-W.; Lee, C.-H. *Tet. Lett.* **2000**, *41*, 4609.

(33) Chadwick, D. J.; Willbe, C. *J. Chem. Soc., Perkin Trans. I* **1977**, *8*, 887.

(34) Cell parameters of $[\text{Na}(\text{dme})_3]_2[\{\text{LNa}\}_2]$: Monoclinic, P21/c, $a = 13.185(3)$ Å, $b = 26.470(5)$ Å, $c = 15.240(2)$ Å, $\beta = 116.074(14)^\circ$, $V = 4777.5(15)$ Å³, G. B. Nikiforov, S. Gambarotta, unpublished results.

(35) a) Stewart, P. J.; Blake, A. J.; Mountford, P. *J. Organomet. Chem.* **1998**, *564*, 209.

b) Wagner, O.; Jansen, M.; Baldus, H. P.; *Anorg. Z.; Allg. Chem.* **1994**, *620*, 366.

c) Smolensky, E.; Kapon, M.; Woollins, J. D.; Eisen, M. S.; *Organometallics* **2005**, *24*, 3255.

d) Iamos, C. Y.; Heeg, M. J.; Winter, C. H.; *Organometallics* **1999**, *18*, 1168.

e) Coles, M. P.; Hitchcock, P. B. *Organometallics* **2003**, *22*, 5201.

f) Cheng, F.; Kelly, S. M.; Clark, S.; Young, N. A.; Archibald, S. J.; Bradley, J. S.; *Chem. Mater.* **2005**, *17*, 5594.

g) Stewart, P. J.; Blake, A. J.; Mountford, P. *Inorg. Chem.* **1997**, *36*, 3616.

(36) Gross, M. E.; Siegrist, T. *Inorg. Chem.* **1992**, *31*, 4898.

(37) Bai, G.; Roesky, H. W.; Noltemeyer, M.; Hao, H.; Schmidt, H. G. *Organometallics* **2000**, *19*, 2823.

(38) Lorber, C.; Choukroun, R.; Vendier, L.; *Eur. J. Inorg. Chem.* **2006**, 4503.

- (39) a) Nielson, A. J.; Glenny, M.W.; Rickard, C. E. F.; Dalton Trans. **2001**, 232.
- b) A. J. Blake, P. E. Collier, L. H. Gade, P. Mountford, J. Lloyd, S. M. Pugh, M. Schubart, M. E. G. Skinner, D. J. M. Tr_sch, Inorg. Chem. 2001, 40, 870.
- c) N. Adams, H. R. Bigmore, T. L. Blundell, C. L. Boyd, S. R. Dubberley, A. J. Sealey, A. R. Cowley, M. E. G. Skinner, P. Mountford, Inorg. Chem. 2005, 44, 2882.
- d) S. C. Dunn, N. Hazari, A. R. Cowley, J. C. Green, P. Mountford, Organometallics 2006, 25, 1755.
- e) A. J. Blake, P. E. Collier, S. C. Dunn, W.-S. Li, P. Mountford, O. V. Shishkin, Dalton Trans. 1997, 1549.
- f) S. C. Dunn, P. Mountford, D. A. Robson, Dalton Trans. 1997, 293.
- (40) Arunachalampillai, A.; Crewdson, P.; Korobkov, I.; Gambarotta, S.; *Organometallics* **2006**, 25, 3856,
- (41) Vol_pin, M. E.; Shur, V. B. *Nature* **1966**, 209, 1236.