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The Search for Low-Valent Transition Metal Complexes for Oligomerization and Polymerization of Ethylene

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The Search for Low-Valent Transition Metal Complexes for Oligomerization and Polymerization of Ethylene

A Thesis Submitted to the

School of Graduate Studies and Research

In Partial Fulfillment of the Requirements

For the Degree of

Master of Science

In the Ottawa-Carleton Chemistry Institute

Department of Chemistry

University of Ottawa

Ottawa, Ontario

Candidate

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Your file Votre référence
ISBN: 978-0-494-65537-5
Our file Notre référence
ISBN: 978-0-494-65537-5

Abstract:

Combination of the potassium salt of the triazenide anion (R)NNN(R)$^-$ with $CrCl_2(THF)_2$ leads to the formation of dimeric complexes {Cr[μ,η,η'-bis-1,3-(2',5'-diisopropylphenyl)triazenide]$_2$}$_2$ **(2.1)**, [Cr(μ,η,η'-1,3-diphenyltriazenide)$_2$]$_2$ **(2.2)**, {Cr[μ,η,η'-bis-1,3-(2'-methoxyphenyl)triazenide]$_2$}$_2$ **(2.3)** which are paddlewheel type structures featuring bridging triazenide anions. These complexes led to very low activity for the polymerization and oligomerization of ethylene upon activation with known activators MAO, TIBAO.

Combination of the potassium salt of the triazenide anion with $CrCl_3(THF)_3$ leads to the formation of mononuclear complexes [bis-1,3-(2',5'-diisopropylphenyl)triazenide]Cr(THF)$_2$Cl$_2$ **(2.5)** and [bis-1,3-(2'-methoxyphenyl)triazenide]Cr(THF)$_2$Cl$_2$ **(2.6)**. These complexes showed high activity for the non-selective oligomerization of ethylene, fitting a Schulz-Flory distribution. Reduction of these complexes lead to the dinuclear Cr^{II} species {[bis-1,3-(2',5'-diisopropylphenyl)triazenide]Cr(THF)(μCl)}$_2$ **(2.7)**, but did not lead to the target Cr^{I} complexes as ligand salts were isolated upon further reduction.

One pot reaction of $ZrCl_4$ with 2 equivalents of mono-pyrrole based ligands and 4 equivalents of AlR_3 leads to the formation of zirconocene type structures (η^5[2,5-$Me_2C_4H_2N${$AlCl_2Et$}])$_2$$ZrCl_2$ **(3.1)**, (η^5[2,5-$Me_2C_4H_2N${$AlClMe_2$}])$_2$ZrClMe **(3.2)**, (η^5[2,5-$Me_2C_4H_2N${$AlClMe_2$}])$_2$$ZrCl_2$ **(3.3)**, (η^5[C_4H_4N{$AlClMe_2$}])$_2$$ZrMe_2$ **(3.4)**. These Zr^{IV} complexes produced lower than expected activity for polymerization of ethylene when activated by MAO, as compared to their Cp analogues.

When dipyrrole ligands were combined with $ZrCl_4$ and 4 equivalents of AlR_3 in one pot, formation of Zr^{III} compounds were observed. Octameric $([\{Ph_2C(C_4H_3N)_2\}Zr_2]_4(\mu\text{-}Cl)_{16})$ $[\mu\text{-}Cl]_2AlCl_2)_4$ **(3.5)** provides a Zr^{III} complex unlike any other observed in literature. Reduction was performed from $Al(Me)_3$ in this case, however coordination of Al in the structure is unlike the previous **3.1,3.2,3.3,3.4.**

The formation of $([AlEtCl\{\mu\text{-}Cl\}_2][\{C_4H_4N\}_2AlClEt]Zr_2(\mu\text{-}Cl)_4)_2 \cdot 4\ (C_7H_8)$ **(3.7)** has many interesting features. The Zr-Zr distance of 3.045(2)Å is the shortest yet observed for Zr. Additionally, the dipyrrole starting material was cleaved during the reaction to basic pyrrole, which suggests insight into the mechanism of formation of **3.5** and suggests the possibility of *in situ* Zr^{II} formation.

This work is dedicated to the life of my good friend Philip LeBlanc. The knowledge that you were watching over me was the driving force that kept me going throughout my time at Ottawa U. I've learned more from you than I could ever learn in any classroom and those lessons will never be forgotten.

"Do not stand at my grave and weep;
I am not there. I do not sleep.
I am a thousand winds that blow.
I am the diamond glints on snow.
I am the sunlight on ripened grain.
I am the gentle autumn rain.
When you awaken in the morning's hush
I am the swift uplifting rush
Of quiet birds in circled flight.
I am the soft stars that shine at night.
Do not stand at my grave and cry;
I am not there. I did not die."

Keep a few cold ones on ice for me, for when we meet again one day.

Acknowledgements

First and foremost, I would like to thank my research supervisor, Dr. Sandro Gambarotta, a talented chemist who finds a way to stay enthusiastic day in and day out. He has provided me with more opportunities and ideas in the last 2 years than imagineable. His life experiences which he has shared with the lab on occasion are truly valuable lessons.

I would like to acknowledge the different professors who have contributed to my experience at Ottawa U. Dr. Rob Duchateau from TU/e (Eindhoven) for his hospitality in the Netherlands and for the incredible tidbits of knowledge he passed my way. Dr. Darrin Richeson and Dr. Muralee Murugesu whose classes were some of the best, and who acted as amazing role models and advisors throughout my time here.

Inorganic synthesis requires technical help from many different areas. I would like to thank the following U of O staff for their help: Dr. Glenn Facey, Cheryl Macdowall, Dr. Tara J. Burchell, Dr. C. W. Kazakoff, Andrew Zlotorzynski, the science store staff any others who have helped contribute to this work.

The many labmates I have had throughout my time here have made things interesting on a day to day basis. Most notable are Indu Vidyaratne who helped from day one when I was a lost soul in the lab, and remained a close friend throughout. I most surely would not have completed my degree should Steve Horvath have not been there to undergo every experience with me, which included a few interesting ones. Dr. Ilia Korobkov provided me with infinite amounts of help on a day to day basis and was a pleasure to share the glovebox (and a few beers) with. Dr. Grigory Nikiforov passed on a wealth of experience to me and made the office extremely exciting. Vladimir Shuster kept me laughing every day and was a pleasure to share an office(desk) with. The undergrad students I worked with, Mike Juba and Yan Sim who are both up and coming scientists must be thanked. And all other labmates, and coworkers, and friends at the university that I have worked with, I would like to thank you for your contributions to my experience.

I would like to thank my highschool friends from Barrhaven who kept me sane and up to date with 'non-chemistry' related news. Your encouragement and friendship helped me see true values in life.

And finally, I would like to thank my family, my Mom and Dad, my sisters Jenn and Julie and brother in law Barry. Your never-ending support and continued faith in me kept me moving forward on my degree. You are all role models that truly illustrate the definition of happiness and success in life.

List of Publications

1 Jabri, A,; Mason, C.B.; Sim, Y.; Gambarotta, S.; Burchell, T.J.; Duchateau, R.; Isolation of Single-Component Trimerization and Polymerization Chromium Catalysts: The Role of the Metal Oxidation State. *Angew. Chem. Int. Ed. Engl.* **2008**, 47, 9717.

List of Abbreviations

Å	Angström
Anal	Analysis
Br	Broad
°C	degrees Celsius
Calcd	Calculated
cm^{-1}	Wave number
Cp	Cyclopentadienyl
Cy	Cyclohexyl
Et	Ethyl
F(000)	Electronic density
FTIR	Fourier transform infrared spectroscopy
g	Grams
G.O.F.	Goodness of fit
h	Hour
K	Kelvin
L	Ligand
LAO	Linear Alpha olefin
MAO	Methylaluminoxane
Me	methyl
MHz	Megahertz
mL	millilitre
mmol	millimole

mol	mole
Mw	molecular weight
NMR	nuclear magnetic resonance
ORTEP	Oak Ridge thermal ellipsoid program
PDI	polydispersity index
Ph	Phenyl
R	Alkyl group
s	Second
T	temperature
THF	tetrahydrofuran
THF-d^8	deuterated tetrahydrofuran
TIBAO	Tetraisobutyldialuminoxane
μ_{eff}	effective magnetic moment in Bohr magnetons
V	volume

Table of Contents

Chapter I

Introduction of Ethylene Polymerization

And Oligomerization

Ziegler-Natta Polymerization

The discovery and subsequent development of alkene polymerization catalysts in the 2nd half of the twentieth century has marked a milestone in our modern lifestyle. The industrial scale synthesis of polyethylene and polypropylene has generated immense possibilities for business in packaging materials, fabrics, materials for construction, medical supplies, etc. and modified our way of living. As a matter of fact, synthetic polyolefins are today ubiquitous. These polymers are commonly prepared with organometallic catalysts, either in solution (homogeneous catalysis) or in heterogeneous phase via preliminary catalyst support on a solid surface.[1] The first observation was due to K. Ziegler who discovered that the combination of $TiCl_4$ and $Al(C_2H_5)_3$ in the presence of $MgCl_2$ could polymerize ethylene.[2a,b] Subsequently, G. Natta successfully used the same system for the stereospecific polymerization of propylene.[3] A Ziegler-Natta catalyst may broadly be defined as a material which consists of a Group 3-8 transition metal together with a Group 1, 2 or 13 organometallic, the combination of which is capable of polymerizing and copolymerizing olefins and dienes under relatively mild conditions of temperature and pressure.[4a,b] In a recent survey of catalyst technology in the USA during the 1980's, polymerisation catalysis was listed as one of four major areas in which innovation has been successfully commercialized.[5a-c] Although the catalysts used in industry are mainly heterogeneous, well defined homogeneous Ziegler-Natta catalysts have been developed in the nearly six decades since the original discovery of these types of catalysts. Today, zirconium catalysts are used wordwide to produce up to 100tons of polyethylene per gram of zirconium.[6] Figures for worldwide production of polyolefins, shown in table 1.1, truly illustrate the impact of this field. Together for their

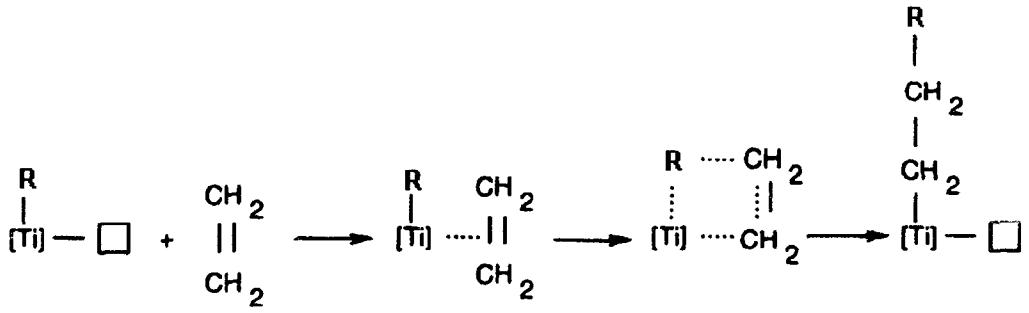
work on olefin polymerization Ziegler and Natta were awarded the Nobel Prize for Chemistry in 1963.

Table 1.1: Worldwide production of polyolefins.[6]

Year	Polyethylene LDPE ($x10^6$ tons)	Polyethylene HDPE/LLDPE ($x10^6$ tons)	Polypropylene (PP) ($x10^6$ tons)	Fraction of plastics production (%)
1983	11.3	7.9	6.4	-
1990	14.0	16.1	12.6	43
1995	14.4	22.1	17.1	47
2005	15.8	36.1	27.7	55

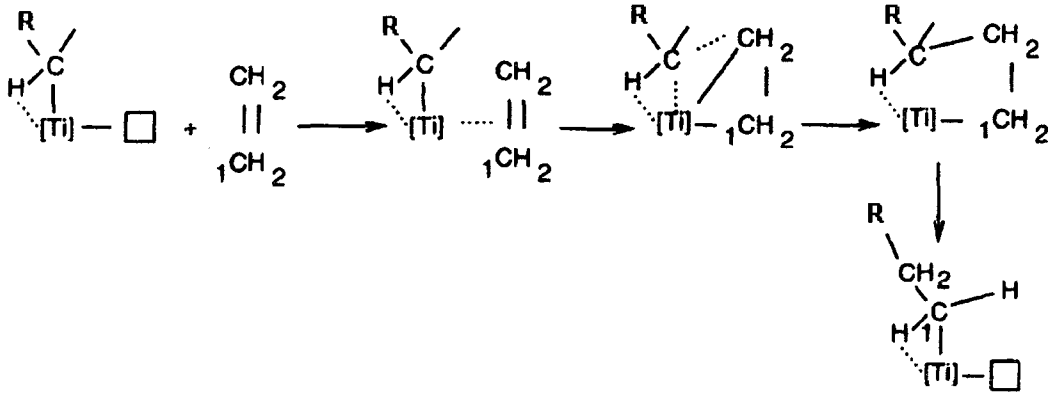
*LDPE = low density polyethylene, HDPE = high density polyethylene, LLDPE = linear low density polyethylene.

The mechanism of Ziegler-Natta polymerization is also known as the Cossee-Arlman mechanism from the name of the discoverers.[7a,b] (scheme 1.1) The mechanism is initiated by alkylation of the metal center by the group 13 activator. This is followed by ligand(halide) extraction by the activator, leaving a cationic metal center and an anionic group 13 species. Ethylene molecules can coordinate to the vacant site on the metal center and undergo a migratory insertion into the previously formed M-C bond.



Scheme 1.1: Chain growth via Cossee-Arlman mechanism.[8]

Several studies supported the idea that that the olefin insertions are assisted by an α-agostic interaction of one of the H atoms of the migrating alkyl chain with the active metal center.[9a-e] This slightly adapts the scheme for the Cossee-Arlman mechanism as it can be seen in scheme 1.2.



Scheme 1.2: α-agostic interaction facilitating ethylene insertion.[8]

The ligand attached to the metal center plays an important role with respect to catalyst polymerization activity, as well as affecting the polymer molecular weight, its polydispersity, tacticity and extent of branching. The ligand basically controls the catalytic center coordination number and geometry, it may determine the formal

oxidation state of the metal center and provides a tunable steric environment around the active site.[10]

Bis cyclopentadienyl anions (Cp) derivatives, also commonly known as metallocene catalysts[6,8,11] and mono Cp (constrained geometry) catalysts are the most commonly encountered and successfully employed catalytic systems in olefin polymerization.[12a,b] However, the variety of ligands goes well beyond the domain of the Cp systems as successful olefin polymerization catalysts have been prepared with several neutral and monoanionic tridentate and bidentate ligands based on N,O,P,S,C and combinations thereof,[13a-e] as well as alkyl and allyl type ligands.[14a-c]

Simple modifications in the ligand can cause dramatic effects on the quality of the polymer produced. Polyolefins with different microstructures and characteristics can be custom made just by varying the ligand substituents on the metallocene.[15a,b] This effect was first observed when chiral, bridged metallocenes were found able to control the stereoregularity of the polymer by forming isotactic polypropylene.[16a,b] Development of this concept led to further discoveries: by combining different olefins and cycloolefins these characteristics can be further broadened. Modified metallocene catalysts were able to produce polyethylene, polypropylene, and copolymers with narrow molecular weight distribution,[17] syndiotactic polypropylene[18] and syndiotactic polystyrene,[19] which were previously impossible to produce.

The greatest improvement made in the field of olefin polymerization was the discovery of the now well known activator, methylaluminoxane (MAO).[20a,b] A stoichiometric addition of water to $Al(CH_3)_3$ produced MAO, the structure of which is still debated but reasoned to be $[Al_4O_3(CH_3)_6]$.[21,a,b] The discovery of MAO to replace

basic aluminum alkyl activators led to enhanced catalyst activity by a factor of four orders of magnitude.

While the generic zirconocene, Cp_2ZrCl_2 has been shown to produce polyethylene at an activity of 3,648,800,000 g PE mol_{Zr}^{-1} h^{-1} upon activation by MAO,[22a-c] other metallocene derivatives had lower activities. The catalyst activity observed when chlorines were replaced by methyl groups and the catalyst activated by MAO[23] was only 2,262,300,000 g PE mol_{Zr}^{-1} h^{-1}. Non-metallocene catalysts of group 4 metals such as contrained geometry catalysts,[12a,b,24] diamide systems,[25] and phosphorus subsitituted Cp, have also displayed very high catalytic activity.[26]

Selective Oligomerization of Olefins

Studies investigating polymer rheology, with respect to polymer density, molecular weight and polydispersity, have found that addition of a short chained linear alpha olefin (LAO) to the polymerization mixture can provide the polymer with highly desirable properties. Therefore, light linear α-olefins (LAO) such as1-butene, 1-hexene, and 1-octene, rapidly became crucial additives in commercial polymerization. The availability of these additives cannot satisfy the market demand, hence the need for developing catalytic systems for their formation from ethylene. Longer LAO have found industrial applications as detergents and lubricants and many other uses are in place for different ranges of molecular weights. Particularly successful is the SHOP process developed by the SHELL laboratories and which is capable of producing, with high turnover frequencies, a polymer-free, statistical distribution of LAO easily fractioned by

distillation. Still, 1-hexene and 1-octene remain the most highly sought after of the LAO since the current production cannot satisfy the demand.

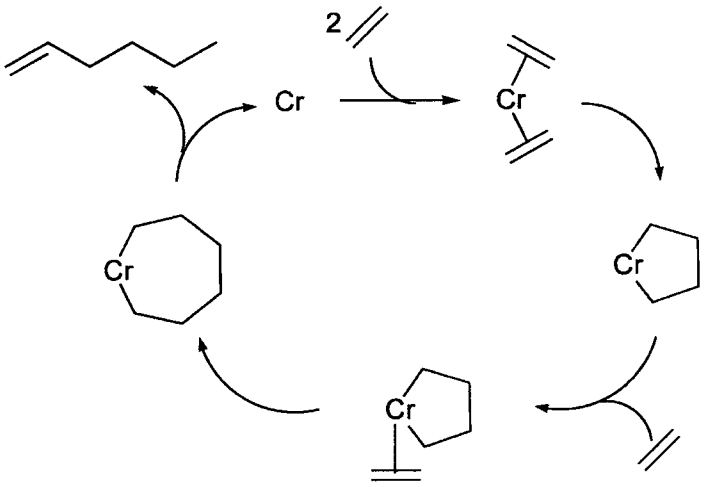
This background explains the steady resurgence of interest during the last decade for finding selective ethylene tri- and tetramerization catalysts. While the number of academic publications on the topic surged steadily through the late 1990's and early 2000's,[27] there are only very few industrial methods used to produce these valuable comonomers: 1-Butene is made by ethylene dimerization in the Middle East by using nickel based catalysts,[27] 1-hexene is made by ethylene trimerization by Chevron Phillips with their plant in Qatar,[28a,b] and 1-hexene and 1-octene are extracted from the Synthol streams at the Sasol facilities in South Africa.[27]

In both patent and academic literature of ethylene oligomerization, chromium catalysts account for more than 90% of the systems discovered. Although selective trimerization has been observed with other transition metals,[29a-c] the activity and product purity exhibited by chromium catalysts is so far unbeatable. On the other hand, chromium provides an ideal substrate to study the factors which drive the C-C bond reaction towards either polymerization or oligomerization since this element has provided commercial catalysts for both processes. The general discussion of ethylene oligomerization is therefore centered around Cr catalysts. One of the characteristics of chromium is the possibility of existing in a variety of oxidation states. Identification of the oxidation state responsible for the particular type of catalytic performance (oligo- versus polymerization) is the center of a vigorous literature debate.

It was 40 years ago that ethylene trimerization was first discovered. Walker and Wilson of the Union Carbide Corporation observed that during ethylene polymerization using Cr^{III} 2-ethylhexanoate under activation of partially hydrolysed tri-isobutylaluminum, a polymer having butyl side chains was formed. In their patent filed on continuous processes for production of polyethylene,[30] the authors claimed that the butyl side chains are a result of some of the ethylene being trimerized to 1-hexene which is then co-polymerized to form the branched PE. This discovery has lead to remarkable improvements in the field, as homogeneous catalysts have since been developed giving remarkably high catalyst activity with high (>90%) selectivity for 1-hexene. For example, the Philips catalytic system, and which is now industrially used for commercial production, is based on the combination of Cr^{III}ethylhexanoate, 2,5-dimethylpyrrole, diethylaluminum chloride and triethylaluminum in toluene.[28] This catalyst system was able to produce activity as high as 156,666 g_{Cr}^{-1} h^{-1} with an overall 93% 1-hexene selectivity. Although the starting material contains chromium in its trivalent state, the oxidation state of the catalytically active species remained unknown until recent work published from our lab.[31] A catalyst system comprising $Ar_2PN(Me)PAr_2$ (Ar =2-methoxyphenyl) and $[CrCl_3(THF)_3]$, activated with methyl aluminoxane (MAO) yielded a highly selective catalyst (89.9 wt% 1-hexene overall) with unprecedented productivity, over 1 million g_{hexene} g_{Cr}^{-1} h^{-1}.[32] Mitsubishi Chemical Corporation further improved the original Philips system. By employing the in situ protocol (using chromium(III) 2-ethylhexanoate, 2,5-dimethylpyrrole, hexachloroethane and triethylaluminium,[33] and by controlling the ratio of 1-hexene/ethylene in the reaction (<0.5:1 mol ratio)

unprecedented catalyst activities were obtained (3,780,000 g/g_{Cr}^{-1} h^{-1} with an overall 95.4% selectivity for 1-hexene).

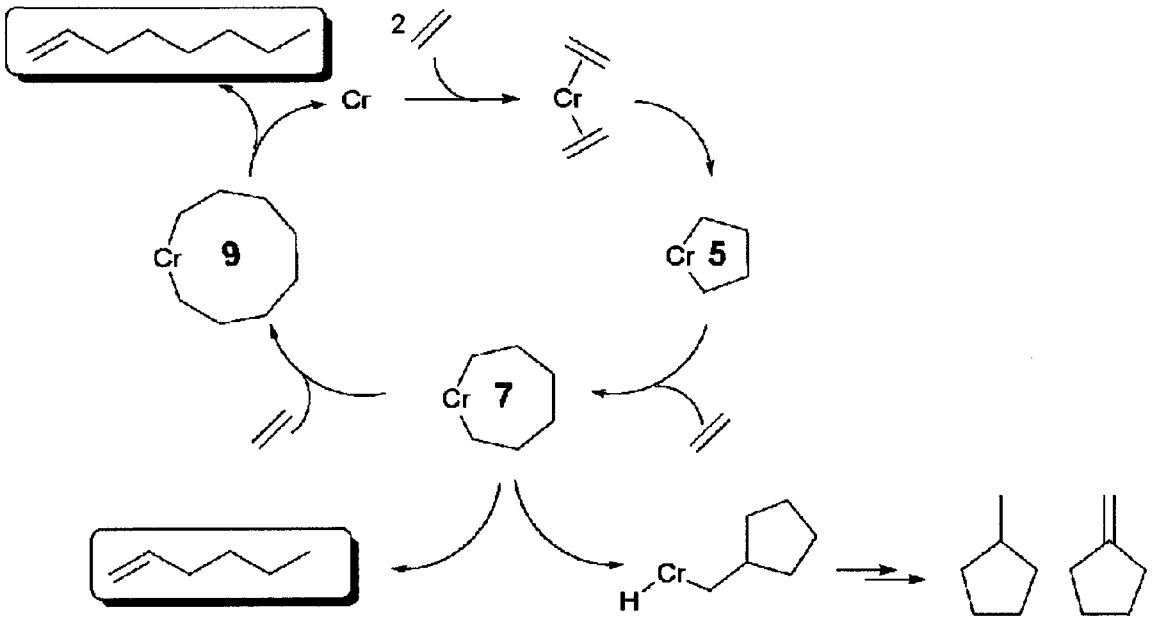
While it is commonly accepted that polymerization of ethylene proceeds via the aforementioned chain-growth mechanism, it is also believed that selective oligomerization proceeds via a metallocycle mechanism. The ring expansion metallocycle mechanism was originally proposed by Manyik and coworkers,[34] but was refined to the currently accepted mechanism by Briggs in 1989.[35] Contrary to polymerization where the metal center remains in the same oxidation state throughout, the metal center in the metallocycle mechanism undergoes a two-electron oxidation when forming the metallocycle and regeneration of the original oxidation state during the final α-olefin reductive elimination process. (Scheme 1.3)



Scheme 1.3: Metallocycle mechanism of selective ethylene trimerization.[36]

A similar mechanism involving further ring expansion was conceived to rationalize the selective formation of 1-octene (Scheme 1.4) This important observation is unique in the

academic and patent literature and was devised by SASOL company in South Africa with the proprietary PNP system. Workers observed that, in this particular system, formation of 1-octene is always accompanied by a non-negligable amount of 1-hexene, with the SASOL patent giving the highest percentage of C_8/C_6 of slightly over 70%.[37]



Scheme 1.4: Mechanism of formation of 1-octene.[36]

Formation of polymeric materials in the catalytic systems for oligomerization are highly undesirable because of serious reactor fouling issues. As mentioned, there are several oligomerization catalysts producing statistical distribution of α-olefins, the so called Shultz-Flory distribution of oligomers.[38a-c] Catalytic systems capable of selectively producing 1-hexene (>99% purity) are instead very rare while catalysts producing 1-octene are limited to the only case of the aforementioned SASOL patent.[37] The current research for new catalysts appears to follow a sort of combinatorial type of

approach where the most diversified ligand systems are combined with $CrCl_3$ and activated with MAO. This is necessarily due to the lack of knowledge about the metal oxidation state which powers the catalytic cycle.

The concept of a Shultz-Flory or statistical distribution of oligomers is now fairly well understood. Unselective oligomerization may well be regarded as a polymerization truncated at the very early stages of the chain growth due to a combination of factors (poor M-C bond stability, rapid chain transfer to Al, β-H elimination processes, etc.).

A method of quantifying the statistical distribution lies on the α-value, defined as the relative probability of termination versus chain propagation. This value is calculated by taking the average of the mole fraction ratios of C_8/C_6, C_{10}/C_8, C_{12}/C_{10}, C_{14}/C_{12} etc. The extent of this value in fact determines the molecular weight distribution for any polymers ranging from short chain α-olefins to ultra high molecular weight polyethylene (UHWMPE) (Figure 1.5). Figure 1.5 shows the molecular weight distribution that will occur as result of the probability of chain growth. If the probability of chain growth is high, the probability of obtaining polymer in the range C_{35}-C_{120} is high whereas if the probability of chain growth is low, the probability of obtaining C_1-C_{11} becomes the highest.

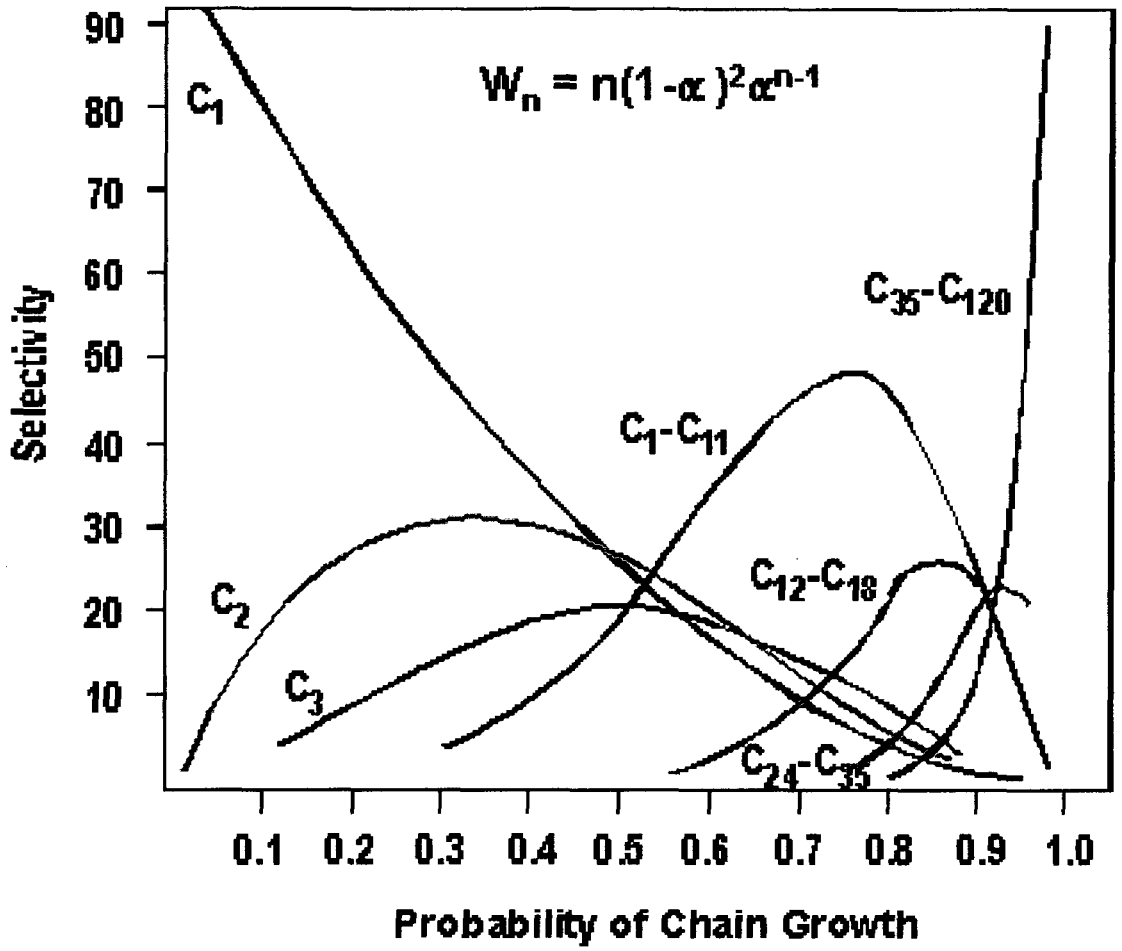


Figure 1.5: Expected molecular weight distributions as related to α-value.[39]

The realization that different mechanisms exist between selective and non-selective ethylene oligomerization reinforces the question about what dictates the type of mechanism and ultimately catalytic behavior that will be adopted by a specific catalyst system. Although ligand sterics and electronics, solvent effects, activator effects, and temperature must be regarded as important factors, the isolation of single component catalysts of the same ligand system and bearing the metal in two different oxidation states has conclusively correlated the metal oxidation state to the type of catalytic behavior.

These results clearly indicated that a statistical (S-F) distribution of LAOs is generated by a Cr^{III} active species, polymerization by Cr^{II} active species, and selective trimerization is the result of a Cr^{I} active species.[39] The finding that Cr^{I} acts as the active species for ethylene trimerization was further supported based on an EPR study recently appearing in the literature.[40] While this information is a potent tool for targeting synthetic efforts, control of the metal oxidation state remains a major challenge. In fact, these three catalytically distinct oxidation states are readily interconvertible via alkylation/reduction and disproportionation, zerovalent chromium remaining so far the only inactive oxidation state being mainly responsible for permanent catalyst deactivation (Figure 1.6).

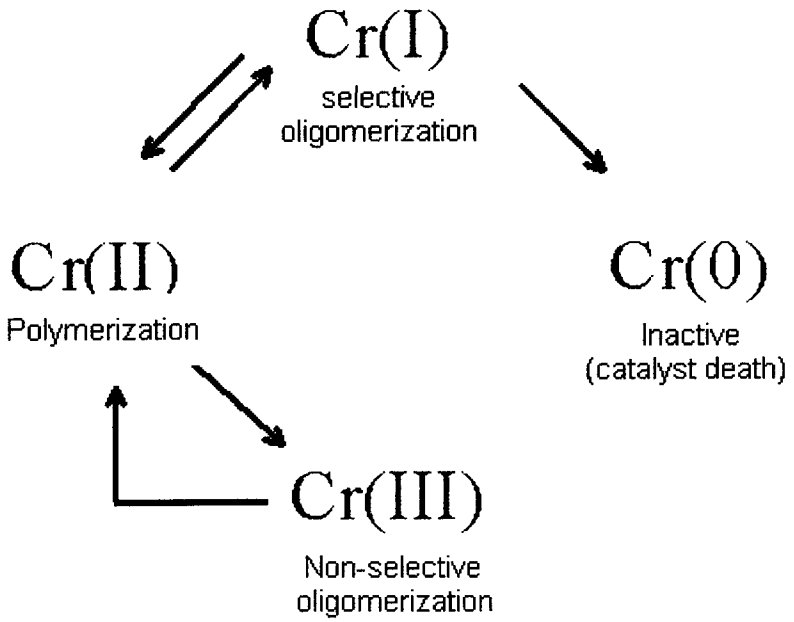


Figure 1.6: Consequences of Cr oxidation state of ethylene catalysis.

Aim Of Thesis

The work of this thesis is aimed at the preparation of new catalysts for ethylene oligomerization (hopefully selective) and polymerization as well as elucidation of mechanistic pathways. The two elements selected for this work, chromium and zirconium were advised as they have produced the best commercial catalysts. For the chromium system targeting selective trimerization catalysts we have focused on one particular ligand which, due to the similarity to other recently discovered in our lab, was giving hope for isolating single component catalysts and allowing the isolation of Cr(I) species. The rationale and the background for this selection is given in Chapter 2. For the zirconium catalysts targeting polymerization we have selected a pyrrole based ligand system given the ability of the corresponding aluminates to generate single component catalysts of very high performance. Details about the background for this research will be amply discussed in Chapter 3.

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Chapter II

Triazenide-Chromium Complexes for Oligomerization of Ethylene

Introduction

The ligand employed to prepare a transition metal complex controls the electronic and steric properties of the metal to the extent that the metal's chemical behavior may be finely tuned by the judicious selection of the ligand's characteristics. In catalysis, the ligand is the key to control four main features: the coordination number of the metal center, the coordination geometry of the metal, the formal oxidation state of the metal, and the appropriate steric environment at the active site.[1] This of course applies to any field of homogeneous catalysis. As stated in the main introduction, one of the goals of this thesis was to carry out exploratory work for the preparation of ethylene polymerization and oligomerization catalysts, which may act as single component systems. The quest for such a system therefore starts with the quest for the appropriate ligand.

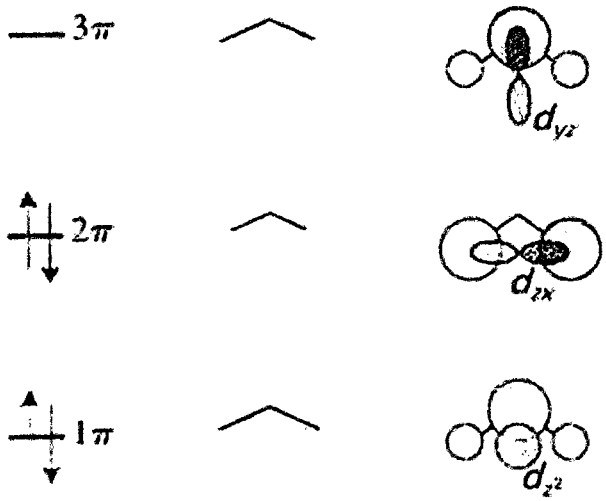
A myriad of ligands have already been shown in literature to produce ethylene oligomerization and polymerization catalysts including the much searched selective tri- and tetramerization catalysts. Common ligands used can be categorized as aromatic ligands and multidentate heteroatomic ligands. Examples of aromatic ligands are pyrrolyl ligands,[2] cyclopentadienyl ligands,[3a,b] and aryloxide ligands[4]. Multidentate heteroatomic ligands comprise of nitrogen donors,[5] sulfur donors,[6] oxygen donors,[7] phosphorus donors,[2] and combinations thereof.[8a,b]

A family of ligands that has played a special role in both coordination chemistry and catalysis is the three-center chelating ligand (Scheme 2.1). These systems consist of a chain of three atoms bearing four π-electrons and one negative charge. In essence it is an allylic-type of anion where any combination of donor atoms can be used. These

ligands have gained considerable attention due to their ability to work as binucleating agents and also to determine a remarkably wide range of intermetallic distances (from non-bonding range to the exceedingly short quintuple bonds).

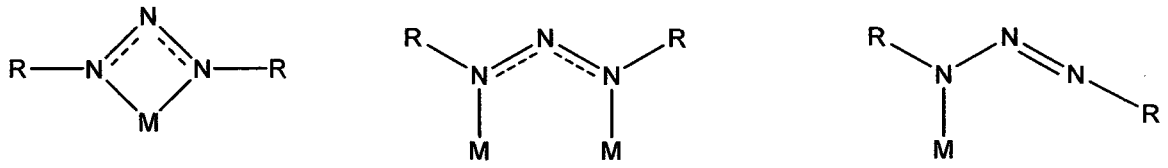
Scheme 2.1: Heteroatomic, Three Centered Chelating Ligands.

The relevant π-orbitals and their possible interaction with the metal *d* orbitals are depicted below (Scheme 2.2).



Scheme 2.2: Molecular Orbitals of the System of the Allyl Group and Symmetry Appropriate Metal d-Orbitals.[9]

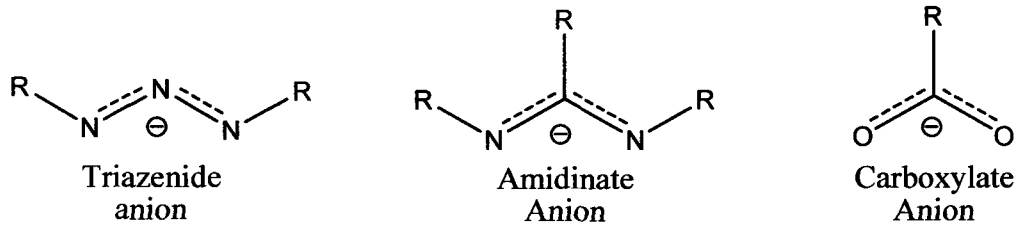
One such ligand is the triazenide (R)NNN(R)$^-$ anion, whose coordination chemistry has been known since the 19th century.[10] Triazenide anions bind metal centers through the hard donor nitrogen atoms, acting as weak electron donors. Triazenide anions can bind to metal centers in three different modes (Scheme 2.3).[11,12]



Scheme 2.3: Known Coordination Modes of Triazenide Anion.

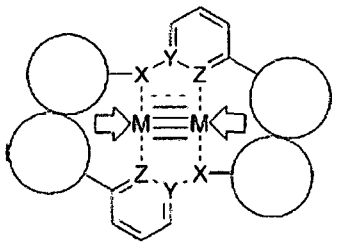
As a standard chelating ligand, it will form a small bite (63-65°) four-centered metallocycle, donating electrons through the terminal nitrogen atoms.[13] As a bridging ligand it forms a three-atom bridge spanning two metal centers, having been known to exhibit unusually strong metal-metal interactions and close metal-metal contacts, and to stabilize unusual oxidation states.[14] The terminal, monodentate bonding mode is instead the least commonly observed.[15]

We were interested in probing the ability of this particular anion in supporting chromium catalysts for ethylene poly- and oligomerization. While the rationale for the selection of chromium is amply discussed in the general Introduction, we shall discuss here the close similarity of the triazenide anion to well-known, established ligands such as the amidinate and carboxylates which have been successfully used in the past not only for stabilizing low oxidation states and facilitating metal-metal bonding but also to perform catalytic transformations.[16,17,18]



Scheme 2.4: Isoelectronic Ligands to the Triazenide

As stated, allylic type ligands have been used in the formation of complexes with short metal-metal contacts. The nature of these intermetallic interactions has been the topic of much debate. Are the short metal-metal contacts the result of the tendency of the metal to form genuine metal-metal bonds capable of holding the polymetallic frame or is it the ability of the ligand to bridge the two transition metals which determines the close proximity?[19] Bridging ligands have without a doubt the ability to impose short metal-metal distances, and it has been now demonstrated that it is the ligand's steric shielding which can force the metal atoms closer together, as shown in scheme 2.5.

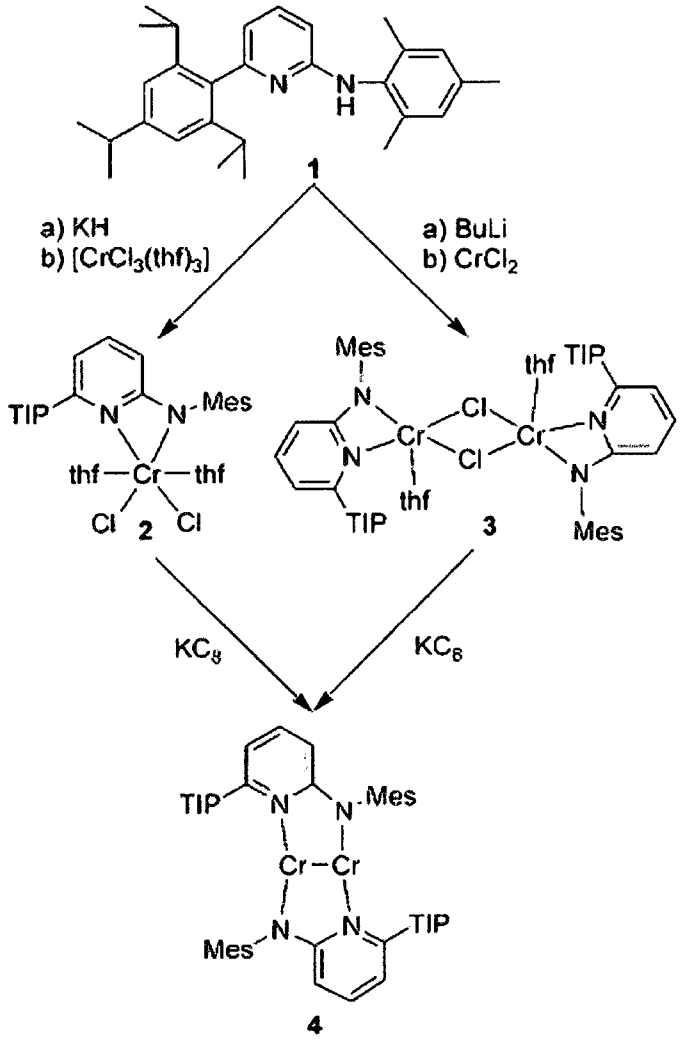


Scheme 2.5: Shortening of Metal-Metal Bond by Steric Shielding of Ligand.[20]

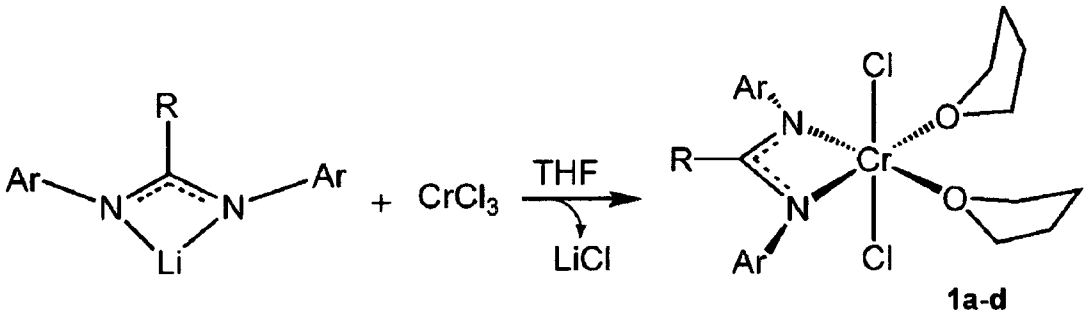
Following the idea that short Cr-Cr contacts might in fact be mainly ligand artifacts, it should be noted that the N-N-N bond angle in triazene is 112°, although some flexibility can be expected this does not lead to a very large intermetallic distance

between the 2 coordinated metal atoms. This knowledge was first observed when 1,3-diphenyltriazene stabilized a Cr-Cr bond of 1.858Å.[21] In this study two interesting features of the triazenide ligand were discussed as possible reasons for the short metal-metal bond observations. It was noted that bulky aryl group substituents could cause a steric barrier to the approach of axial ligands, as it was noted that in most short metal-metal bonded complexes no axial ligands were present. Additionally, it was suggested that the high basicity of nitrogen atoms compared to carboxylate oxygen donor atoms facilitated formation of shorter M-M contacts. Triazenides have been used in studies of short metal-metal bonds on different elements include Cr, Ag, Cu, Ru, Pd.[22,23,24,25,26] Whether or not these metal-metal contacts may be used to diagnose the strength of the M-M interaction, we were interested to probe their ability to provide a large electron pool which might be beneficial to catalytic performance and hopefully some selectivity.

A further encouragement to pursue the coordination chemistry of these ligands was provided by the most recent results appearing in the literature about the behavior of the closely related amidinate ligands. Most notably, monovalent chromium complexes have been stabilized by amidinate,[27,20](Schemes 2,6, 2.7) which basically resemble the target species for selective oligomerization catalysts, the ultimate target of this project. It was felt that the triazenide anion could also stabilize Cr(I) dimeric species due to its close electronic and steric similarities. The strategy used for the isolation of these complexes is illustrated below, and will be followed systematically throughout this project:



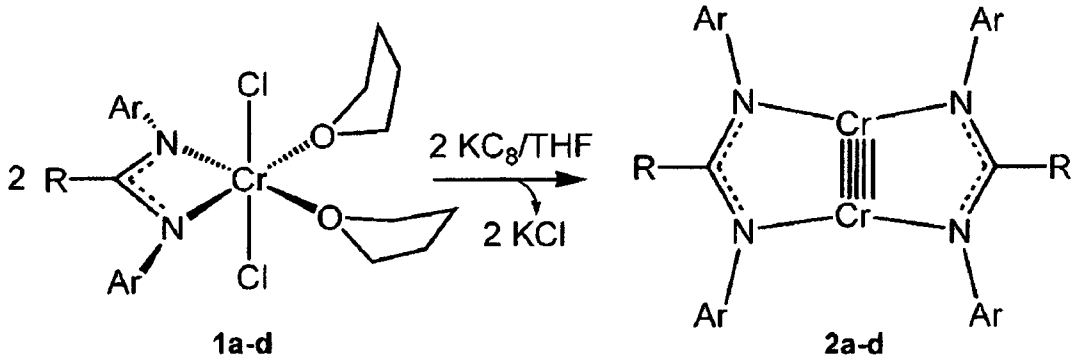
Scheme 2.6: Formation of Cr(I) Dimer Via Reduction of Cr(III) and Cr(II) Amidinate Complexes.[20]



1a-d

1a: R = H, Ar = 2,4,6-$Me_3C_6H_2$ **1b:** R = H, Ar = 2,6-$Et_2C_6H_3$

1c: R = H, Ar = 2,6-*i*$Pr_2C_6H_3$ **1d:** R = Me, Ar = 2,6-*i*$Pr_2C_6H_3$



1a-d **2a-d**

2a: R = H, Ar = 2,4,6-$Me_3C_6H_2$ **2b:** R = H, Ar = 2,6-$Et_2C_6H_3$

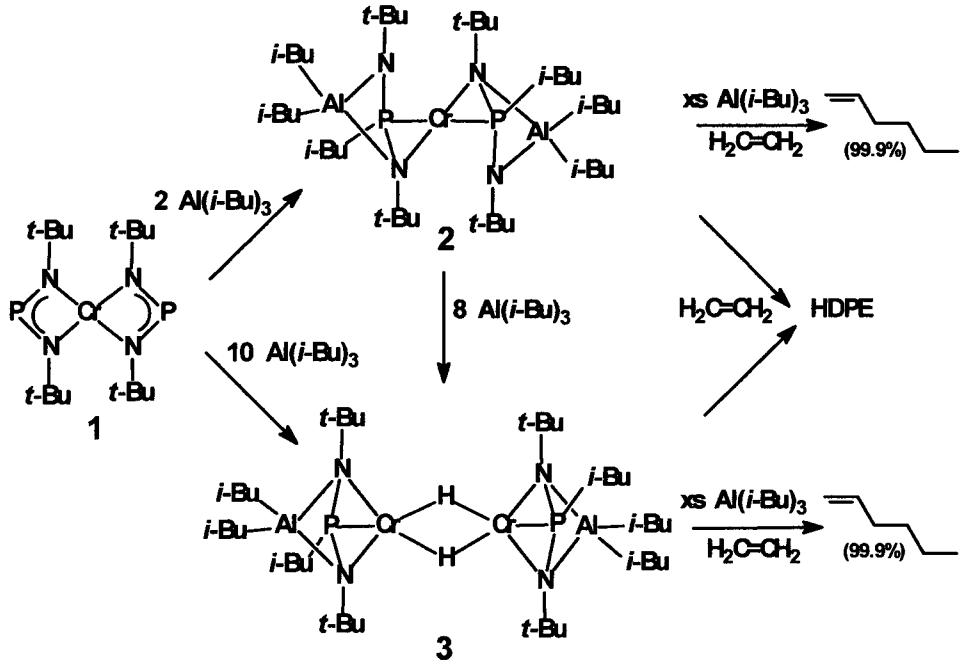
Scheme 2.7: Formation of Cr(I) Dimer From Reduction of Cr(III) Amidinate Species.[27]

When making the comparison to the well established coordination chemistry of amidinates, there are many features of triazenides that must be understood. The central carbon atom of the ligand backbone being replaced by a nitrogen atom has a few different effects. The central nitrogen atom on triazene makes the N-H hydrogen much more acidic, as pKa has been established for 1,3-diphenyltriazene to be 8.4-9.1[28,29] compared to

amidinate which would be expected to be upwards of 17.[30] This makes the triazenide anion much less electron donating than its counterparts.

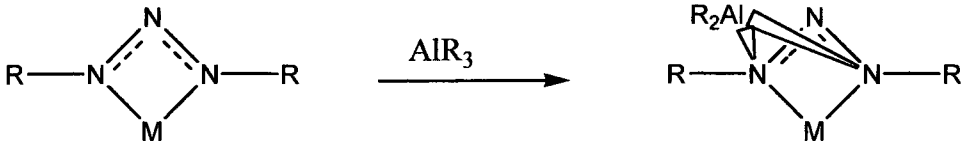
The central R group on the amidinate can be used to tune the ligand bite angle, whereas on triazenide this possibility is not present. Deforming the ligand backbone via sterics has been shown to have a strong effect on catalysis as it can cause the ligand to resist bis-chelation which might be a deactivation pathway for catalytic cycles. It was demonstrated that bis-1,3-(2,6-diisopropylphenyl)triazenide is not sufficiently large to support mono(triazenide)divalent metal complexes.[31]

As discussed in Chapter 1, ethylene oligomerization and polymerization catalysts are commonly activated by aluminum alkyl reagents such as MAO, TIBAO, $Al(CH_3)_3$, $Al(C_2H_5)_3$. Ligands bearing Lewis donor atoms such as nitrogen atoms can act as hosts for the incorporation of AlR_3 residues. In turn this may introduce zwitterionic electronic structures and ultimately afford self activating catalysts (single-component). This strategy has been observed on different instances.[32,33]



Scheme 2.8: Addition of Aluminum Alkyl Reagents Over PNP Ligand System.[32]

For example, the NPN ligand system, which shares with the triazenide the three-atom bite, was able to host AlR_2 bridging across the 2 nitrogen donor atoms. This in turn afforded a self-activating HDPE catalyst. We wished to probe the possibility that such a desirable behavior might also be displayed by the triazenide anion.



Scheme 2.9: Proposed Addition of AlR_3 to Transition Metal Triazenide Complexes.

One possible pitfall behind this strategy is the fact that triazenides are well known to form stable complexes with aluminum.[13,34] This could be problematic as structures of aluminum and the ligand may be observed rather than incorporation of aluminum into the transition metal complex.

The strongest evidence for triazenide ligand system being a good candidate for exploration with transition metals in hopes of isolating self activating catalysts lies in the fact that there is a patented process for its usage with transition metal and aluminum and boron activators.[35] Although very general and not providing much information regarding catalytic performance, the patent indicated that triazenide complexes of formulation $(\text{Triazenide})_n\text{MX}_y\text{L}_z$ once activated by any aluminum and boron reagents, gives rise to good catalytic behavior. It is this patent that gave the motivation for an exploratory investigation aimed at understanding the catalytic process involving the polymerization and oligomerization of olefins by triazenide complexes.

As discussed in Chapter 1, the great majority of patent and academic literature of selective trimerization of olefins shows the use of chromium as the transition metal of preference for more than 90% of the cases. Chromium is indeed versatile with respect to reactivity since it may readily span a variety of oxidation states. Based on this knowledge, triazenide complexes of chromium have been investigated and the results are accounted in this chapter. We were specifically targeting the stabilization of monovalent chromium, which is suspected to be the oxidation state responsible for selective trimerization of olefins.

Experimental

All operations were performed under an inert atmosphere using Schlenk techniques with a nitrogen-vacuum line or a nitrogen filled dry box. All solvents were dried using a column of Al_2O_3 under nitrogen atmosphere, degassed *in vacuo* and stored over molecular sieves under inert atmosphere. $CrCl_3(THF)_3$ and $CrCl_2(THF)_2$ were prepared according to standard procedures. Bis-1,3-(2',5'-diisopropylphenyl)triazine,[31] and bis-1,3-(2'-methoxyphenyl)triazine[36] were also prepared according to published literature procedures. $Al(CH_3)_3$, $Al(CH_2CH_3)_3$, $Al(^iBu)_3$, 1,3-diphenyltriazine were purchased from Sigma Aldrich and used as received. KH suspension in mineral oil was purchased from Sigma Alrich, washed with hexanes, dried and stored under inert atmosphere. Magnetic susceptibility measurements were recorded at room temperature using a Johnson Matthey Gouy balance and corrected for diamagnetism. NMR spectra were recorded on a Bruker AVANCE 300 spectrometer using sealed NMR tubes prepared inside a drybox. Elemental Analyses were performed using a Perkin-Elmer Series II CHN/O 2400 analyser.

Catalyst testing was done in a 300 mL high pressure Büchi reactor containing a heating/cooling jacket. A pre-weighed amount of catalyst was dissolved in 100 mL of toluene under N_2 prior to loading the reaction vessel. Solutions were heated using a thermostatted bath and charged with ethylene, maintaining the pressure 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. Gel permeation chromatography (GPC) analysis of the polyethylene was referenced to polystyrene standards.

Preparation of {Cr[μ,η,η'-bis-1,3-(2',5'-diisopropylphenyl)triazenide]$_2$}$_2$ (2.1).

A solution of bis-1,3-(2',5'-diisopropylphenyl)triazine (731 mg, 2 mmol) at room temperature and in THF (10 mL) was treated with KH (80 mg, 2 mmol) affording a clear light brown solution and visible gas evolution. Stirring was continued at room temperature for 1h. Addition of $CrCl_2(THF)_2$ (258 mg, 1 mmol) produced a dark red solution. Following 1h of stirring, insoluble materials were removed by centrifugation, and dark red oil was obtained upon allowing the resulting solution to stand for 24 hours at –37°C. The oily material was washed with cold hexanes (5 mL), and recrystallized from THF (10 mL), producing **2.1** as a dark red powder (367 mg, 0.24 mmol, 47%). NMR($CDCl_3$): ^{1}H: 7.0(1H,m,*m*-CH), 6.8(2H,d,*o*-CH), 3.0(1H,m,C*H*$(CH_3)_2$, 1.2(6H,d,CH(C*H*$)_3$. Anal Calcd for $C_{48}H_{68}Cr_2N_6$: C, 69.20, H, 8.23, N, 10.09. Found: C, 69.51, H, 8.29, N, 10.01.

Preparation of [Cr(μ,η,η'-1,3-diphenyltriazenide)$_2$]$_2$ (2.2)

A solution of 1,3-diphenyltriazine (394 mg, 2 mmol) at room temperature and in THF (10 mL) was treated with KH (80 mg, 2 mmol) producing a bright red solution and visible gas evolution. After 1h stirring, $CrCl_2(THF)_2$ (258 mg, 1 mmol) was added to the mixture affording darkening of the color towards brown. Following a further 1h of stirring, insoluble materials were removed by centrifugation and the resulting solution was allowed to stand at –37°C overnight. The oily material so formed was subsequently washed with hexanes (5 mL), and cold THF (3 mL) yielding **2.2** as a dark red powder (269 mg, 0.30 mmol, 60 %). NMR($CDCl_3$):^{1}H: 7.0(3H,br,*m,p*-CH), 6.5(2H,d,*o*-CH).

Anal Calcd for $C_{24}H_{20}Cr_2N_6$: C, 58.06, H, 4.06, N, 16.93. Found: C, 57.52, H, 3.29, N, 13.06.

Preparation of {Cr[μ,η,η'-bis-1,3-(2'-methoxyphenyl)triazenide]$_2$}$_2$ (2.3)

A solution of bis-1,3-(2'-methoxyphenyl)triazine (514 mg, 2 mmol) at room temperature and in THF (10 mL) was treated with KH (80 mg, 2 mmol) producing a bright red solution accompanied by visible gas evolution. Further stirring for 1h gave a golden yellow mixture. Subsequent addition of $CrCl_2(THF)_2$ (258 mg, 1 mmol) afforded a dark red mixture which was stirred for 1h. The insoluble materials were removed by centrifugation and the light red crystalline **2.3** (406 mg, 0.36 mmol, 72 %) was formed from a dark red solution after 24h at –37°C. NMR($CDCl_3$): ^{1}H: 6.4-6.9 (4H,m,Ar-CH), 3.4(3H,br,OCH_3). Anal Calcd for $C_{28}H_{28}Cr_2N_6O_4$: C, 54.55, H, 4.58, N, 13.63. Found: C, 53.58, H, 4.21, N, 12.98.

Preparation of (1,3-diphenyltriazenide)$_3$Al (2.4).

A solution of 1,3-diphenyltriazine (394 mg, 2 mmol) at room temperature and in toluene (10 mL) was treated with $Al(CH_3)_3$, (2.1 mL, 1.9 M toluene solution, 4 mmol) and $CrCl_2(THF)_2$ (258 mg, 1 mmol). Stirring was continued for 1h, after which time insoluble materials were removed by centrifugation. Light red crystals of **2.4** (484 mg, 0.79 mmol, 79 %) were obtained from the light brown solution after 24h at –37°C. NMR(C_6D_6, 300MHz): ^{1}H: 7.2(12H,m,*m*-CH_3), 7.1(6H,m,*p*-CH), 3.1(12H,m,C*H*(CH_3)$_2$), 1.3(72H,d,CH(C*H*$_3$)$_2$. Anal Calcd for $C_{36}H_{30}AlN_9$: C, 70.23, H, 4.91, N, 20.48. Found: C, 70.31, H, 4.99, N, 20.43.

Preparation of [bis-1,3-(2',5'-diisopropylphenyl)triazenide]$Cr(THF)_2Cl_2$ (2.5)

Method A. A solution of bis-1,3-(2',5'-diisopropylphenyl)triazine (731 mg, 2 mmol) at room temperature and in THF (10 mL) was treated with $LiAlH_4$ (1.27 mL, 1.57 M THF solution, 2 mmol) giving light gas evolution while affording a light brown solution. Stirring was continued for a period of 24 h, at which time $CrCl_2(THF)_2$ (258 mg, 1 mmol) was added. The resulting slightly darker brown color suspension was stirred for additional 24h. The resulting clear solution was allowed to stand for 24 hours at –37°C yielding dark purple crystals of **2.5** (112 mg, 0.14 mmol, 14 %) accompanied by both black and clear intractable materials. μ_{eff}=3.81μ_B. Anal. Calcd for $C_{32}H_{50}Cl_2CrN_3O_2$: C, 60.85, H, 7.98, N, 6.65. Found: C, 61.20, H, 8.22, N, 6.84.

Method B. A solution of bis-1,3-(2',5'-diisopropylphenyl)triazine (365 mg, 1 mmol) at room temperature and in THF(10 mL) was treated with KH (40 mg, 1 mmol) producing an orange solution and visible gas evolution. Stirring was continued for 1h, at which time $CrCl_3(THF)_3$ (374 mg, 1 mmol) was added to the clear light brown solution. Further stirring for a period of 1h gave a dark brown solution. The insoluble materials were removed by centrifugation, and the solution concentrated under reduced pressure. Dark purple crystals of **2.5** were obtained upon standing for a period of 48h at –37°C (614 mg, 0.79 mmol, 79 %).

Preparation of [bis-1,3-(2'-methoxyphenyl)triazenide]$Cr(THF)_2Cl_2$ (2.6)

A solution of bis-1,3-(2'-methoxyphenyl)triazine (257 mg, 1 mmol) in THF(10 mL) at room temperature was treated with KH (40 mg, 1 mmol) forming a bright red solution

and visible gas evolution. Stirring was continued for 1h at which time the resulting golden yellow solution was treated with $CrCl_3(THF)_3$ (374 mg, 1 mmol) producing a dark red/brown solution. Stirring was continued for a period of 1h and the insoluble materials were removed by centrifugation. Light brown powder of **2.6** (397 mg, 0.76 mmol, 76%) was obtained from slow evaporation of solvent over a 48 hour period at room temperature. . $\mu_{eff}=3.92\mu_B$ Anal Calcd for $C_{22}H_{30}Cl_2CrN_3O_4$: C, 50.49, H, 5.78, N, 8.03. Found: C: 50.68, H, 6.01, N, 7.84.

Preparation of {[bis-1,3-(2',5'-diisopropylphenyl)triazenide]Cr(THF)(μCl)}$_2$ (2.7)

Method A. A purple solution of 5 (775 mg, 1 mmol) at room temperature and in toluene(10 mL) was treated with a solution of $Al(CH_3)_3$ (2.1 mL, 1.9 M toluene solution, 4 mmol) by dropwise addition over a period of 1min. Stirring was continued for 1h at which time a dark brown solution was formed. The insoluble materials were removed by centrifugation and brown crystals of **2.7** (508 mg, 0.90 mmol ,90%) were obtained at room temperature following concentration of solvent under reduced pressure. . $\mu_{eff}=2.97\mu_B$ Anal Calcd for $C_{56}H_{84}Cl_2Cr_2N_6O_2$: C, 64.17, H, 8.08, N, 8.02. Found: C, 65.11, H, 8.59, N, 7.89.

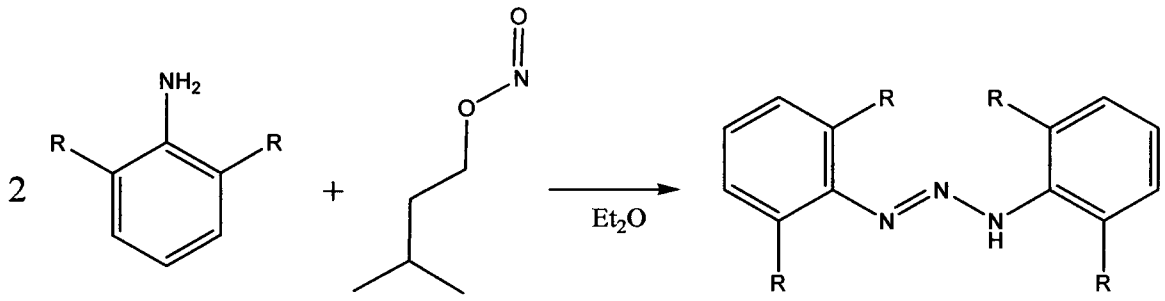
Method B. A purple solution of 5 (775 mg, 1 mmol) at room temperature and in toluene (10 mL) was treated with a solution of $Al(^iBu)_3$ (2.0 mL, 1.0 M toluene solution, 2mmol) by dropwise addition over a period of 1min. Stirring was continued for 1h at which time a dark brown solution was obtained. The insoluble materials were removed by centrifugation and brown crystals of **2.7** (491 mg, 0.86 mmol ,86%) were grown at room temperature following concentration of the solvent under reduced pressure.

Preparation of [bis-1,3-(2',5'-diisopropylphenyl)triazenide]Al(CH_3)$_2$ (2.8)

A purple solution of **2.5** (775 mg, 1 mmol) at room temperature in toluene (10 mL) was treated with Al(CH_3)$_3$ (5.3 ml, 1.9 M toluene solution, 10 mmol) affording a dark brown solution and vigorous gas evolution. The solvent was removed *in vacuo* to give a saturated solution which yielded clear crystals of **2.8** (260 mg, 0.61 mol, 61%) upon standing –37°C over a 48 hour period. NMR(C_6D_6, 300MHz): ^{1}H, 7.2(4H,m,*m*-CH), 7.1(2H,m, *p*-CH), 3.1(4H,m,C*H*(CH_3)$_2$, 1.3(24H,d,CH(C*H*$_3$)$_2$. 0.7(6H,s,AlCH_3). Anal Calcd for $C_{26}H_{40}AlN_3$: C, 74.07, H, 9.56, N, 9.97. Found: C, 74.14, H, 9.61, N, 9.96.

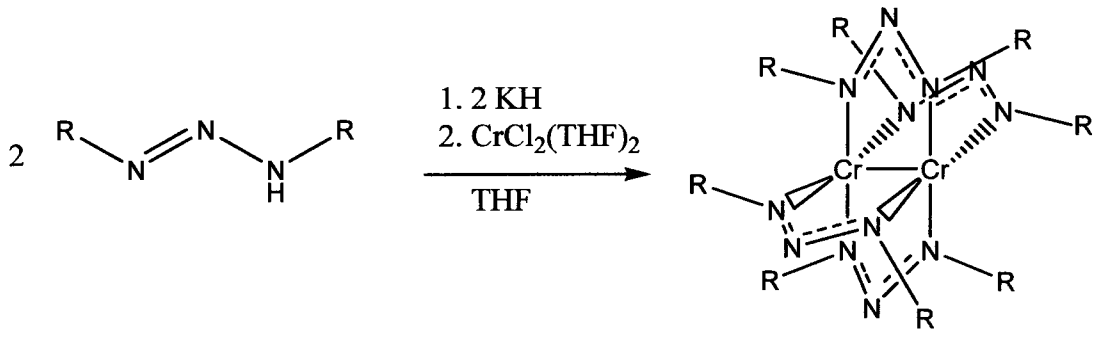
Results and Discussion

Aryl triazenes were synthesized using the literature procedure[31] requiring the combination of two equivalents of secondary amine with isopentyl nitrate in ether(Scheme 2.10). This was followed by recrystallization in nitromethane.



Scheme 2.10: Synthesis of Triazenes:

Triazenide anion chromium complexes were obtained by reacting $CrCl_2(THF)_2$ as starting salt with the deprotonated form of the ligand (Scheme 2.11):



Complex 2.1,2.2,2.3

R= 2,5-diisopropylphenyl (**2.1**), Ph (**2.2**), 2-methoxyphenyl (**2.3**),

Scheme 2.11: Formation of Cr^{II} triazenide complexes.

Deprotonation of the ligand was carried out with KH in THF affording visible gas evolution during the formation of light, pale brown solutions. The reaction mixtures were typically allowed to stir at room temperature for 1h. Except for the few cases where crystalline materials have been obtained, more often the products appeared as oily materials, which after attempts of recrystallization gave fine powders. Characterization proved difficult in the absence of crystalline products, however ^{1}H NMR, analytical, measurements were obtained. Some of the products had a precedent in the literature[21] and in all cases the data were in agreement with the structural assignment as [Cr(μ,η,η'-triazenide)$_2$]$_2$.

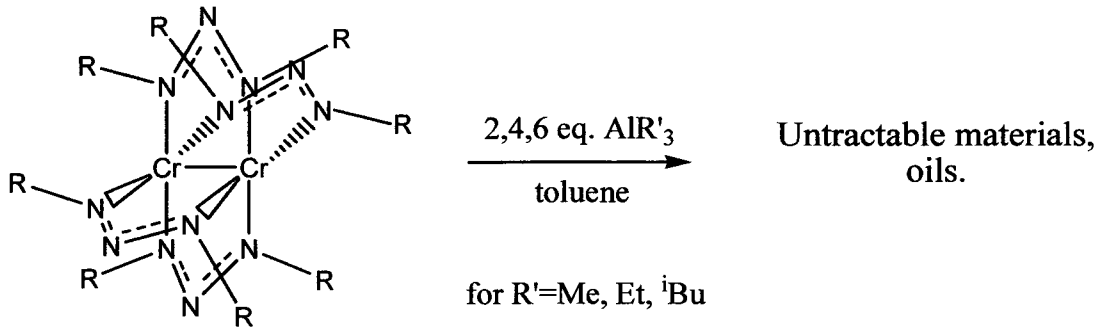
Where pure powdered product could be obtained, catalyst testing was performed to check the ability of these complexes to oligomerize or polymerize ethylene. The complexes were activated by known alkyl aluminum activators such as MAO, TIBAO and TIBA, in toluene. The results are summarized in Table 2.1.

Table 2.1: Catalytic testing of (Cr(μ,η,η'-triazenide)$_2$)$_2$complexes – Cr^{II} Species.

Run	Complex	Loading (μmol)	Co-Catalyst	Yield	Activity (g mmol^{-1} h^{-1} bar^{-1})
1	2.2	10	500 eq TIBAO	2.65g PE	6.6
2	2.2	10	500 eq MAO	1.0 g PE	2.5
3	2.3	30	250 eq TIBAO	0.80g PE	0.67
4	2.3	30	10 eq (^{i}Bu)$_3$Al	1.20g PE	1.0

All runs were performed for 1 hour at 40 bar ethylene pressure and at a temperature of 70°C in toluene. It was observed that the activity was only moderate. In the simple case of a phenyl ring as the ligand substituent, TIBAO led to 2.65g of PE from 10μmol of catalyst where MAO led to 1g of PE from 10μmol. These translate into activities of 6.6 g $mmol^{-1}$ h^{-1} $bar^{-1}$and 2.5 g $mmol^{-1}$ h^{-1} bar^{-1}, which are regarded as being in the range of low activity.[1] In the case where the aromatic ring was bearing a methoxy group in the *ortho* position, TIBAO led to less than 1g of PE formation, and $(^{i}Bu)_3Al$ led to 1.2 g PE. These activities of 0.67 and 1.0 are regarded as borderline.

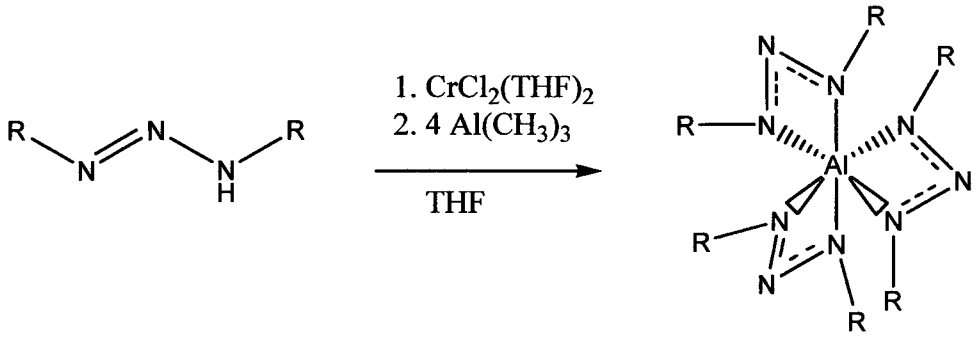
Although this behavior was disappointing, we were primarily interested in testing the ability of these complexes to entrap alkyl aluminum reagents. Therefore, the complexes were reacted with different alkyl aluminum activators with the purpose of isolating Cr-Al dimetallic complexes. We were hoping that this would shed some understanding into the mechanism of catalyst activation and possibly into the low activity observed for these catalysts. Ultimately, these isolated complexes could also act as self-activating catalysts. The complexes were exposed to different stoichiometric amounts (2,4,6) of $Al(CH_3)_3$, $Al(C_2H_5)_3$, and $Al(^{i}Bu)_3$, as represented below. Unfortunately, all these reactions proved fruitless as oils and mixtures of products were persistently obtained as the only products.



Complex 2.1,2.2,2.3

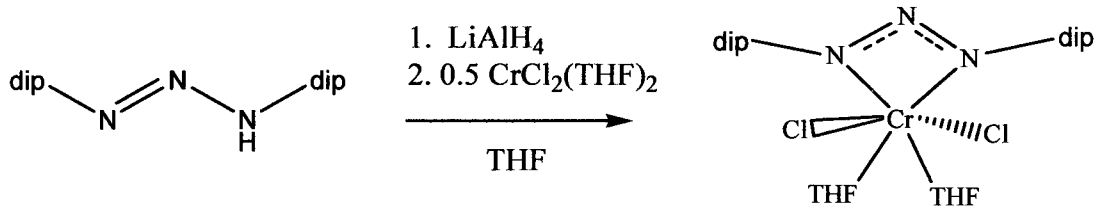
Scheme 2.12: Reactions of Cr^{II} triazenide complexes with Aluminum alkyl reagents.

Reactions via one-pot synthesis of the Cr complex followed by addition of aluminum alkyl reagents were also attempted. However, this strategy was quickly abandoned as a complex was isolated showing that the ligand simply complexed with aluminum rather than chromium [R= 2,6-diisopropylphenyl]. Evidence was found in the literature indicating that the same reaction takes place for triazenide ligands bearing different aryl substituents.[34]



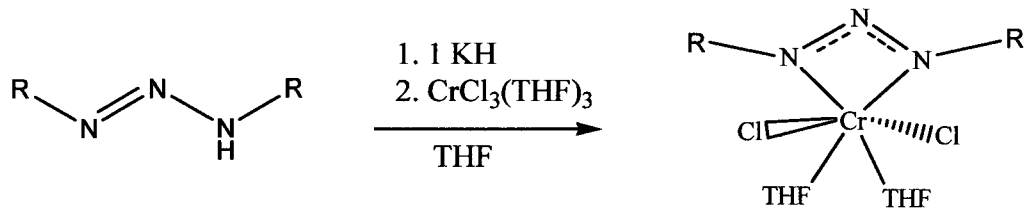
Scheme 2.13: One-pot synthesis of Cr, Al, triazenide containing complexes.

The lack of catalytic activity and crystallinity of the triazenide ligand on Cr^{II} led to a need for new ideas. In an attempt to explore the possibility of forming Chromium hydrides or hydrogenating the ligand to see new possibilities, reactions with $LiAlH_4$ were attempted. A surprising observation was made when bis-1,3-(2',5'-diisopropylphenyl) triazine was exposed to $LiAlH_4$ followed by addition of $CrCl_2(THF)_2$. From a mixture of products, purple crystals were isolated and characterized as a Cr^{III} complex of the ligand, alongside with the formation of black intractable materials. The fact that a trivalent species was generated by a divalent precursor and by using a strong reductant can be explained only by assuming the occurrence of a disproportionation reaction. The black tarry material was in fact identified as metallic chromium in its colloidal state therefore substantiating this proposal.



Scheme 2.14: Synthesis of Complex 2.5. Method A

Preliminary catalyst testing of complex **2.5** showed this species to be a desirable catalyst. It therefore became a target to rationally synthesize this compound to improve its yield and availability. Reaction of one equivalent of deprotonated ligand with equimolar amount of $CrCl_3(THF)_3$ accomplished this task, giving good yield of purple crystals of **2.5**. The reaction proceeded similarly by using bis-1,3-(2'-methoxyphenyl)triazine (Scheme 2.15).



R= 2,5-diisopropylphenyl (complex **2.5**), and 2-Methoxyphenyl(complex **2.6**).

Scheme 2.15: Direct synthesis of $LCrCl_2(THF)_2$ Cr^{III} Complexes.

Catalytic testing was performed on both complex **2.5** and **2.6** to see their ability to polymerize and oligomerize ethylene. Aluminum alkyl activators were used for this process, namely MAO and TIBAO in ratios between 500-1000 equivalents. The results of these tests are reported in Table 2.2.

Table 2.2: Catalytic Testing of Complex 2.5, 2.6.

Run	Complex	Loading (μmol)	Co-Catalyst	Yield (g PE)	Yield (ml) oligomers	Activity (g $mmol^{-1}$ h^{-1} bar^{-1})
5	2.5	15	1000 eq. MAO	4.85	38	53.8
6	2.5	15	500 eq. TIBAO	23.0	0	38.3
7	2.6	30	1000 eq. MAO	10.5	14	17.2
8	2.6	15	1000 eq. TIBAO	2.11	0	3.5

These data clearly show that complex **2.5** is a switchable catalyst since, depending on the nature of the activators, the catalytic system produces either large amounts of oligomers or only polymer. It can be noted that for both complexes, the use of MAO as co-catalyst resulted in the formation of some polyethylene, accompanied by a large amount of liquid oligomers. The use of TIBAO resulted instead in the exclusive formation of polymers. Complex **2.6** is a poorer performing catalytic system.

Table 2.3: Analysis of Polyethylene

Run	Mp	Mn	Mv	Mw	Mz	Mz+1	PD
5	503	358	656	707	1223	1891	1.97
6	46248	3585	135028	233190	3489613	8666836	65.04
7	2432	947	2695	3084	6454	10245	3.25

The GC-MS analysis of the large amount of oligomers generated by **2.5** (Run 5) showed a statistical distribution ranging from C_4(1-butene) to higher α-olefins, $>C_{16}$. This indicates the presence of a Schultz-Flory distribution with an α-value of 0.71. The 4.85g of polyethylene that was obtained was analyzed by gel-permeation chromatography. It was measured that this polymer had a molecular weight of 707g/mol and a polydispersity index of 1.9749. This implies that the polymer is very low Mw, consisting of chains of approximately 50 carbon atoms in length. Furthermore the NMR shows the presence of olefinic termini and that the chains are highly linear (Figure 2.1). Therefore, it can be speculated that the polymer formed is from the same mechanism as the liquid oligomers, a Schulz-Flory distribution producing α-olefins of lengths large enough to become a waxy solid. These results are consistent, as the range of α-olefins observed (C_4-~C_{60}) are what can be expected for a Schulz-Flory distribution bearing an α-value of 0.71.

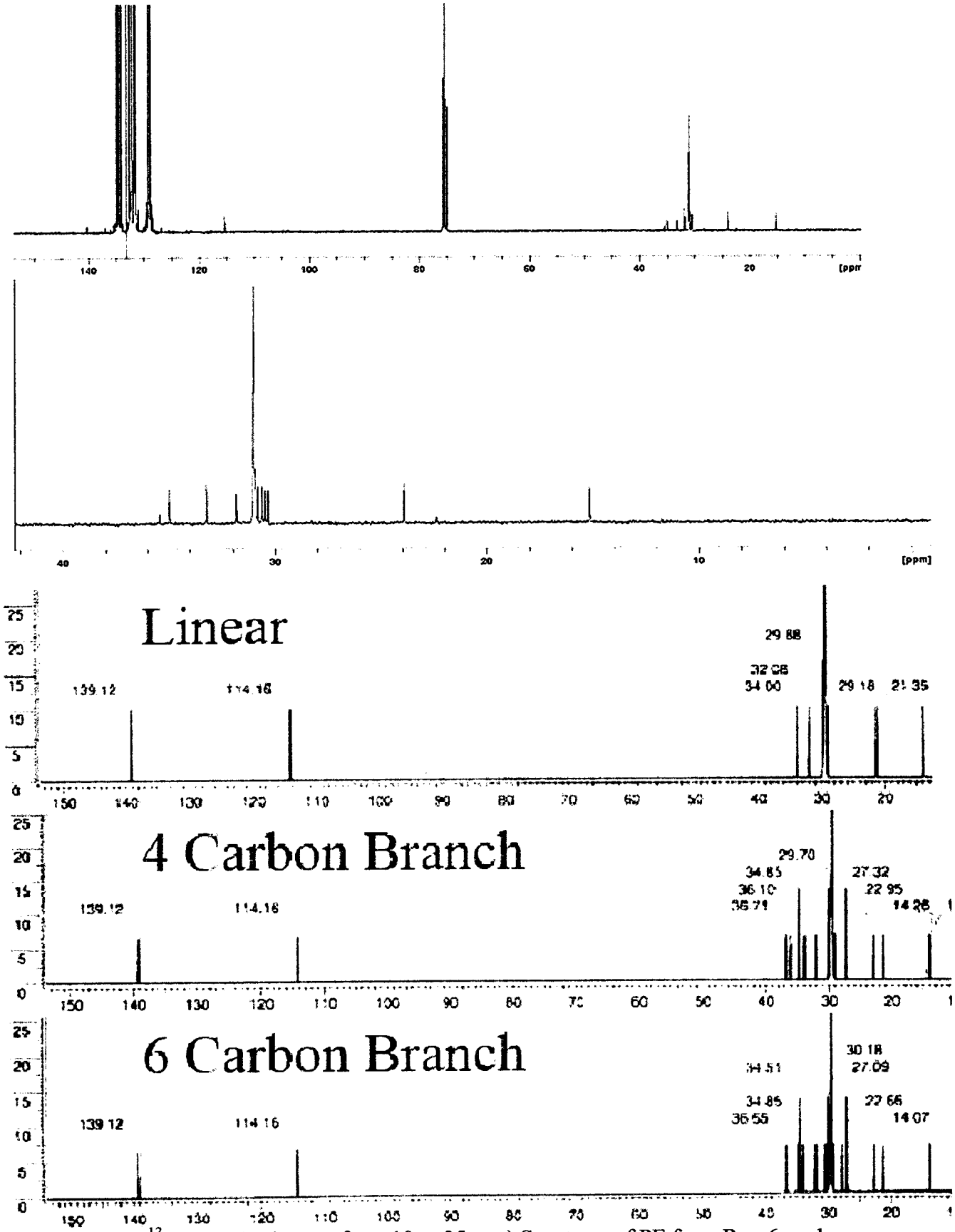


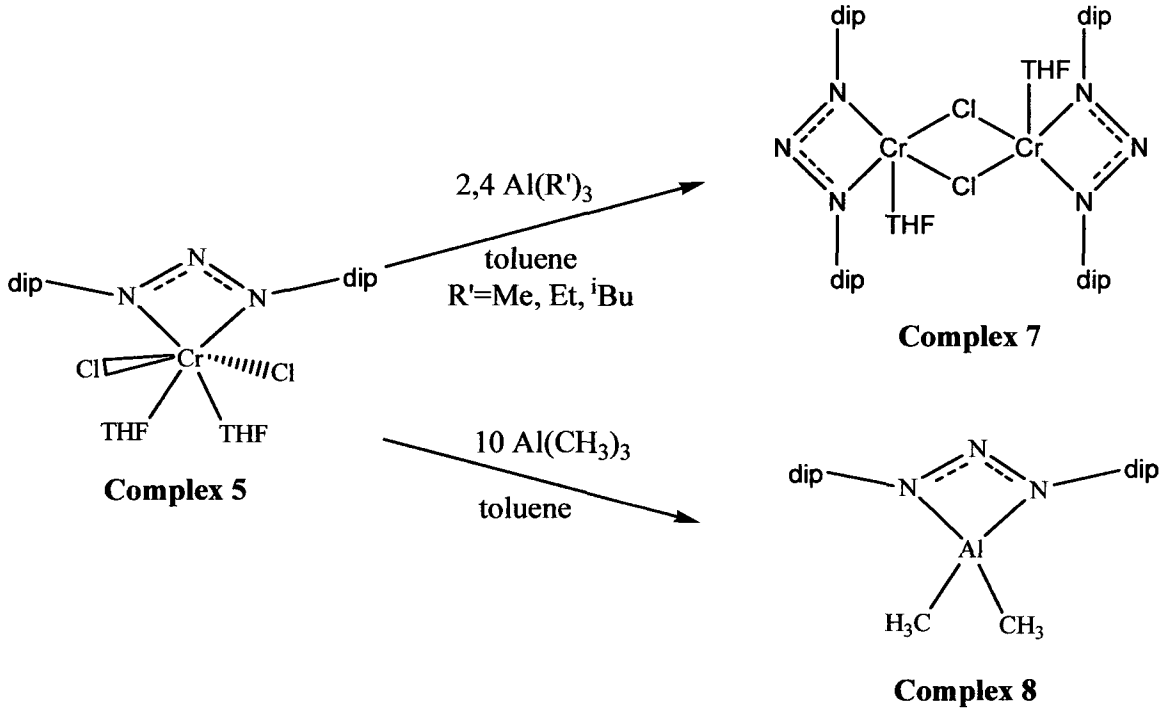
Figure 2.1: ^{13}C NMR(and zoom from 10 to 35ppm) Spectrum of PE from Run 6, and Comparison to Simulated Spectrum of Linear, and Branched PE.

Similar results were obtained when complex **2.6** was activated by MAO (Run 7), producing some polymer and some liquid α-olefins. In this case however, more polyethylene and less α-olefins were observed. Analysis of the liquid oligomers by GC-MS showed once again a statistical distribution of α-olefins, with an α-value of 0.75. GPC analysis of the polymer once again showed low molecular weight polymer, in this case 3084g/mol, with a PDI of 3.25, meaning that polymer chains had an average of 220 carbons in length. It seems as though the selectivities of complex **2.5** and **2.6** activated by MAO are comparable, simply with the mean molecular weight shifted higher for the case of complex **2.6**.

Analysis of the large amount of polymer obtained from activation of **2.5** by TIBAO (Run 6) by GPC indicated that the polymer was of high molecular weight, with a very broad molecular weight distribution (M_w = 233,190g/mol, PDI 65.04). Such behavior is very similar to what is commonly referred to as 'naked Chromium'.[37] It can be explained by assuming that the co-catalyst is extracting the ligand from Cr resulting in naked Chromium polymerizing ethylene without any control of selectivity. Interpretation of these data leads to the suggestion that the triazenide ligand cannot possibly stabilize Cr^I complexes in a sufficient manner when treated with large amounts of MAO or TIBAO (common co-catalysts for olefin oligo- and polymerization).

To better elucidate this behavior, attempts to isolate complexes bearing aluminum were performed by reacting **2.5** and **2.6** with stoichiometric amounts of alkyl aluminum reagents. Isolation of low-valent complexes could prove to be valuable as catalysts, most notably if a Cr^I complex could be isolated or, even more desirably, complexes retaining

Al in the ligand backbone. The reaction with **2.5** and **2.6** were carried out with 2, 4 and 10 equivalents of $Al(Me)_3$, $Al(Et)_3$, $Al(^iBu)_3$).



Scheme 2.16: Reaction of Complex 2.5 with Alkyl Aluminum Reagents.

Regardless of the Al reagent used, low stoichiometric amounts of aluminum alkyl reagents such as 2 or 4 equivalents per chromium led to reduction to the divalent state as for example in the case of the formation of complex **2.7**. Complex **2.7** was characterized crystallographically (Figure 2.4) and the magnetic moment and elemental analysis agreed with this formulation.

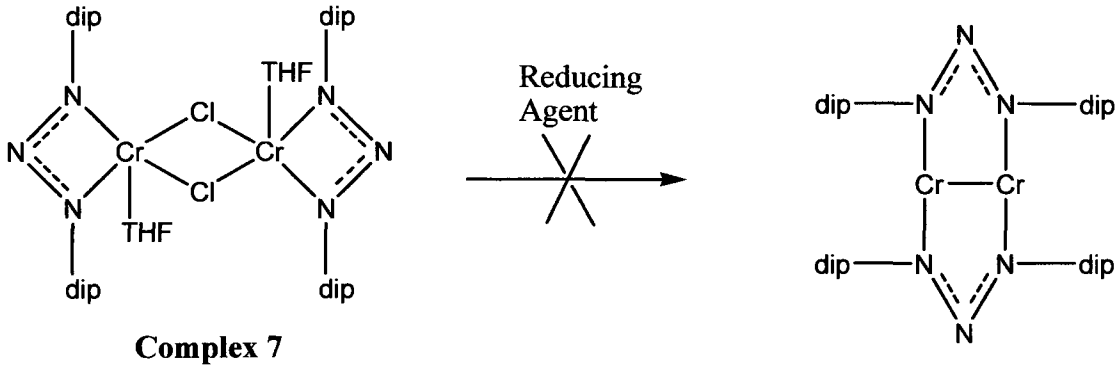
As illustrated in scheme 2.16, more reducing conditions were also examined for complex **2.5** in hope of obtaining a Cr^{I} species. The results of the reactions carried out with two and four equivalents of AlR_3 indicated that larger amounts of $Al(CH_3)_3$ simply extracted the ligand from chromium, destroying the complex and generating a chromium-free aluminate species.

Table 2.2 summarized the catalytic testing of complexes **2.4** and **2.5**. The molecular weight distribution of the products from catalytic runs showed a complete absence of selectivity, and extremely broad molecular weight distributions. This is indicative of the formation of "naked" chromium as the active species, meaning that indeed the ligand was extracted from the transition metal. On the other hand, the behavior highlighted in Scheme 2.16 provided ideas for new attempts in catalytic testing. Complex **7** was tested using the well known activators, TIBAO and MAO. Additionally, complex **5** was retested using lower loading of co-catalyst. The results of these tests are tabled below.

Table 2.4: Catalytic Testing of Complexes 2.7, 2.5.

Run	**Catalyst**	**Loading (μmol)**	**Co-catalyst**	**Yield (g PE)**	**Oligomeric Yield (mL)**	**Activity (g $mmol^{-1}$ h^{-1} bar^{-1})**
9	2.7	15	500 eq. MAO	2.3	8.1	13.4
10	2.7	15	500 eq. TIBAO	5.9	0	9.8
11	2.5	15	50 eq. MAO	1.2	0	2.0
12	2.5	15	50 eq. TIBAO	3.2	0	5.3

Complex **2.5** and Complex **2.7** have similar catalytic behavior with respect to selectivity and mechanism, however their activities are dramatically different. It can be observed (run 9) that complex **2.7** produces polyethylene (2.3g) and liquid oligomers (8.1mL) when activated by 500 equivalents of MAO. The distribution of liquid oligomers fits a Schulz-Flory distribution with α-value of 0.59. In run 10, complex **2.7** produces 5.9g of polyethylene exclusively when activated by TIBAO. Comparison of runs 9 and 10 to runs 5 and 6 shows that complex **2.5** and **2.7** have similar catalytic behavior with regards to selectivity and mechanism, however complex **2.5** has a much higher activity. However, when activated by only 50 equivalents of either MAO or TIBAO, complex **2.5** produced nearly negligible activity. This is clearly indicating that the constant for the alkylation equilibrium is rather unfavorable in this case, requiring the employment of larger amount for the alkylation of chromium to occur at significant rate. We speculate that the lack of selectivity in the catalytic performances described above has probably to be ascribed to the robustness of the divalent state which prevents reaching the monovalent state via simple alkylation. In turn, this advised us to pursue deliberate reduction of **2.7** with non-alkyl based reducing agents such as potassium/graphite, potassium metal, potassium mirror and sodium amalgam.



Complex 7

Scheme 2.17: Attempted Reduction of Cr^{II} dimeric Complex 2.7.

All reactions produced dark brown colored mother liquors, but no tractable materials were isolated in spite of repeated attempts and use of different solvents and reaction conditions.

Conclusions:

We conclude that simply the triazenide monoanion is not providing sufficient stability to the monovalent state of chromium. However, although the original target of obtaining selective trimerization catalysts of the triazenide anion was not achieved, the outstanding oligomerization activity of **2.5** opens interesting perspective for the use of three-center chelating ligands. We believe that the use of these ligands for the preparation of monovalent single component chromium catalysts is still a valuable strategy since monovalent complexes could indeed be stabilized by similar ligand systems. Accordingly, when this work was in progress a report appeared in the literature describing the use of a bulky amidinate for the preparation and characterization of a quintuply bonded Cr(I) complex.[27,20]

Crystal Structure Data

A single crystal suitable for X-ray diffraction measurements was mounted on a glass fibre. Unit cell measurements and intensity data collections were performed on a Bruker-AXS SMART 1 k CCD diffractometer at 202K using graphite monochromatized Mo K_α radiation (λ = 0.71073 Å). Unit cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. The data reduction included a correction for Lorentz and polarization effects, with an applied multi-scan absorption correction (SADABS). Crystal structures were solved and refined using the SHELXTL program suite. Direct methods yielded all non-hydrogen atoms which were refined with anisotropic thermal parameters. All hydrogen atom positions were calculated geometrically and were riding on their respective atoms.

Crystals of $C_{57}H_{54}AlN_9$ (Complex **2.4**) were grown from toluene. The crystal data and refinement parameters for complex **2.4** can be found in table 2.5, and interatomic distances and angles are listed in figure 2.2. The reflection data were consistent with a monoclinic system; C2/c. The largest residual electron density peak (0.239 e/Å^3) was associated with the N1 atom. Full-matrix least-squares refinement on F^2 gave R_1 = 0.0581 and wR_2 = 0.1388 at convergence.

Crystals of $C_{40}H_{66}Cl_2CrN_3O_4$ (complex **2.5**) were grown from THF. The crystal data and refinement parameters for complex **2.5** can be found in table 2.5, and interatomic distances and angles are listed in figure 2.3. The reflection data were consistent with an orthorhombic system; Fdd2. The uncoordinated THF solvent molecule

was disordered and modeled over two positions as a 50:50 mixture. The largest residual electron density peak (0.445 e/Å^3) was associated with a disordered Cr1 atom. Full-matrix least-squares refinement on F^2 gave $R_1 = 0.0581$ and $wR_2 = 0.1440$ at convergence.

Crystals of $C_{70}H_{100}Cl_2Cr_2N_6O_2$ (complex **2.7**) were grown from toluene. The crystal data and refinement parameters for complex **2.7** can be found in table 2.5, and interatomic distances and angles are listed in figure 2.4. The reflection data were consistent with a triclinic system, P-1. The largest residual electron density peak (1.084 e/Å^3) was associated with a Cr atom. Full matrix least-squares refinement on F^2 gave $R_1 = 0.0667$ and $wR_2 = 0.1827$ at convergence.

Crystals of $C_{26}H_{40}AlN_3$ (Complex **2.8**) were grown from toluene. The crystal data and refinement parameters for complex **2.8** can be found in table 2.5 and interatomic distances and angles are listed in figure 2.5. The reflection data were consistent with a monoclinic system, C2/c. The largest residual electron density peak (0.211 e/Å^3) was associated with the N1 atom. Full matrix least-squares refinement on F^2 gave $R_1 = 0.0582$ and $wR^2 = 0.1446$ at convergence.

Table 2.5: Crystal Data and Refinement Parameters for Complex 4,5,7,8.

Identification Code	**Complex 2.4**	**Complex 2.5**	**Complex 2.7**	**Complex 2.8**
Empirical Formula	$C_{57}H_{54}AlN_9$	$C_{40}H_{66}Cl_2CrN_3O_4$	$C_{70}H_{100}Cl_2Cr_2N_6O_2$	$C_{26}H_{40}AlN_3$
Formula Weight	892.07	775.86	1232.46	421.59
Temperature	201(2) K	203(2) K	203(2)K	203(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal System	Monoclinic	Orthorombic	Triclinic	Monoclinic
Space Group	C2/c	Fdd2	P-1	C2/c
Unit cell Dimensions	a = 19.978(2) Å b = 17.337(2) Å	a = 29.334(4) Å b = 30.173(4) Å	a = 12.447(7) Å b = 15.553(9) Å	a = 17.758(3) Å b = 9.0900(16) Å

	c = 15.2718(18) Å α = 90° β= 109.570(2)° γ = 90°	c = 9.7129(12) Å α= 90°. β= 90°. γ = 90°	c = 20.068(11) Å α = 87.554(7)° β= 76.474(7)° γ= 71.820(7)°	c = 16.537(3) Å α = 90°. β = 91.916(3)° γ = 90°
Volume	4984.0(10) $Å^3$	8596.8(19) $Å^3$	3587(4) $Å^3$	2667.8(8) $Å^3$
Z	4	8	2	4
Density (calculated)	1.189 Mg/m^3	1.199 Mg/m^3	1.141 Mg/m^3	1.050 Mg/m^3
Absorption Coefficient	0.088 mm^{-1}	0.430 mm^{-1}	0.422 mm^{-1}	0.092 mm^{-1}
F(000)	1888	3336	1320	920
Crystal Size	0.25 x 0.10 x 0.08 mm^3	0.10 x 0.02 x 0.02 mm^3	0.80 x 0.80 x 0.50 mm^3	0.10 x 0.10 x 0.05 mm^3
Theta Range for Data Collection	1.60 to 25.19°.	2.31 to 25.68°.	1.70 to 24.11°	2.30 to 23.52°
Index Ranges (h,k,l)	±22, ±19, ±18	±35, ±36, ±11	±14, ±17, ±23	±19, ±10, ±18
Reflections Collected/Independent	20277/4466	22970/4081	26629/11280	8828/1977
R(int)	0.0873	0.0963	0.0394	0.0370
Completeness to theta =	25.19° =99.7%	25.68° = 99.8%	24.11° =99.0%	23.52° = 99.5%
Max. and Min. Transmission	0.9930 and 0.9784	0.9914 and 0.9582	0.8168 and 0.7289	0.9954 and 0.9909
Data/Restraints/ Parameters	4466 / 0 / 320	4081 / 143 / 272	11280 / 7 / 695	1977 / 0 / 138
Goodness-of-Fit on F^2	1.040	1.057	1.067	1.081
Final R indices [I>2sigma(I)]	R1 = 0.0581, wR2 = 0.1388	R1 = 0.0581, wR2 = 0.1440	R1 = 0.0667, wR2 = 0.1827	R1 = 0.0582, wR2 = 0.1446
R indices (all data)	R1 = 0.1442, wR2 = 0.1771	R1 = 0.1057, wR2 = 0.1696	R1 = 0.0944, wR2 = 0.2074	R1 = 0.0777, wR2 = 0.1552
Largest Diff. Peak and Hole	0.239 and -0.219 e.Å^{-3}	0.445 and -0.354 e.$Å^{-3}$	1.084 and -0.441 e. $Å^{-3}$	0.210 and -0.186 e. $Å^{-3}$

The homoleptic **2.4** (figure 2.1)contains an Aluminum atom bearing three 1,3-diphenyltriazenide ligands. The ligand is coordinated to the metal via the expected 1,3 σ-coordination. The geometry surrounding Aluminum is distorted octahedral, due to the small bite angles of the ligands [N(1)-Al(1)-N(3) = 63.80(10)°; N(4)-Al(1)-N(4A) = 64.06(16)°]. The distortion also allows the bulky phenyl rings to orient themselves in a propeller-type of shape to minimize steric hindrance. The consistent bond distances between N atoms [N(1)-N(2) = 1.314(3) Å; N(2)-N(3) = 1.318(3)Å; N(4)-N(5) = 1.317(3)Å; N(4A)-N(5) = 1.317(3)Å] indicate that there is delocalization of the π-electron amongst the three N-atoms. However, the shortness of the N-C bond distances observed [N(4)-C(13)=1.411(4)Å; N(1)-C(1)=1.419(4)Å] suggest that it may also be delocalization over the phenyl rings as they are slightly shorter than a standard N-C bond distance of 1.472Å. The rotation of the helix generated by the 3 chelating ligands gives the complex Λ-configuration as it is a chiral complex.

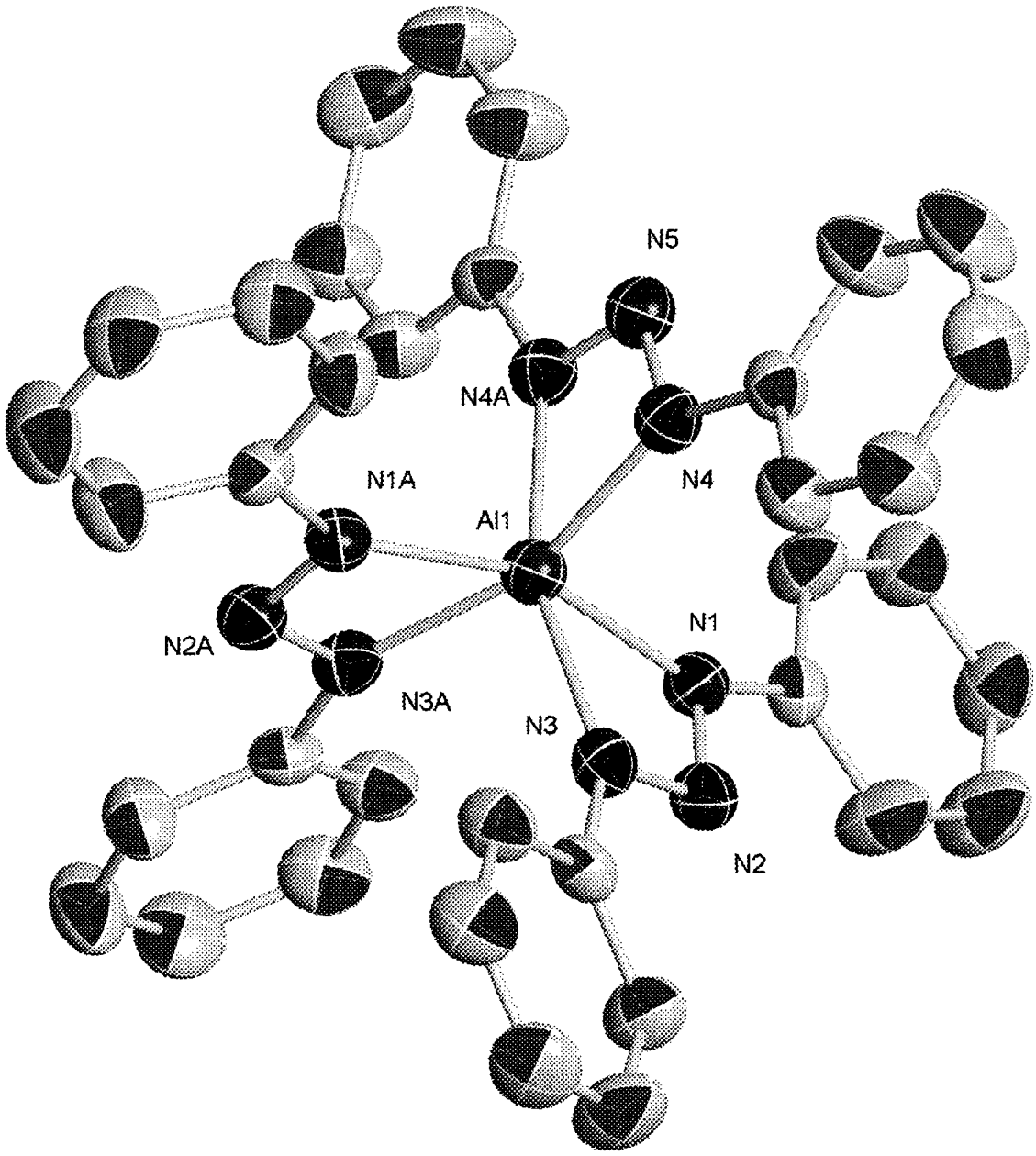


Figure 2.2: X-ray crystal structure of ((1,3diphenyltriazenide)$_3$Al) (**2.4**). Thermal ellipsoids are drawn at the 30% probability level.

Selected Bond Distances(Å) and Angles(°): Al(1)-N(4) =1.976(3), Al(1)-N(4A) =1.976(3), Al(1)-N(1) =1.979(2), Al(1)-N(1A) =1.979(2), Al(1)-N(3) =1.984(3), Al(1)-N(3A) =1.985(3), N(1)-N(2) =1.314(3), N(1)-C(1) =1.419(4), N(2)-N(3) =1.318(3),

N(3)-C(7) =1.411(4), N(4)-N(5) =1.317(3), N(4)-C(13) =1.411(4), N(5)-N(4A) =1.317(3), N(4)-Al(1)-N(4A) =64.06(16), N(4)-Al(1)-N(1) =97.45(10), N(4A)-Al(1)-N(1A) =97.45(10), N(1)-Al(1)-N(3) =63.80(10), N(1A)-Al(1)-N(3A) =63.80(10), N(3)-Al(1)-N(3A) =94.72(16), N(2)-N(1)-C(1) =116.9(2), N(1)-N(2)-N(3) =105.5(2), N(2)-N(3)-C(7) =117.5(3), N(5)-N(4)-C(13) =117.1(3), N(4)-N(5)-N(4A) =105.4(4).

The monomeric **2.5** as seen in figure 2.3 contains a trivalent chromium atom in an octahedral coordination environment defined by one triazenide ligand, two chlorine atoms and two coordinated THF molecules. The equatorial plane is comprised of the chelating triazenide ligand and the two THF oxygen donor atoms while the two chlorine atoms occupy the axial *trans* positions. The Cr-N bond lengths are in the expected range [Cr(1)-N(1) = 2.032(4)Å; Cr(1)-N(1A) = 2.031(4)Å] with a ligand bite angle [N(1)-Cr(1)-N(1A) = 62.5(2)°] causing some distortion of the octahedron. Two additional molecules of solvent per molecule (THF) are retained in the lattice, each disordered over two positions.

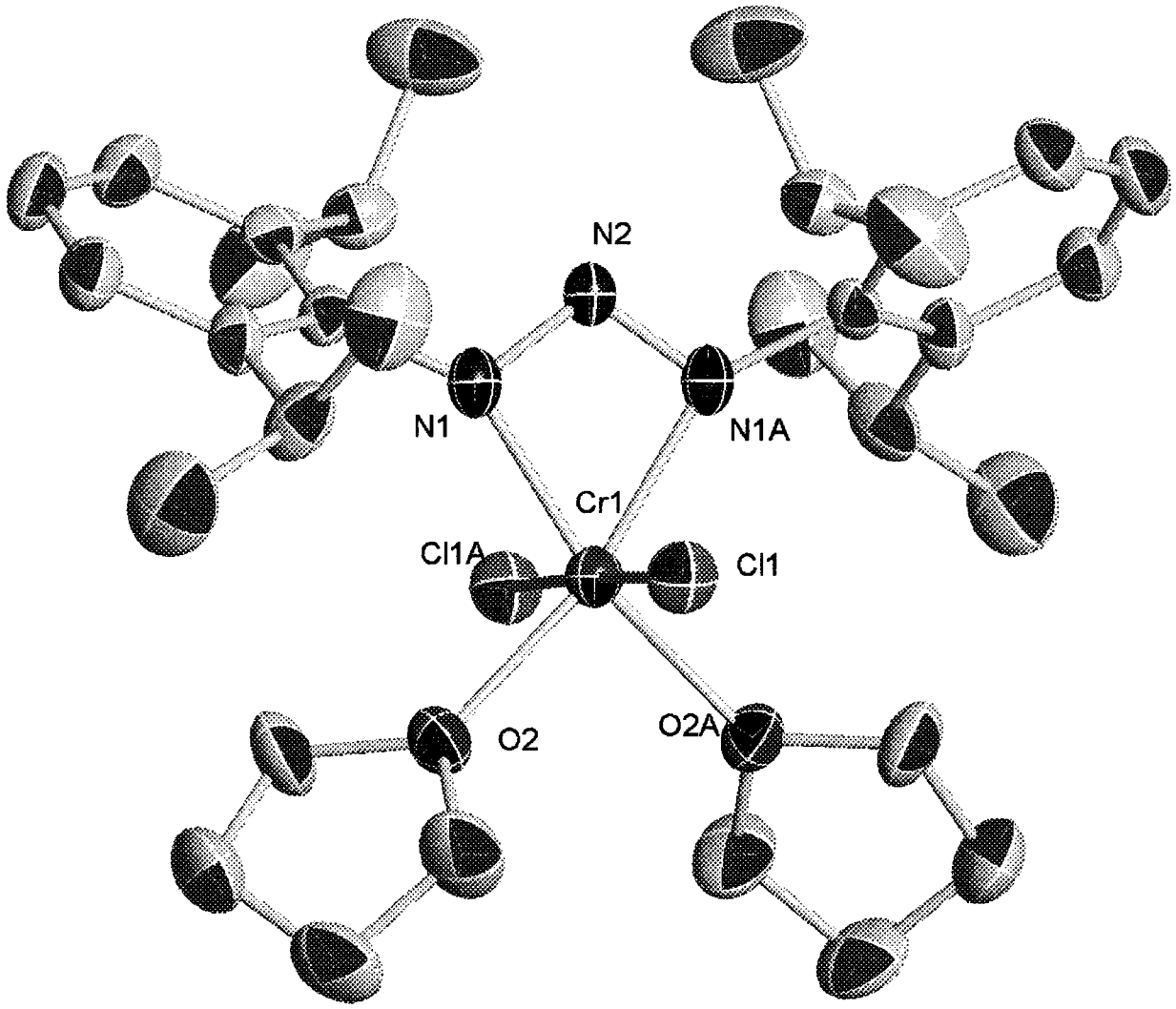


Figure 2.3 X-ray Crystal Structure of ((bis-1,3-(2',5'-diisopropylphenyl)triazenide)Cr(THF)$_2$Cl$_2$) (**2.5**) Thermal ellipsoids are drawn at the 30% probability level.

Selected Bond Distances(Å) and Angles(°): Cr(1)-N(1A) =2.031(4), Cr(1)-N(1) =2.032(4), Cr(1)-O(2) =2.050(4), Cr(1)-O(2A) =2.050(4), Cr(1)-Cl(1) =2.3095(12), Cr(1)-Cl(1A) =2.3095(12), N(2)-N(1A) =1.307(5), N(2)-N(1) =1.307(5), N(1A)-Cr(1)-N(1) =62.5(2), N(1A)-Cr(1)-O(2) =165.78(16), N(1)-Cr(1)-O(2)

=103.69(16), N(1A)-Cr(1)-O(2A) =103.69(16), N(1)-Cr(1)-O(2A) =165.79(16), O(2)-Cr(1)-O(2A) =90.3(2), N(1A)-Cr(1)-Cl(1) =88.60(12), N(1)-Cr(1)-Cl(1) =93.58(12), O(2)-Cr(1)-Cl(1) =89.20(11), O(2A)-Cr(1)-Cl(1) =89.00(11), N(1A)-Cr(1)-Cl(1A) =93.58(12), N(1)-Cr(1)-Cl(1A) =88.61(12), O(2)-Cr(1)-Cl(1A) =89.00(11), O(2A)-Cr(1)-Cl(1A) =89.21(11), Cl(1)-Cr(1)-Cl(1A) =177.45(10), N(1A)-N(2)-N(1) =107.4(5), N(2)-N(1)-C(1) =117.1(4), N(2)-N(1)-Cr(1) =95.1(3), C(1)-N(1)-Cr(1) =145.3(3).

The structure of complex **2.7** (Figure 2.4) consists of a symmetry generated dimer with two identical chromium containing moieties bridged by two chlorines. The coordination geometry around the Cr center is distorted trigonal bypiramidal with the two nitrogen atoms of the ligand occupying one axial and one equatorial position [Cr(1)-N(3) =2.048(3)Å; Cr(1)-N(1) =2.090(3)Å]. The oxygen atom of the coordinated THF molecule is in equatorial position [Cr(1)-O(1) = 2.048(3) Å] while the two bridging chlorines occupy the last axial and equatorial positions [Cr(1)-Cl(1) = 2.6279(16)Å; Cr(1)-Cl(1A)= 2.3939(15)Å]. The bonding of the bis-1,3-(2',5'-diisopropylphenyl)triazenide) to chromium is typical, only displaying a slightly sharper bite angle, [N(3)-Cr(1)-N(1) = 61.46(13)°]. The delocalization of the π-electron as indicated by the N-N bond distances appears to be slightly different from previously observed in complex **5** [N(1)-N(2) = 1.308(5)Å; N(2)-N(3) =1321(5)Å] as a probable result of the different oxidation state.

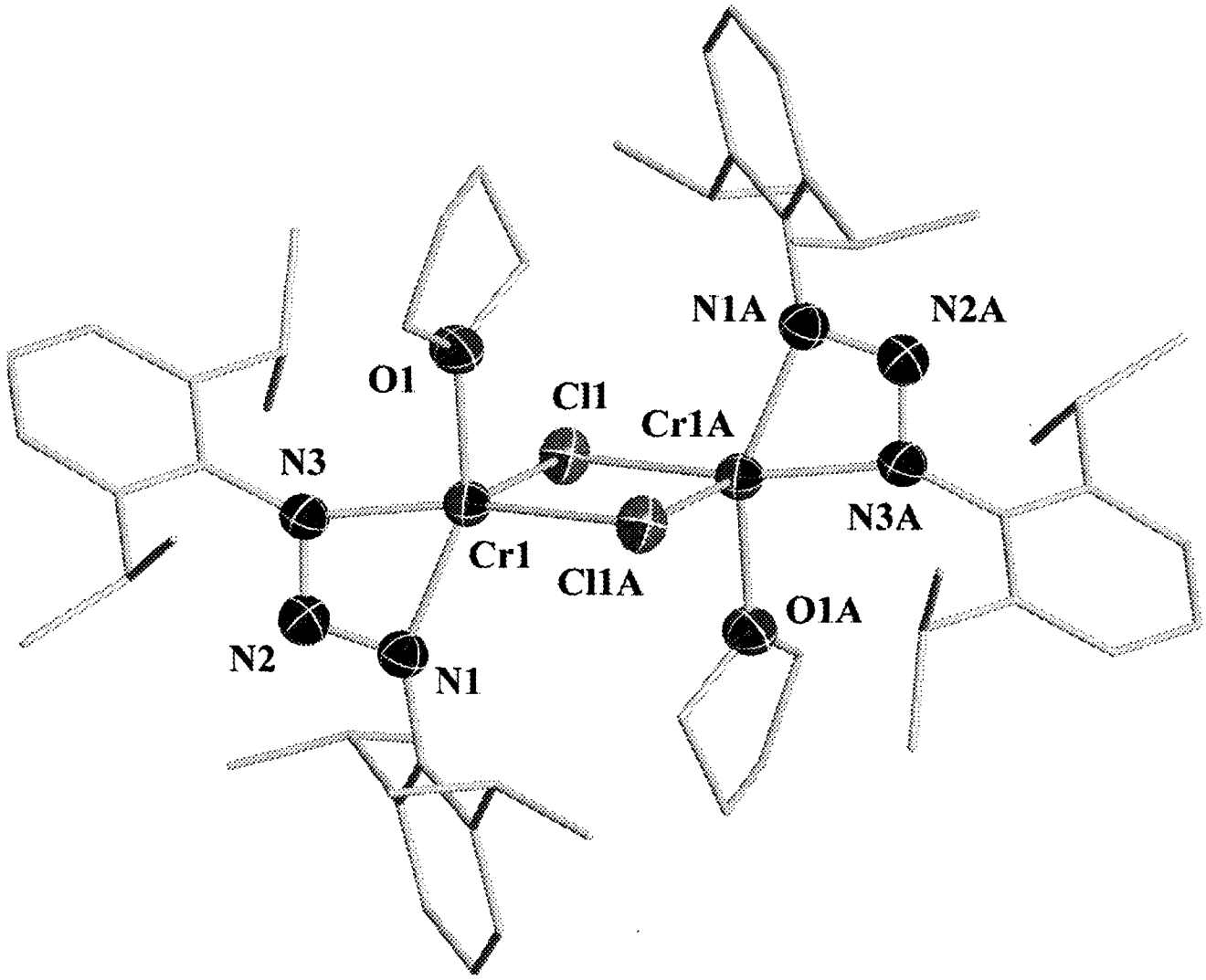


Figure 2.4: X-ray Crystal Structure of (((bis-1,3-(2',5'-diisopropylphenyl)triazenide)Cr(THF)(μCl))$_2$) (**2.7**). Thermal ellipsoids are drawn at the 30% probability level.

Selected Bond Distances (Å) and Angles (°): Cr(1)-O(1) =2.048(3), Cr(1)-N(3) =2.048(3), Cr(1)-N(1) =2.090(3), Cr(1)-Cl(1A) =2.3939(15), Cr(1)-Cl(1) =2.6279(16), N(1)-N(2) =1.308(5), N(1)-C(1) =1.431(5), N(2)-N(3) =1.321(5), O(1)-Cr(1)-N(3) =93.92(13), O(1)-Cr(1)-N(1) =153.04(13), N(3)-Cr(1)-N(1) =61.46(13), O(1)-Cr(1)-Cl(1A) =91.58(10), N(3)-Cr(1)-Cl(1A) =161.49(10), N(1)-Cr(1)-Cl(1A)

=108.65(10), O(1)-Cr(1)-Cl(1) =95.34(9), N(3)-Cr(1)-Cl(1) =108.83(11), N(1)-Cr(1)-Cl(1) =102.72(11), Cl(1A)-Cr(1)-Cl(1) =88.19(5), Cr(1A)-Cl(1)-Cr(1) =91.81(5), Cr(1A)-Cl(1A)-Cr(1) =91.80(6), N(1)-N(2)-N(3) =107.1(3).

Figure 2.5 reveals a trivalent tetrahedrally coordinated aluminum atom, where a methyl group has been replaced by the chelating (bis-1,3-(2',5'-diisopropylphenyl) triazenide) ligand. No unusual intermolecular contacts have been observed. The distortion of the tetrahedral geometry is due to the narrow bite angle of the ligand [N(1)-Al(1)-N(1A) = 65.12(14)°]. The ligation of the triazenide ligand is almost identical to that observed in the aluminum triazenide complex reported above (complex **2.4**). The two aluminum-carbon bond distances were identical and fall in the expected range [Al(1)-C(14)=1.944(4)Å].

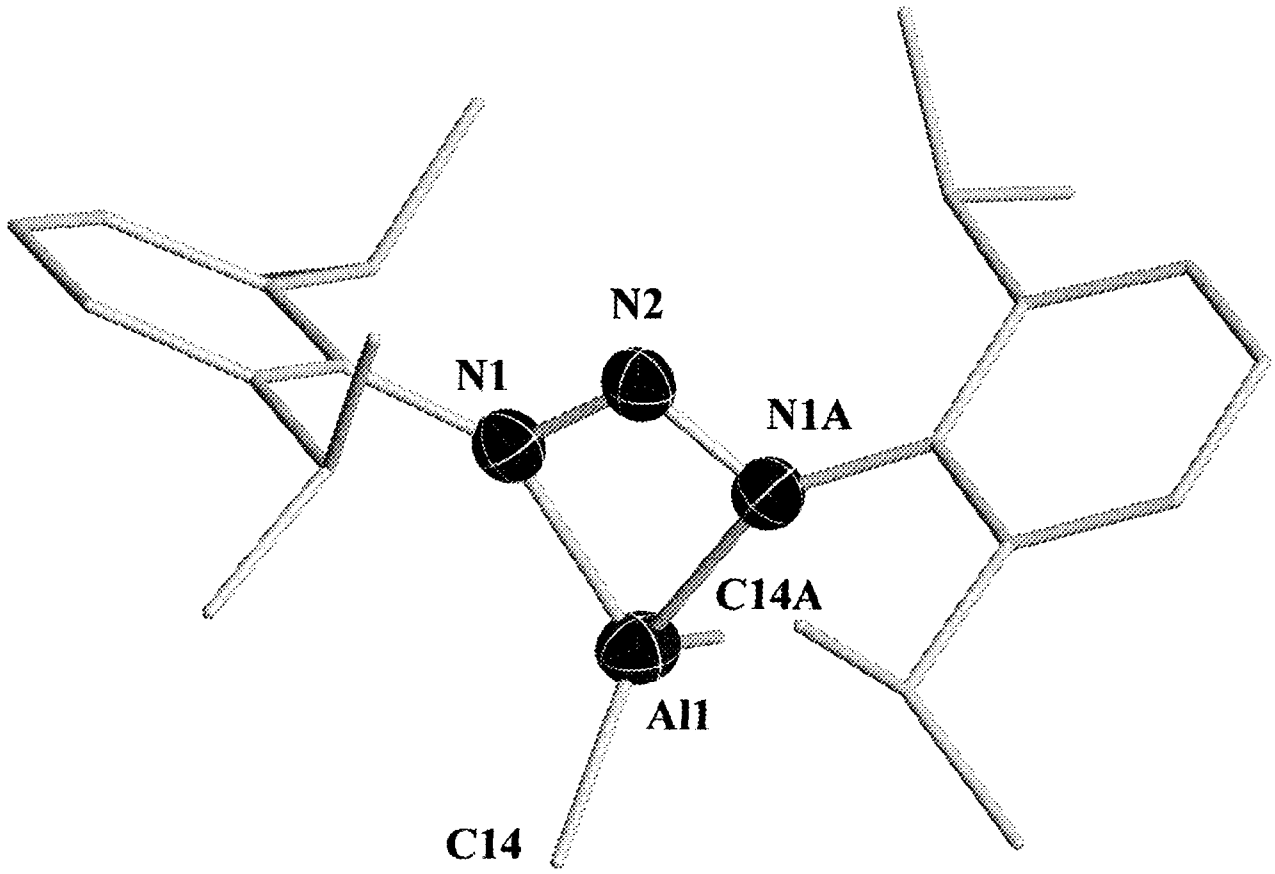


Figure 2.5: X-Ray Crystal Structure ((((bis-1,3-(2',5'-diisopropylphenyl)triazenide)Al(CH_3)$_2$).**(2.8)**. Thermal ellipsoids are drawn at the 30% probability level.

Selected Bond Distances (Å) and Angles (°): N(2)-N(1A) =1.315(3), N(2)-N(1) =1.315(3), N(2)-Al(1) =2.437(4), Al(1)-C(14A) =1.944(4), Al(1)-C(14) =1.944(4), Al(1)-N(1) =1.956(2), Al(1)-N(1A) =1.956(2), N(1)-C(1) =1.432(3), N(1A)-N(2)-N(1) =106.3(3), N(1A)-N(2)-Al(1) =53.16(15), N(1)-N(2)-Al(1) =53.16(15), C(14A)-Al(1)-C(14) =122.5(3), C(14A)-Al(1)-N(1) =112.52(14), C(14)-Al(1)-N(1)

=115.30(13), C(14A)-Al(1)-N(1A) =115.30(13), C(14)-Al(1)-N(1A) =112.52(14), N(1)-Al(1)-N(1A) =65.12(14), C(14A)-Al(1)-N(2) =118.74(13), C(14)-Al(1)-N(2) =118.74(13), N(1)-Al(1)-N(2) =32.56(7), N(1A)-Al(1)-N(2) =32.56(7), N(2)-N(1)-C(1) =117.4(2), N(2)-N(1)-Al(1) =94.28(17), C(1)-N(1)-Al(1) =147.02(19), C(2)-C(1)-C(6) =122.3(3), C(2)-C(1)-N(1) =119.8(3), C(6)-C(1)-N(1) =117.7(2).

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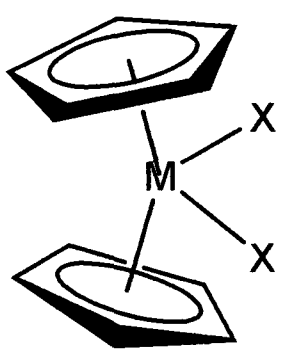
Chapter III

Pyrrole-Zirconium Complexes for Polymerization of Ethylene

Introduction

Ziegler and Natta's discovery that the combination of $TiCl_4$ and $Al(C_2H_5)_3$ in the presence of $MgCl_2$ can polymerize ethylene in high yield and efficiency has marked a milestone,[1a-c] as polyethylene is today an integral part of everyday life. Since then, much research has been focused on the design of new catalysts with higher activity, control over molecular weight, and control over polymer stereochemistry. Following the discovery by Wilkinson et.al. of the bis-cyclopentadienyl derivatives, it was found that catalysts featuring transition metals sandwiched by cyclopentadienyl ligands $(Cp)^{3a-c}$ much commonly referred to as metallocene complexes, or their related constrained geometry catalysts,[4a,b] were highly active olefin polymerization catalysts. (Scheme 3.1). More recently, group 4 metallocenes and half-sandwich titanium amide complexes (constrained-geometry catalysts) have been at the forefront of these developments[2], and have found very competitive industrial applications.



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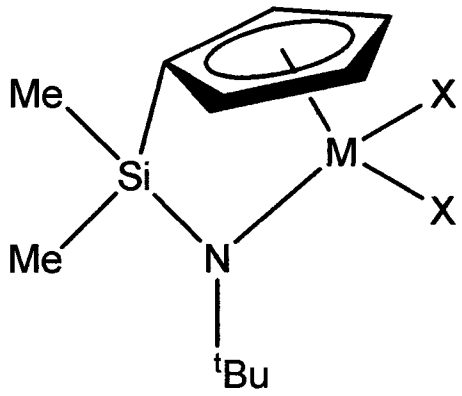
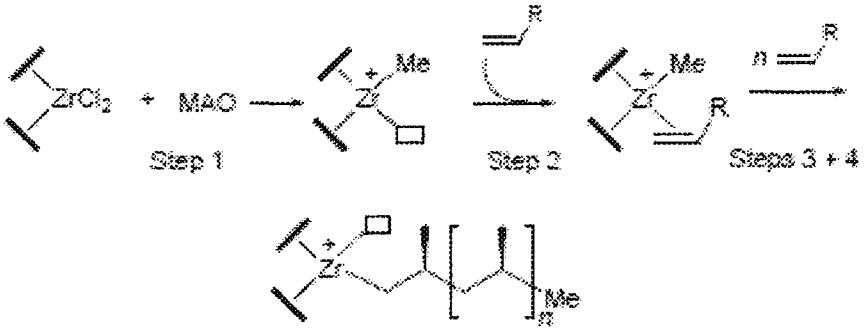


2

Scheme 3.1: Metallocene (1) and Constrained Geometry (2) Catalysts.

Halide replacement with methyl groups in metallocene catalysts, [i.e. $Cp_2Zr(CH_3)_2$] led to a complex that was catalytically inactive even in combination with large amounts of Me_3Al. However, the controlled addition of water to this mixture afforded a highly active polymerization catalyst, and in turn led to the discovery of the most effective activator, today known as MAO.[5] The mechanism of activation of group 4 metallocene catalysts is known and is summarized in scheme 3.2.

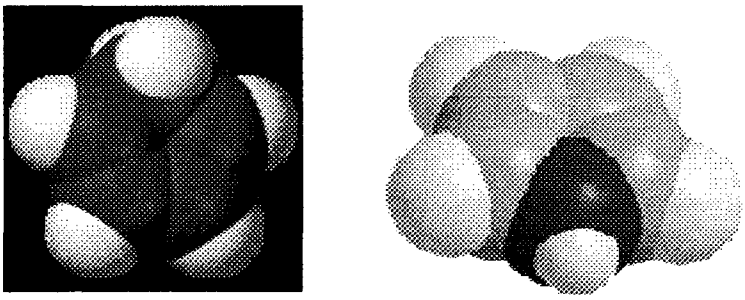


Scheme 3.2: Activation of metallocene catalysts by MAO.[6]

This activation can be summarized in 4 steps. In Step 1, the co-catalyst MAO alkylates the metal center and generates a free coordination position for the monomer and stabilizes the latter. In Step 2, the monomer (olefin) is added to the empty coordination sites. In Step 3, insertion of the olefin into the zirconium alkyl bond starts the chain growth and regenerates a new free coordination position ready for the coordination of a second molecule of monomer. In Step 4, repetition of step 3 in a very short period of time (about 2000 substrate molecules per catalyst molecule per second), grows the polymer chain.

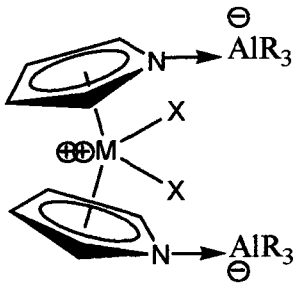
It is proposed that one important requirement for active polymerization is having at one stage the formation of either a cationic metal center or a zwitterionic structure to ensure that the metal center is sufficiently electrophilic to coordinate olefins. As presented in scheme 3.2, MAO is believed to possess adequate Lewis acidity to abstract a methyl group and generate a cationic metal center. Following these seminal findings, much research has been invested into the study of weakly coordinating anions which can result in the formation of well characterized zwitterionic structures.[7a,b] The formation of an electrophilic metal center is indeed essential to initiation of polymerization.

Given the versatility and performance of the Cp ligands, it comes without surprise that molecules maintaining their primary characteristics have been widely examined. Among the possible alternatives, the pyrrolide anion has attracted the attention of researchers in the field[8] given the close similarity of geometry and electronic configuration. However, the presence of the nitrogen atom in the ring introduces an asymmetry in the corresponding anion which is a substantial deviation from the perfect symmetry of the cyclopentadienyl anion. (Scheme 3.3)



Scheme 3.3: HOMO of Cyclopentadiene(left) and pyrrole (right).

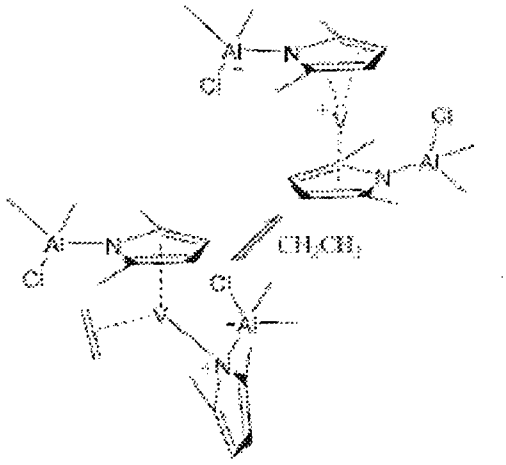
As a result, the sp^2 nitrogen orbital may be competitive with the aromatic π-system for interacting with the transition metal. As a matter of fact, the η^1-bonding mode may be preferential to the η^5 coordination,[9a,b] depending on the nature of the metal. It was reasoned that once a strong Lewis acid such as AlX_3 would lock the N atom through σ-bonding, the η^5 bonding mode of pyrrole could be forced upon the metal center.[10] The isolation of transition metal complexes bearing pyrrole retaining an aluminum alkyl residue could satisfy the prerequisites of active polymerization catalysts. The Lewis acidity of Al could pull electrons away from the metal center, creating a zwitterionic structure (Scheme 3.4). Additionally, the Al residue could perform many of the roles of MAO such as methylation of the metal center and abstraction of halides.



Scheme 3.4: Illustration of partial charge location in transition metal pyrrole complexes bearing aluminum residues.

This strategy has in fact been confirmed and has allowed the preparation of self activating, single site catalyst capable of producing ultra high molecular weight polyethylene.[11] These findings have shown an additional advantage in using pyrrole versus Cp. Pyrrole is a hemilabile ligand in the sense that the π-bonding mode may rapidly interconvert into the σ-bonding. However, while in non-coordinating solvent, this

process opens coordination sites for polymerization and favors the shuttling of one alkyl from aluminum towards the metal center. In the end, the catalytically active metal center becomes cationic, gains the alkyl initiating function and the positive charge. A good catalytic activity is naturally to be expected. The ring slippage, highlighted in scheme 3.4, allows the original catalyst to be regenerated once the growing polymer chain has been eliminated so that polymerization can carry on. The resulting π-bonded complex would have the benefit that its π-bonding and hemilability could be tuned through choice of the Lewis acid coordinated to the N atom of the pyrrolide unit.



Scheme 3.4: Hemilabile ligand; ring slippage of pyrrole during polymerization.[11]

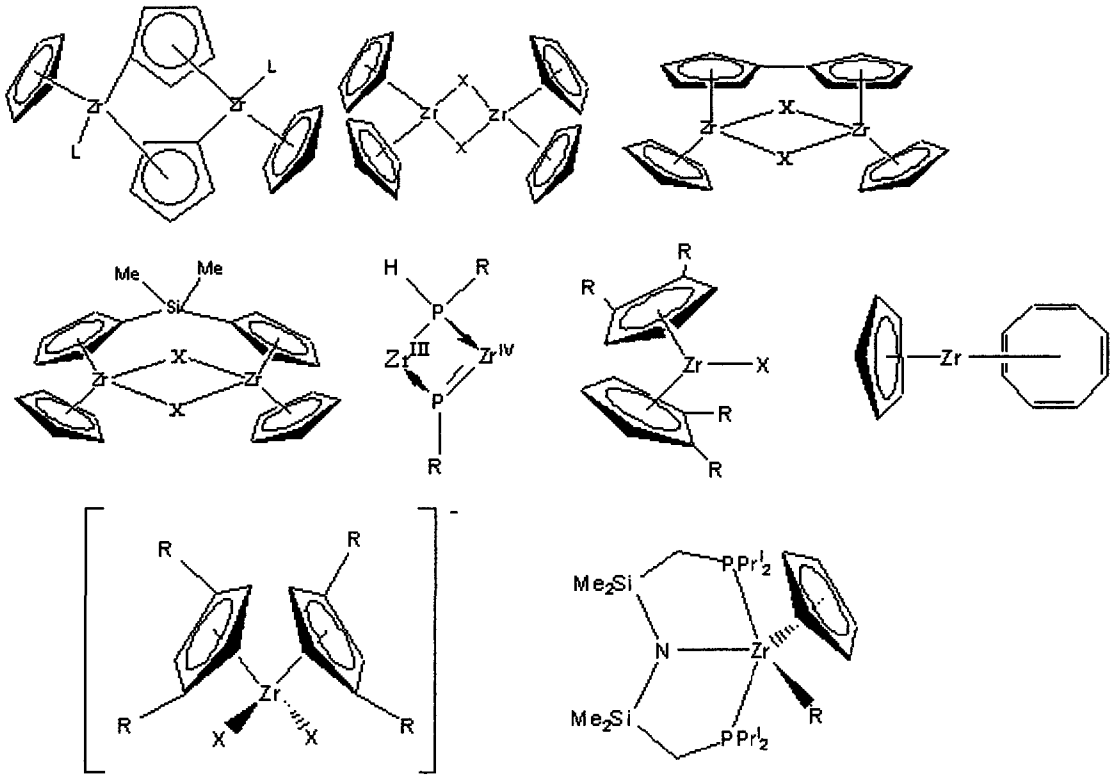
This behavior was initially observed for vanadium, a metal which is notorious for poor activity as an ethylene polymerization catalyst. Even further, the activity was observed for the divalent state and which in the case of vanadium is commonly regarded as the deactivated state. More recently, these findings have been generalized by extending the

investigation to chromium, a better performing element for ethylene polymerization. Two more recent studies have shown a close similarity of behavior to that of vanadium and allowed for elucidation of the factors which allowed chromium to provide active catalysts for either ethylene polymerization or selective trimerization. Therefore, it was natural to extend this research work to group 4 elements which provide the most potent catalytic systems. Zirconium in particular is characterized by an exceedingly robustness of its tetravalent state. By not embarking in redox chemistry it provides the most active, robust and long lasting catalytic systems.

As mentioned above, zirconium is most commonly observed in its +4 oxidation state. The lower valent states +3 and +2, albeit rare, have been characterized. An enormous reactivity is the primary characteristic of divalent zirconium commonly being able to reduce dinitrogen and to perform reduction of a variety of organic substrates, including metallocycle formation upon exposure to ethylene.[12a,b] Instead, a great instability towards disproportionation is the behavior commonly observed for Zr^{III}. Nonetheless, the large negative reduction potential for the Zr^{IV}/Zr^{III} couple ranging from E^0= -1.6 to –2.1V[13a,b] gives expectation for a great reactivity to be found for these derivatives. For example, a simple $[ZrCl_3(PR_3)_2]_2$ has been found capable of reacting with ethylene to form an ethylene bridged dinuclear complex with a bonding mode similar to that observed for samarocene. Since ethylene bridged samarocene provides one of the most spectacular polymerization catalysts capable of producing PE of molecular weight so high that it cannot be measured, expectations are naturally placed by workers in the field for finding interesting Zr(III) based catalytic systems.[14] Additionally,

it has been demonstrated that Zr^{III} complexes are sufficiently reactive to form complexes with dinitrogen.[15a,b]

The first well characterized formally Zr^{III} complexes were the dinuclear species prepared by reduction of $ZrCl_4$ in the presence of trialkylphosphines by Na/Hg.[16a,b] Examples of Zr^{III} complexes seen in literature generally fit into a few families. Most are diamagnetric dimeric, [16a,17a-p] however monomeric examples [14,18a-f] stabilized by phosphorus or nitrogen-based ligand systems also exist. The known families of Zr^{III} complexes are shown in scheme 3.5.



Scheme 3.5: General families of known Zr^{III} complexes.

The observation of diamagnetism in dimeric Zr^{III} structures raises the question of zirconium metal-metal bonds, most notably sparked by the publication of $\{Cp_2Zr[\mu\text{-}P(CH_3)_2$.[17f] Contradicting views of this idea have been published: Bond lengths of 3.233Å,[17d] 3.099 Å, 3.127 Å[17b] have been claimed as containing a Zr-Zr single bond, where 3.420 Å and 3.472 Å[17h] were claimed to lack a metal-metal bond. the d^1 electron count is sufficient to provide for a metal-metal bond and at the same time achieve an 18-electron count for each Zr. The current understanding, based on DFT studies,[19a,b] is that the diamagnetism can only be explained by "superlong" metal-metal σ-bonds, with the superlong length being attributed to ligand steric repulsions. This is a bond in that the electrons are spin paired, however a weak bond since the atomic orbitals do not strongly overlap. It is nearly impossible to unravel completely the metal-metal bonding from the metal-ligand bonding in these bridging complexes. It is believed that the length of the bond does not dictate bonding or non-bonding, as the length is an effect of ligand sterics.

Given the ubiquity of the cyclopentadienyl ligand system among trivalent zirconium complexes, we reasoned that perhaps the iso-electronic pyrrolide anions could be able to provide useful and catalytically active trivalent complexes. In case the trivalent state could not be achieved, even straightforward tetravalent analogues would be interesting due to the close similarity with the classical zirconocene catalysts.

Herein we report our findings.

Experimental:

All operations were performed under an inert atmosphere using Schlenk

üü♣♥ └<p– techniques with a nitrogen-vacuum line or a nitrogen filled dry box. All solvents were 80

Experimental:

All operations were performed under an inert atmosphere using Schlenk techniques with a nitrogen-vacuum line or a nitrogen filled dry box. All solvents were dried using a column of Al_2O_3 under nitrogen atmosphere, degassed *in vacuo* and stored over molecular sieves under inert atmosphere. $ZrCl_4$ was purchased from Strem Chemicals and used as received. $ZrCl_4(THF)_2$ was prepared according to standard procedures. 2,3,4,5-tetramethylpyrrole,[20] 2,3,4,5-tetraphenylpyrrole,[21] diphenyldi(2-pyrrolyl)methane, 1,1(2-pyrrolyl)cyclohexane[22] were also prepared according to published literature procedures. All aluminum alkyl reagents, pyrrole, 2,5-dimethylpyrrole, were purchased from Sigma Aldrich and used as received. Magnetic susceptibility measurements were recorded at room temperature using a Johnson Matthey Gouy balance and corrected for diamagnetism. NMR spectra were recorded on a Varian INOVA 500MHz spectrometer using sealed NMR tubes prepared inside a drybox. Elemental Analyses were performed using a Perkin-Elmer Series II CHN/O 2400 analyser.

Catalyst testing was carried out in a 300 mL high pressure Büchi reactor containing a heating/cooling jacket. A pre-weighed amount of catalyst was dissolved in 100 mL of toluene under N_2 prior to loading the reaction vessel. Solutions were heated using a thermostatted bath and charged with ethylene, maintaining the pressure throughout the run. Polymerization mixtures were quenched by addition of MeOH and HCl. The resulting polymer was isolated by filtration, sonicated with a solution of HCl,

Preparation of (η^5[2,5-$Me_2C_4H_2N${$AlCl_2Et$}])$_2ZrCl_2$ (3.1)

A suspension of $ZrCl_4$ (200mg, 0.85mmol) in toluene (5mL) and at room temperature was combined with a clear solution of 2,5-dimethylpyrrole (163mg, 1.71mmol) in toluene (5mL) and at room temperature affording a light orange solution. A solution of $(C_2H_5)_2AlCl$ (1.9 mL, 1.8 M in toluene, 3.4 mmol) was subsequently added, dropwise over a period of 1 minute producing gas evolution and a dark brown solution. Stirring was maintained for a period of 1h and insoluble materials were removed by centrifugation affording a brown solution. Light yellow crystals of **3.1** (303 mg, 0.50 mmol, 59%) were grown after 24h at -37°C. NMR(C_6D_6, 500MHz): ^{1}H: 5.6(4H, br, Ar-*H*), 2.2(12H, s, Ar-CH_3), 1.3(4H, quartet, Al-CH_2), 0.8(6H,t,$AlCH_2CH_3$). Anal Calcd for $C_{16}H_{26}Al_2Cl_6N_2Zr$: C, 34.08, H, 5.08, N, 4.42. Found: C, 34.15, H, 5.21, N, 4.29.

Preparation of (η^5[2,5-$Me_2C_4H_2N${$AlClMe_2$}])$_2ZrClMe$ (3.2)

A clear solution of $ZrCl_4(THF)_2$ (200 mg, 0.53 mmol) in toluene (5 mL) and at room temperature was combined with a clear solution of 2,5-dimethylpyrrole (100 mg, 1.06 mmol) in toluene (5 mL) and at room temperature producing a light orange solution. A solution of $(CH_3)_2AlCl$ (1.59 mL, 2.0 M in toluene, 3.18 mmol) was subsequently added dropwise over a period of 1 minute giving gas evolution and affording an orange solution. Stirring continued for 1h and the insoluble materials were removed by centrifugation. The orange solution was concentrated to 1/3 volume *in vacuo* and crystals of **3.2**(205mg, 0.38mmol, 64%) were grown after 48 h period at room temperature. NMR(C_6D_6, 500MHz): ^{1}H: 5.6(2H, br, pyr-*H*), 5.5(2H, br, pyr-*H*), 5.4(4H, br, pyr-*H*),

0.4(3H, s, Zr-CH_3), -0.2(6H, s, Al-CH_3). Anal Calcd for $C_{19}H_{37}Al_2Cl_3N_2Zr$: C, 41.87, H, 6.84, N, 5.14. Found: C, 42.31, H, 7.11, N, 5.03.

Preparation of (η^5[2,5-$Me_2C_4H_2N${$AlClMe_2$}])$_2ZrCl_2$ (3.3)

A clear solution of $ZrCl_4(THF)_2$ (200 mg, 0.53 mmol) in toluene (5 mL) and at room temperature was combined with a clear solution of 2,5-dimethylpyrrole (100 mg, 1.06 mmol) in toluene (5 mL) and at room temperature forming a light orange solution. A solution of $Al(CH_3)_3$ (1.05 mL, 2.0M in toluene, 2.1 mmol) was subsequently added, dropwise over a period of 1 minute producing gas evolution and an orange solution. Stirring continued for 1h and then insoluble materials were removed by centrifugation. The orange solution was concentrated to 1/3 volume *in vacuo* and crystals of **3.3**(212mg, 0.323mmol, 61%) were grown after 48h period at room temperature. NMR(C_6D_6, 500MHz): ^{1}H: 5.6(2H, br, pyr-*H*), 5.5(2H, br, pyr-*H*), 5.4(4H, br, pyr-*H*), 0.4(6H, s, Zr-CH_3), -0.2(6H, s, Al-CH_3). Anal Calcd for $C_{18}H_{34}Al_2Cl_2N_2Zr$: C, 38.23, H, 6.06, N, 4.95. Found: C, 45.65, H, 6.44, N, 4.26.

Preparation of (η^5[C_4H_4N{$AlClMe_2$}])$_2ZrMe_2$ (3.4)

A suspension of $ZrCl_4$ (200mg, 0.85mmol) in toluene (5mL) and at room temperature was combined with a clear solution of pyrrole (107 mg, 1.7 mmol) in toluene (5mL) producing a pale yellow solution. A solution of $(CH_3)_2AlCl$ (3.4 mL, 2M in toluene, 6.8 mmol) was added dropwise with stirring affording gas evolution and a dark brown colored solution. Following 1.5h stirring, insoluble materials were removed by centrifugation. Pale yellow, microcrystalline **3.4** (283mg, 0.60mmol ,71%) was obtained

upon allowing the resulting orange solution to stand at –37°C for 48 h. NMR(C_6D_6, 500MHz): ^{1}H: 5.4-5.6(8H,m,pyr-*H*), 0.4(6H, s, Zr-CH_3), -0.2(12H, s, Al-CH_3). Anal Calcd for $C_{12}H_{20}Al_2Cl_4N_2Zr$: C, 41.02, H, 6.88, N, 5.98. Found: C, 41.47, H, 7.08, N, 5.89.

Preparation of ([{$Ph_2C(C_4H_3N)_2$}Zr_2]$_4$(μ-Cl)$_{12}$) ([μ-Cl]$_2$Al{CH_3}$_2$)$_4$ (3.5)

Method A. A suspension of $ZrCl_4$ (200 mg, 0.85 mmol) in toluene (5 mL) was combined at room temperature with a clear solution of diphenyldi(2-pyrrolyl)methane (256 mg, 1.70 mmol) in toluene (5 mL) producing a clear yellow solution. A solution of $Al(CH_3)_3$ (1.7 mL, 2M in toluene, 3.4 mmol) was subsequently added affording a dark green solution. Stirring continued for 1.5 h and the insoluble materials were removed by centrifugation. Dark green crystals of **3.5** (182mg,0.434mmol, 51%) were grown from the resulting dark green solution after 2 weeks at –37°C. NMR(THF-d_8, 500MHz): ^{1}H: 7.1(40H, m, Ar), 6.7(8H, s, pyr-*H*), 6.0(8H, s, pyr-*H*), 5.8(8H, s, pyr-*H*), -0.6(24H, s, Al-CH_3). Anal Calcd for $C_{92}H_{96}Al_4Cl_{20}N_8Zr_8$: C, 38.63, H, 3.38, N, 3.92. Found: C, 48.85, H, 4.21, N, 3.07.

Method B. A suspension of $ZrCl_4$ (200 mg, 0.85 mmol) in toluene (5mL) and at room temperature was combined with a clear solution of diphenyldi(2-pyrrolyl)methane (128 mg, 0.85 mmol) in toluene (5 mL) producing a clear yellow solution. A solution of $Al(CH_3)_3$ (1.7 mL, 2M in toluene, 3.4 mmol) was subsequently added producing a dark green solution. Stirring was continued for 1.5h and the insoluble materials were removed by centrifugation affording a dark green solution. Dark green crystals of **3.5** were grown

after 2 weeks at –37°C.

Preparation of ([{Cy(C_4H_3N)$_2$}Zr_2]$_4$(μ-Cl)$_{12}$)([μ-Cl]2Al{CH_3}$_2$)$_4$ (3.6).

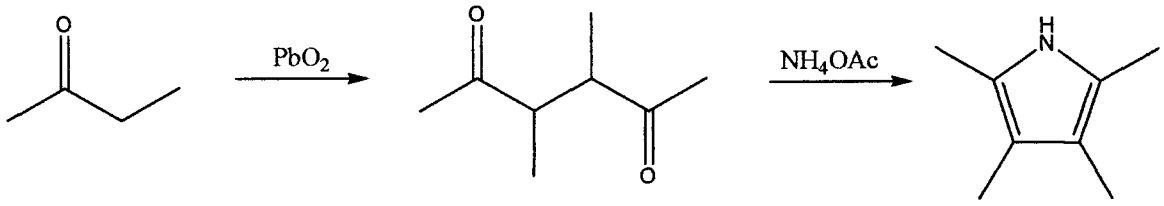
A suspension of $ZrCl_4$ (200 mg, 0.85 mmol) in toluene (5 mL) and at room temperature was combined with a clear solution of 1,1(2-pyrrolyl)cyclohexane (184 mg, 1.70 mmol) in toluene (5 mL) producing a clear yellow solution. The subsequent addition of a solution of $Al(CH_3)_3$ (1.7 mL, 2M in toluene, 3.4 mmol) afforded a dark green solution. Stirring continued for 1.5h and the insoluble materials were removed by centrifugation giving a dark green solution. Dark green crystals of **3.6** (150mg, 0.478mmol, 56%) were grown after 2 weeks at –37°C. NMR(THF-d_8, 500MHz): ^{1}H: 6.0-6.8 (24H, m, pyr-*H*), 1.4 (40H,m, Cy-*H*), -0.4(24H, s, Al-CH_3). Anal Calcd for $C_{64}H_{96}Al_4Cl_{20}N_8Zr_8$: C, 30.45, H, 3.83, N, 4.44. Found: C, 32.02, H, 4.23, N, 4.25.

Preparation of ([AlEtCl{μ-Cl}$_2$][{C_4H_4N}$_2$AlClEt]Zr_2(μ-Cl)$_4$)$_2$ · 4 (C_7H_8) (3.7)

A suspension of $ZrCl_4$ (200 mg, 0.85 mmol) in toluene (5 mL) and at room temperature was combined with a solution of diphenyldipyrromethane (256 mg, 1.70 mmol) in toluene (5 mL) and at room temperature. A solution of $(C_2H_5)_2AlCl$ (2.0 mL, 1.9 M in toluene, 3.8 mmol) was subsequently added dropwise producing a caramel brown solution. Following 1h stirring, a dark brown solution was obtained and insoluble materials were removed by centrifugation. Dark brown crystals of **3.7** (267mg, 0.577mmol, 68%) were grown at room temperature following slow evaporation of solvent over a 48h period. Anal Calcd for $C_{52}H_{68}Al_4Cl_{16}N_4Zr_4$: C, 22.71, H, 3.27, N, 3.78. Found: C, 35.47, H, 4.32, N, 3.05.

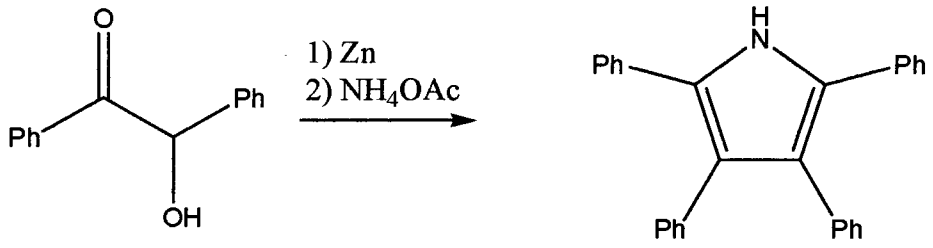
Results and Discussion:

Some pyrrole ligands are commercially available. The 2,3,4,5-tetramethylpyrrole was deemed to be particularly interesting for this study aiming at zirconium chemistry given the close similarity with the permethylated cyclopentadienyl systems. It is worth reminding that the combination of alkylated Cp with zirconium or lanthanides has produced one of the largest and richest chapters of organometallics chemistry. Unfortunately this ligand is not available from a commercial source. It was therefore synthesized via dimerization of 2-butanone by extraction of lead dioxide over a 48 hour period. The ring closing condensation reaction was carried out via simple addition of excess ammonium acetate affording the desired pyrrole which was recrystallized from 50/50 water/methanol mixture(Scheme 3.6).



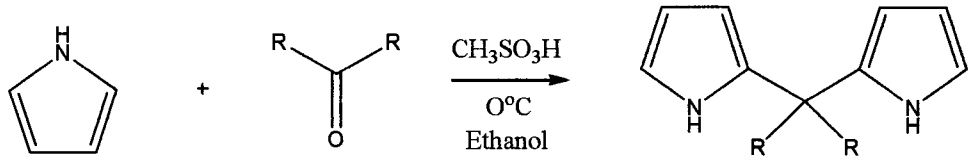
Scheme 3.6: Synthesis of 2,3,4,5-tetramethylpyrrole.

The 2,3,4,5-Tetraphenylpyrrole was also regarded as an interesting sterically demanding ligand and whose electronic properties were hard to predict. In any event, the preparation could be readily be performed with one-pot reaction of 2-hydroxy-1,2-diphenylethanone with excess zinc dust and ammonium acetate under reflux(Scheme 3.7).



Scheme 3.7: Synthesis of 2,3,4,5-tetraphenylpyrrole.

Another interesting variation of theme in this family of ligands was provided by the dipyrrole ligands. Should both rings be π-bonded to the same metal, the dipyrrole will adopt a geometry closely reminiscent of the *ansa*-metallocene type of motif. Ansa-zirconocenes have shown the greatest improvement of the reactivity and catalytic behavior amongst metallocenes, due to the ring bending constraints. The preparation of a series of dipyrroles was readily accomplished through acid catalyzed condensation reaction of ketone with 2 equivalents of pyrrole in ethanol at low temperature, as shown (Scheme 3.8).



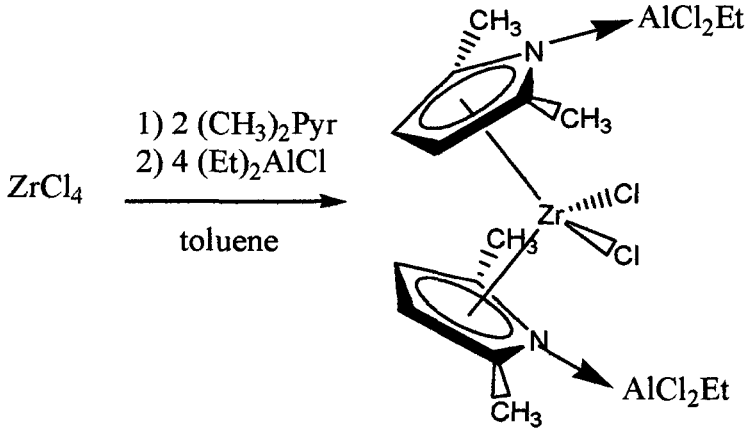
R=Ph, Et, Me.

Scheme 3.8: Synthesis of dipyrrole ligands.

The complexations have been carried out via preliminary deprotonation of the N-H groups with potassium hydride followed by reaction with the metal starting material. The possibility of carrying out one-pot reactions of metal starting material, pyrrole and alkyl aluminum reagents was also probed. This procedure proved to be particular versatile for enforcing the π-bonding mode of the ring around the transition metals. In fact, pyrrolide anions are known to be fluxional and to readily interconvert the σ- and π– bonding mode. We reasoned that by coordinating a strong Lewis acid, such as alkyl aluminum, to the sp^2 nitrogen atom of the deprotonated pyrrole, the π-bonding mode to the zirconium metal center would naturally occur as the sole bonding possibility.

The reactions between 2,5-dimethylpyrrole, 2,3,4,5-tetramethylpyrrole, and 2,3,4,5-tetraphenylpyrrole were carried out in toluene and at room temperature with either starting materials $ZrCl_4$ or $ZrCl_4(THF)_2$ and in the presence of a moderate excess of aluminum alkyl reagents, $AlR_{3-x}Cl_x$. Where crystalline materials were obtained, the compounds were tested for possible catalytic behavior.

When two equivalents 2,5-dimethylpyrrole were combined in toluene with $ZrCl_4$ and four equivalents of Et_2AlCl, the Zr^{IV} sandwich complex ($C_{16}H_{26}Al_2Cl_6N_2Zr$) **3.1** was obtained (Scheme 3.9). This complex contained the two pyrrolide rings bearing aluminum residues and adopting the expected π-bonding mode.



Complex 3.1

Scheme 3.9: Synthesis of complex 3.1.

Complex 3.1 was characterized crystallographically (figure 3.3). NMR spectra and elemental analysis agreed with the formulation. It was assumed that complex **3.1** was an excellent candidate to act as a self-activating ethylene polymerization catalyst, as the aluminum residue could possibly shuttle ethyl groups to zirconium thus initiating polymerization. This expectation was based on the behavior of the chromium and vanadium analogues which were self activating catalysts producing good quality UHMWPE.[11,23]. However complex 3.1 is not a self-activating catalyst as a possible result of the fact that the metal rests in this complex in its highest oxidation state. However, upon activation with one thousand equivalents of MAO (Table 3.1) some moderate activity was observed which is comparable to similar Zr^{IV} metallocene catalysts, however it is nowhere near the highest activities observed.[6,4b]

One pot combination of $ZrCl_4(THF)_2$ with two equivalents of 2,5-dimethylpyrrole and six equivalents of $(CH_3)_2AlCl$ in toluene once again produced crystals of the Zr^{IV} sandwich complex ($C_{17}H_{31}Al_2Cl_3N_2Zr$) **3.2,** which was also crystallographically

characterized (Figure 3.4). The appearance of this complex is very similar to 3.1 the only difference consisting of the 50/50 occupancy of the chlorine atoms with methyl groups (Scheme 3.10). Integration of the NMR(figure 3.1) resonances and elemental analysis data were in agreement with the formulation. Although figure 3.2 shows that the pyrrole rings are eclipsed with respect to the direction that their methyl groups extend from the ring at low temperature, a VT NMR study shows that at 70°C coalescence of pyrrole aromatic and pyrrole methyl group protons occur (figure 3.1).

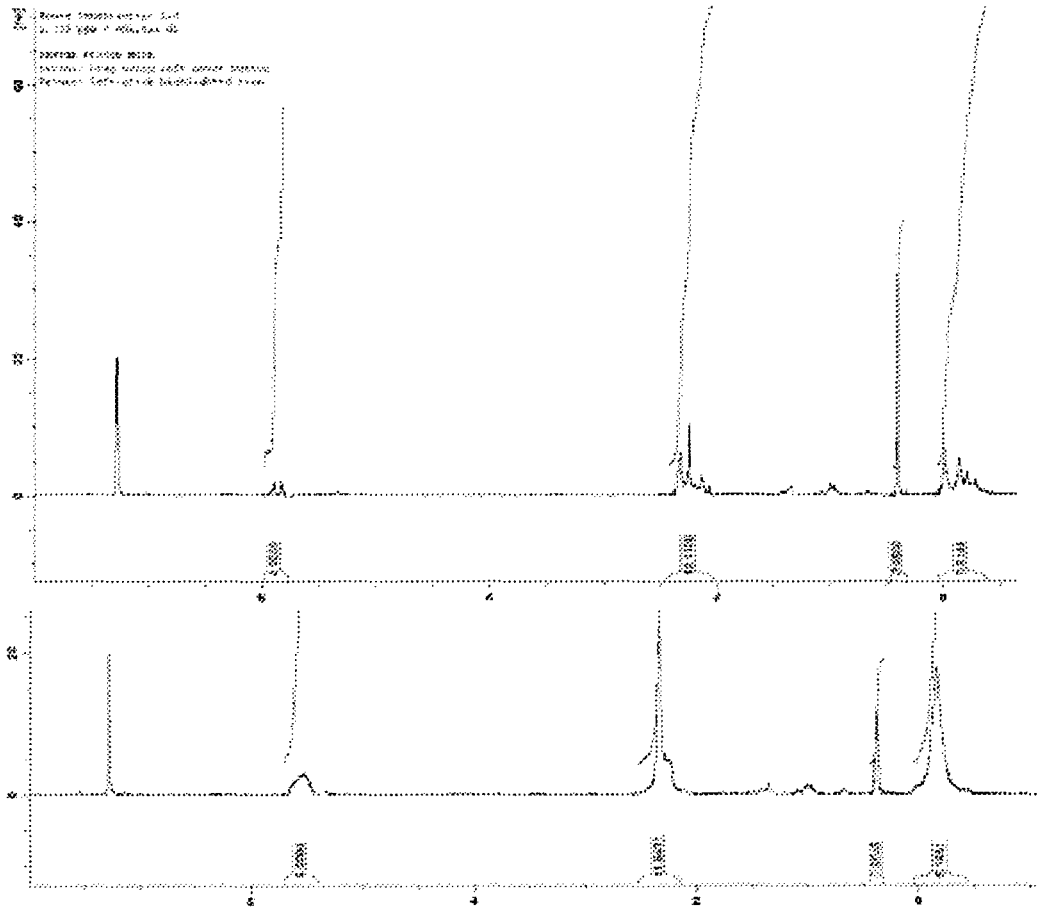
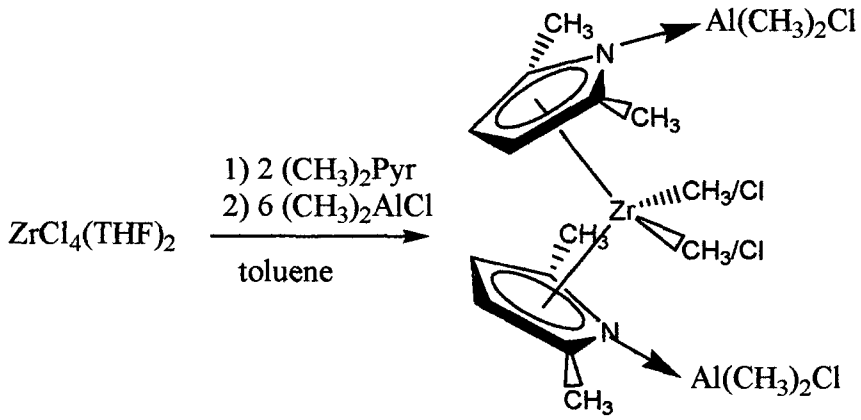


Figure 3.1: ^{1}H NMR of complex 3.2 at RT (top) and 70°C(bottom).

This indicates that the rings freely rotate, possibly indicating lability of the ring and hopefully enabling single-component catalytic behavior.

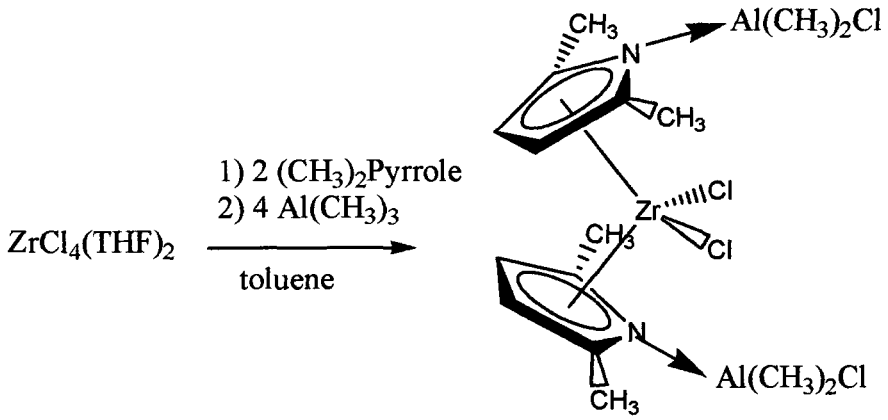


Complex 3.2

Scheme 3.10: Synthesis of complex **3.2**.

Catalytic testing of complex **3.2** revealed that even this species is not a self activating catalyst. Similar to the case above, moderate activity can be only observed upon activation with one thousand equivalents of MAO (Table 3.1).

Another Zr^{IV} sandwich compound ($C_{16}H_{28}Al_2Cl_4N_2Zr$) **3.3** was prepared from combination of $ZrCl_4(THF)_2$ with two equivalents of 2,5-dimethylpyrrole and four equivalents of trimethylaluminum (Scheme 3.11)

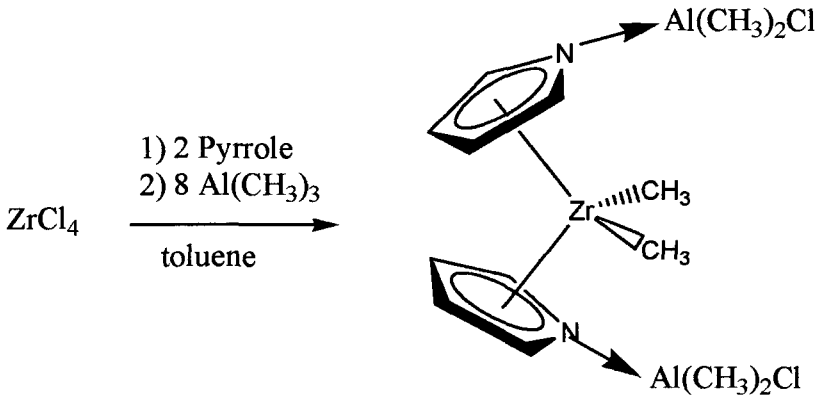


Complex 3.3

Scheme 3.11: Synthesis of complex 3.3.

Once again, Zr was coordinated to two π-bound, aluminum containing pyrrole rings. This time the other two sites were occupied solely by chlorine atoms, as determined by X-ray crystallographic methods(figure 3.5), NMR, and elemental analysis. It was hoped that in comparison to **3.1**, the methyl groups bound to Al would more readily shuttle towards the transition metal center than ethyl groups thus triggering self activating behavior. However, catalytic testing showed that complex **3.3** also was not a self activating catalyst. In line with complexes **3.1** and **3.2**, catalytic testing using one thousand equivalents of MAO produced low activity for polymerization of ethylene (Table 3.1).

Combination of $ZrCl_4$ with two equivalents of pyrrole and eight equivalents $(CH_3)_2AlCl$ in toluene produced microcrystals of complex ($C_{14}H_{26}Al_2Cl_2N_2Zr$) **3.4**. Although in this case the crystallinity did not allow undertaking an X-ray crystallographic determination, a convincing structural assignment was obtained on the basis of NMR spectra and comparison to those of previously characterized compounds **3.1, 3.2, 3.3**. (Scheme 3.12).



Complex 3.4

Scheme 3.12: Synthesis of complex **3.4**.

In these preparations the stoichiometric Al/Zr ratio dictates the methyl occupancy of the chlorine atoms. Catalytic testing of **3.4** showed that when activated by one thousand equivalents of MAO, 30μmol catalyst can produce up to 13.2 g PE in 1h. This catalytic activity appears to be more substantial even though far from that of the most active zirconium catalysts.

Table 3.1: Catalyst activity of isolated Zr^{IV} complexes **3.1, 3.2, 3.3, and 3.4.**

Run	Complex	Loading (μmol)	Co-Catalyst	Yield (g PE)	Activity (g $mmol^{-1}$ h^{-1} bar^{-1})
1	3.1	30	None	Negligable	0
2	3.1	30	1000 eq. MAO	9.3	8.9
3	3.2	30	None	Negligable	0
4	3.2	30	1000 eq. MAO	7.9	7.5
5	3.3	30	None	Negligable	0
6	3.3	30	1000 eq. MAO	8.1	7.7
7	3.4	30	1000 eq. MAO	13.2	12.6

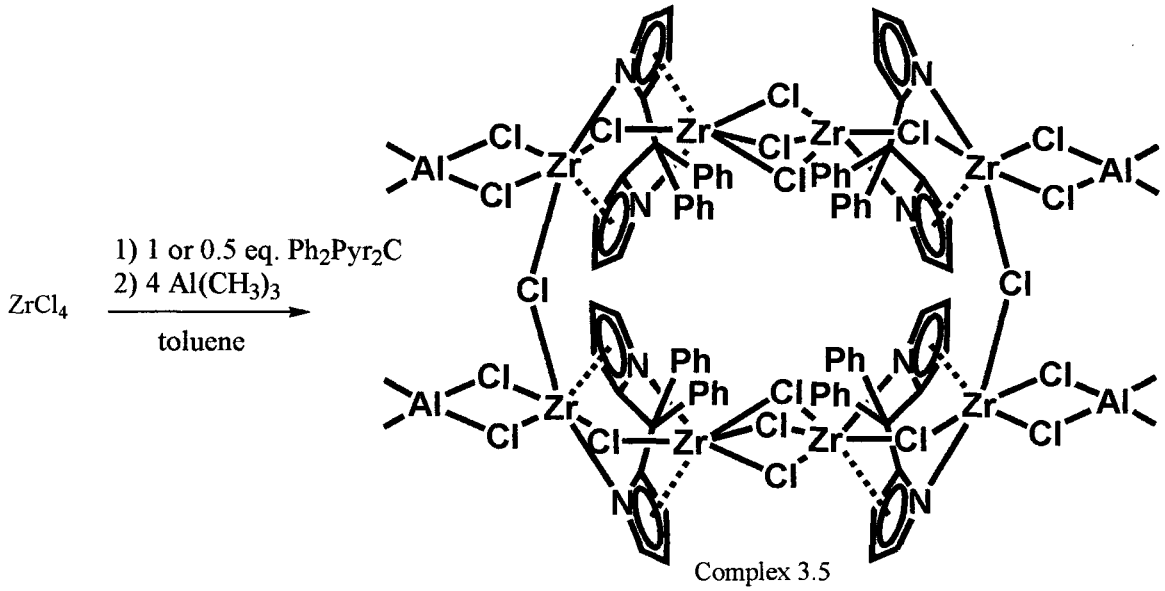
All runs were performed for 1 hour at 35 bar ethylene pressure and at a temperature of 70°C in 100mL toluene.

Attempts to coordinate 2,3,4,5-tetramethylpyrrole with zirconium and aluminum alkyl reagents were unsuccessful as only intractable materials could be isolated. Combination of 2,3,4,5-tetraphenylpyrrole, zirconium starting materials, and aluminum alkyl reagents always led to isolation of unreacted pyrrole. It was assumed that the phenyl rings are too bulky to allow deprotonation and coordination of Al to the pyrrole nitrogen atom.

A few generalizations can be drawn regarding the one pot coordination of Zr^{IV} starting materials with two equivalents of pyrrole ligands, and variable amount of aluminum alkyl reagents. Formation of tetravalent sandwich compounds was systematically observed. The complexes always contained two π-bound pyrrolide rings bearing aluminum alkyl residues, and either Cl or CH_3 on the remaining two coordination sites. These complexes are not self-activating catalysts, and even upon activation proved to be unexciting polymerization catalysts.

Therefore, we turned our attention to the dipyrrolide systems since the constrained bend geometry has been a key to success in boosting the catalytic activity of metallocene systems. The one pot reaction of the intact ligand with Zr salt and in the presence of a variety of alkyl aluminum reagent allowed some interesting observations.

The reaction of $ZrCl_4$ with one equivalent of diphenyl di(2-pyrrolyl)methane and four equivalents of trimethylaluminum afforded the octameric complex ($C_{92}H_{96}Al_4Cl_{20}N_8Zr_8$) **3.5**. The fascinating feature of this complex is that the zirconium atom is present in its very rare trivalent oxidation state (Scheme 3.13).



Scheme 3.13: Synthesis of complex **3.5.**

The assembly of the octameric structure is not surprising *per se* since the very same ligand has afforded macrocyclic polymetallic structures with a variety of lanthanides[22,24] and transition metals such as Mn.[25] By contrast, the reduction of zirconium to its trivalent state is a rare event which requires always the use of strongly reducing agents such as alkali or alkaline-earth metals.[14,17p,18c] In addition, there is an inherent inclination of the trivalent state towards disproportionation as indicated by the thermal instability of these derivatives. Since the disproportionation proceeds via dimerization,[19a,b] the employment of sterically demanding ligands , which may prevent aggregation in favor of mononuclear species, remains the only strategy to prepare monomeric form of these d^1 paramagnetic compound. The commonly observed diamagnetism of trivalent zirconium has been explained with the presence of superlong Zr-Zr bonds although the presence of efficient ligand mediated superexchange is the most realistic scenario.[19a,b]

While the mechanism of formation of 3.5 is unclear, the σ-,π-bridging interaction formed by the ligand system is not surprising on the ground of literature precedents. What is surprising is that the Al residues are not coordinated to pyrrole but remained bridged to the zirconium center via chlorine. Still the reduction of the metal center can be only caused by the alkyl groups carried by aluminum. The thought that alkyl aluminum reagents may work as reductants is not terribly surprising provided that thermally labile metal alkyl functions are generated. This is for example normally encountered in Ti[26] and Cr[23] chemistry. However, in the case of zirconium, which like lanthanides is normally providing thermally robust alkyls, the spontaneous reduction via alkylation is utterly rare and documented only in the preparation of one case of Zr^{III} metallocene[17n] and in situ formation of Zr(II) derivatives.[12a,b] The structure however contains no N-Al bonds, unlike previously observed in **3.1, 3.2, 3.3.** Solubility in non-coordinating deuterated solvents was low and NMR spectrum was obtained only in THF-d_8 as it appeared that the complex did not dissociate in the presence of THF.

It was speculated that the low-valent, highly reactive Zr^{III} oxidation state would be an excellent candidate for a self-activating ethylene polymerization catalyst (Table 3.2). However all attempts at catalysis proved futile as the complex appeared to be too stable and ligands not sufficiently labile to allow coordination of ethylene. Additionally, when the activator MAO was used to initiate polymerization, merely 1.3g of polyethylene were obtained. Again, the lability of the dipyrrole ligand bonded to Zr^{III} was not high enough to allow coordination of ethylene and starting polymerization.

When other dipyrrole ligands were used in place of diphenyldi(2-pyrrolyl)methane, such as 1,1(2-pyrrolyl)cyclohexane, and diethyldi(2-pyrrolyl)methane,

in the analogous reaction, similar observations were made. The distinct dark green colour was observed when the reagents were combined, however crystalline samples were not obtained. In the case of 1,1(2-pyrrolyl)cyclohexane, an NMR (Figure 3.2) in THF-d_8 appeared to indicate that the analogous compound ($C_{64}H_{96}Al_4Cl_{20}N_8Zr_8$) **3.6** had been formed.

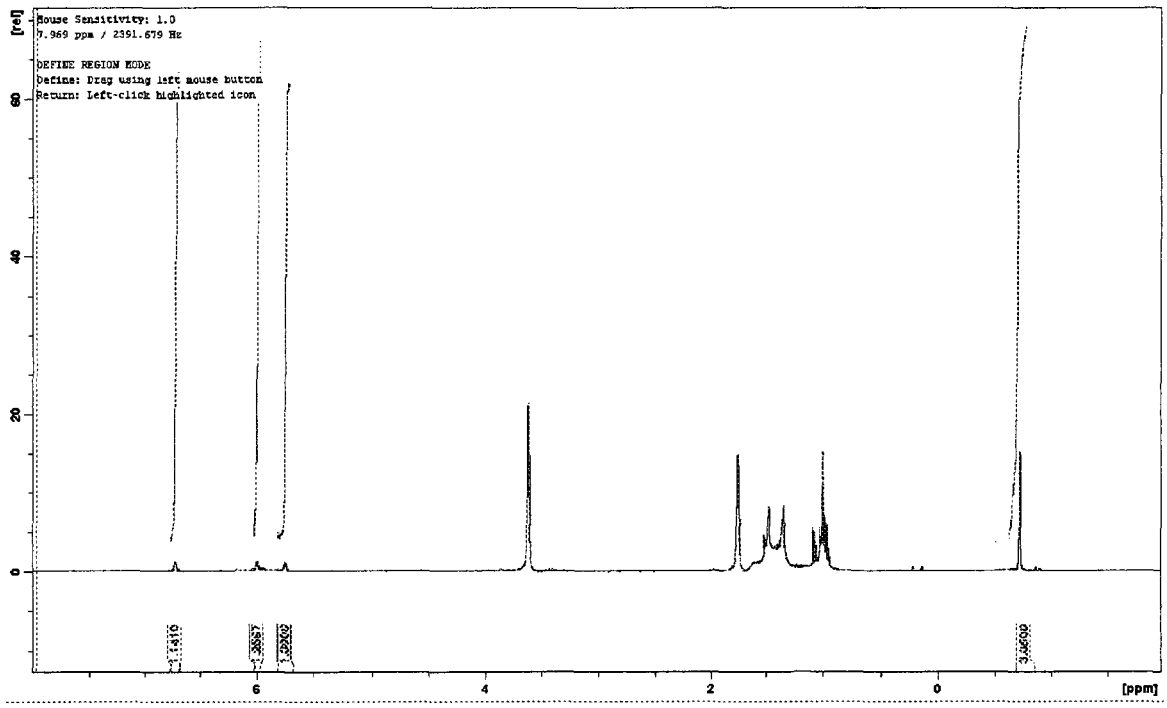
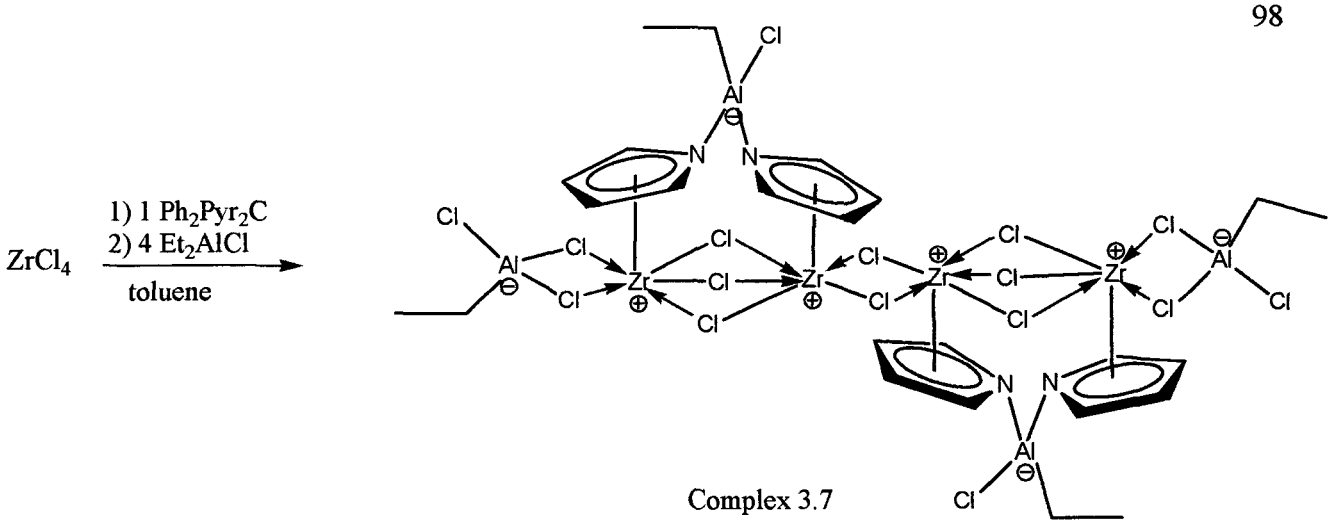


Figure 3.2: ^{1}H NMR of complex 3.6 in thf d^8.

Further experimentation to follow up this encouraging observation was performed by replacing $Al(CH_3)_3$ with other aluminum alkyl reagents such as the more reducing $(C_2H_5)_2AlCl$ and $Al(C_2H_5)_3$. When $ZrCl_4$ was combined with 1 equivalent of diphenyldi(2-pyrrolyl)methane and four equivalents of $(C_2H_5)_2AlCl$ in toluene, another low valent Zr complex was obtained (Scheme 3.14).



Scheme 3.14: Synthesis of complex **3.7.**

Diamagnetic **3.7** indicates that a Zr-Zr bond is in fact present, or that antiferromagnetic superexchange is taking place. Examination of the Zr-Zr distances shows the shortest ever recorded, [Zr(1)-Zr(2) = 3.045(2)Å]. Since, as previously stated, the length of the bond is not conclusive indication of the presence of a bond, we cannot conclude that a σ-bond is in fact present. The pyrrolide-Al-pyrrolide bridging framework is capable of bringing Zr atoms together to an unprecedented short distance.

The crystal structure revealed that during this transformation the dipyrrole ligands have been transformed into regular pyrrole. In turn this implies that R_2C units have been eliminated somehow. It was speculated that the formation of ($C_{52}H_{68}Al_4Cl_{16}N_4Zr_4$) **3.7** proceeded via intermediate formation of Zr^{II} species, as it was also further corroborated by initial observation of formation of dark brown colors. Unstable Zr^{II} could then have provided the electrons necessary to cleave dipyrrole while being oxidized to trivalent state of the final compound. In that scenario, tetraphenylethylene was expected to accompany the formation of the trivalent final complex. Quenching of the mother liquor

followed by organic separation techniques did not lead to isolation of tetraphenylethylene and so the mechanism of formation remains unknown.

When $ZrCl_4$ was combined with one equivalent of diphenyldi(2-pyrrolyl)methane and four equivalents of the more reducing $(C_2H_5)_3Al$, in line with schemes 3.8 and 3.9. Very dark brown (almost black) solutions and oils were formed.

Catalytic testing showed that complexes **3.5**, **3.7** were not self-activating catalysts (Table 3.2). However this complex, when activated with one thousand equivalents of MAO showed some moderate activity towards polymerization of ethylene as it produced 5.6 g PE from 30 μmol of catalyst.

Table 3.2: Catalytic testing of complex **3.5, 3.7**.

Run	**Complex**	**Loading(μmol)**	**Co-Catalyst**	**Yield (gPE)**	**Activity (g $mmol^{-1}$ h^{-1} bar^{-1}**
8	3.5	30	None	Negligable	0
9	3.5	30	1000eq. MAO	1.3	1.2
10	3.7	30	None	Negligable	0
11	3.7	30	1000eq. MAO	6.5	6.2

All runs were performed for 1 hour at 35 bar ethylene pressure and at a temperature of 70°C in 100mL toluene.

Conclusions:

This exploratory work on the use of pyrrole and dipyrrole based ligand systems for the preparation of zirconocene and *ansa* zirconocene analogues afforded the expected compounds. Although the catalytic behavior was disappointing, the ability to stabilize the trivalent state is remarkable. The successful structural characterization of the first octameric(**3.5**) and tetrameric(**3.7**) Zr^{III} compounds open new perspective for the use of these ligands to enter the rare domain of low-valent zirconium. Even more remarkable was the degradation of the dipyrrole ligand framework performed by Et_3Al and which necessarily implies formation of even lower valent intermediate species, and led to the shortest known Zr-Zr intermetallic distance. We also obtained some tenuous evidence about possible stabilization of divalent zirconium complexes, which will be the target of future work in the view of the established ability of divalent zirconium to perform dinitrogen activation and possibly ethylene selective trimerization.

Crystal Structure Data:

A single crystal suitable for X-ray diffraction measurements was mounted on a glass fibre. Unit cell measurements and intensity data collections were performed on a Bruker-AXS SMART 1 k CCD diffractometer at 202K using graphite monochromatized Mo K_α radiation (λ = 0.71073 Å). Unit cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. The data reduction included a correction for Lorentz and polarization effects, with an applied multi-scan absorption correction (SADABS). Crystal structures were solved and refined using the SHELXTL program suite. Direct methods yielded all non-hydrogen atoms which were refined with anisotropic thermal parameters. All hydrogen atom positions were calculated geometrically and were riding on their respective atoms.

Crystals of complexes **3.1, 3.2, 3.3, 3.5, 3.7** were grown from toluene solutions. A single crystal suitable for X-ray diffraction measurements was mounted on a glass fibre. The crystal data and refinement parameters for **3.1, 3.2, 3.3, 3.5, 3.7** are listed in table 3.3. Selected interatomic distances and angles for **3.1, 3.2, 3.3, 3.5, 3.7** are listed in figures 3.3, 3.4, 3.5, 3.6, 3.7 respectively. The reflection patterns for **3.1, 3.2, 3.3** were consistent with a monoclinic system, C2/c, and for **3.5, 3.7** were consistent with a triclinic system, P-1.

Table 3.3: Crystal data and refinement parameters for complex **3.1, 3.1, 3.3, 3.5, 3.7.**

Identification Code	**3.1**	**3.2**	**3.3**	**3.5**	**3.7**
Empirical Formula	$[C_{16}H_{26}Al_2Cl_6N_2Zr]$	$C_{17}H_{31}Al_2Cl_3N_2Zr$	$C_{16}H_{28}Al_2Cl_4N_2Zr$	$C_{296}H_{304}Al_8Cl_{40}N_{16}Zr_{16}$	$C_{52}H_{68}Al_4Cl_{16}N_4Zr$
Formula Weight	604.27	513.74	535.38	7178.91	1789.10
Temperature	201(2) K	203(2) K	202(2) K	201(2)K	203(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal System	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space Group	C2/c	C2/c	C2/c	P-1	P-1
Unit cell Dimensions	a = 0.0633(13) Å b= 13.2556(17) Å c = 18.485(2) Å α = 90° β = 92.122(2)° γ = 90°	a = 9.5130(19) Å b = 13.316(3) Å c = 19.035(4) Å α = 90° β= 90.853(3)° γ = 90°	a = 9.527(9) Å b = 13.335(9) Å c = 19.051(14) Å α= 90°. β= 90.583(14)°. γ = 90°	a = 16.878(3) Å b = 21.680(4) Å c = 23.191(4) Å α = 76.838(3)° β= 74.243(2)° γ= 81.163(3)°	a = 10.844(5) Å b = 10.936(5) Å c = 16.234(8) Å α = 72.666(7)°. β = 83.816(7)° γ = 85.847(7)°
Volume	2439.5(5) $Å^3$	2411.0(8) $Å^3$	2420(3) $Å^3$	7914(2) $Å^3$	1825.5(15) $Å^3$
Z	4	4	4	1	1
Density (calculated)	1.645 Mg/m^3	1.415 Mg/m^3	1.469 Mg/m^3	1.506 Mg/m^3	1.627 Mg/m^3
Absorption Coefficient	1.186 mm^{-1}	0.859 mm^{-1}	0.972 mm^{-1}	0.915 mm^{-1}	1.225 mm^{-1}
F(000)	1216	1054	1088	3616	892
Crystal Size	0.25 x 0.15 x 0.10 mm^3	0.40 x 0.40 x 0.10 mm^3	0.10 x 0.10 x 0.05 mm^3	0.35 x 0.10 x 0.06 mm^3	0.10 x 0.10 x 0.05 mm^3
Theta Range for Data Collection	2.76 to 26.39°	2.14 to 24.76°.	2.14 to 24.83°.	2.11 to 24.71°	1.95 to 22.21°
Index Ranges (h,k,l)	±12, ±16, ±23	±11, ±15, ±22	±11, ±15, ±22	±19, ±25, ±27	±11, ±11, ±17
Reflections Collected/Independent	10821/2480	8665/2027	10796/2040	65540/26744	14648/4598

R(int)	0.0302	0.0289	0.0528	0.1216	0.1431
Completeness to theta =	26.39° =98.6%	24.76° =97.5%	24.83° = 96.9%	24.71° =99.1%	22.21° = 99.8%
Max. and Min. Transmission	0.8906 and 0.7558	0.9190 and 0.7251	0.9530 and 0.9091	0.9472 and 0.7402	0.9413 and 0.8873
Data/Restraints/ Parameters	2480 / 0 /126	2027 / 0 / 123	2040 / 0 / 114	26744 /546 / 1640	4538 / 0 / 307
Goodness-of-Fit on F^2	1.103	1.056	1.036	0.974	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0323, wR2 = 0.0802	R1 = 0.0401, wR2 = 0.1135	R1 = 0.0569, wR2 = 0.1503	R1 = 0.0717, wR2 = 0.1547	R1 = 0.0718, wR2 = 0.1174
R indices (all data)	R1 = 0.0417, wR2 = 0.0841	R1 = 0. 461, wR2 = 0.1202	R1 = 0.0668, wR2 = 0.1599	R1 = 0.1771, wR2 = 0.1950	R1 = 0.1524, wR2 = 0.1272
Largest Diff. Peak and Hole	0.605 and –0.244 e.$Å^{-3}$	0.481 and -0.907e.$Å^{-3}$	0.640 and -1.238e.$Å^{-3}$	1.002 and -0.715 e. $Å^{-3}$	0.773 and -0595 e $Å^{-3}$

The structure of 3.1 consists of a neutral monomeric zirconium species in a sandwich arrangement (Figure **3.3**). The zirconium's coordination sphere consists of two chlorine atoms and two π-bound dimethylpyrrole units in an overall pseudo-tetrahedral arrangement. Each dimethylpyrrole retains at the N atom an aluminum bearing two chlorine atoms and one ethyl group. The two dimethylpyrrole rings adopt a bent sandwich conformation [$N(1)_{centroid}$-Zr(1)-$N(1A)_{centroid}$ = 134.95(8)]. The Zr-chlorine bond lengths [Zr(1)-Cl(1) = 2.3747(8)] are comparable to those of cyclopentadienyl structures known in literature[4], and the Zr-pyrrole centroid bond length is [Zr(1)-$N1_{centroid}$ = 2.295(4)]. In the solid state structure the dimethylpyrrole rings are eclipsed with respect to the methyl groups and aluminum atoms which extend from the ring.

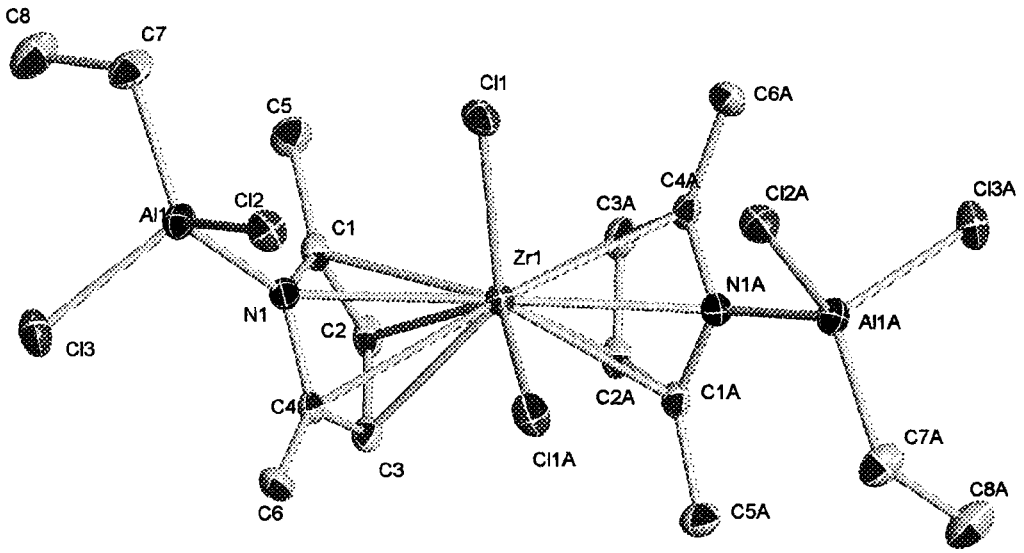


Figure 3.3: X-ray crystal structure of $[C_{16}H_{26}Al_2Cl_6N_2Zr]$ **(3.1)**. Thermal ellipsoids are drawn at the 30% probability level. Selected Bond Distances(Å) and Angles(°): Zr(1)-$N1_{centroid}$ =2.295(4), Zr(1)-Cl(1) =2.3747(8), N(1)-Al(1) = 1.989(3), Al(1)-N(1) =1.989(3), Al(1)-Cl(3) =2.1527(12), Al(1)-Cl(2) =2.1573(12), C(7)-C(8) = 1.556(5), $N(1)_{centroid}$-Zr(1)-$N(1A)_{centroid}$ = 134.95(8), $N(1)_{centroid}$-Zr(1)-Cl(1) = 134.95, $N(1)_{centroid}$-Zr(1)-Cl(1A) =107.64(7), Cl(1)-Zr(1)-Cl(1A) = 103.24(5), Zr(1)-$N(1)_{centroid}$-N(1) = 94.51(8), Zr(1)-$N(1)_{centroid}$-(C1) = 91.78(9), Zr(1)-$N(1)_{centroid}$-(C2) = 83.10(11), Zr(1)-

$N(1)_{centroid}$-C(3) = 80.92(11), Zr(1)-$N(1)_{centroid}$-C(4) = 88.98(7).

Figure 3.4 reveals a neutral monomeric zirconium sandwich compound (**3.2**). Zirconium's coordination sphere consists of two π-bound dimethylpyrrole units, and the other 2 positions occupied 50/50 by Cl and a methyl group. Disorder was resolved and modeled as one chlorine atom and one methyl group(figure 3.2) as that fits the correct formulation. Each dimethylpyrrole retains at the N atom an aluminum bearing two methyl groups and one chlorine atom. The dimethylpyrrole rings adopt a bent sandwich formation as the chlorine atoms/methyl groups have pushed them outwards [$N(1)_{centroid}$-Zr(1)-$N(1A)_{centroid}$ = 125.57(9)]. The Zr-chlorine bond length [Zr(1)-Cl(2) =2.418(9)] is comparable to cyclopentadienyl structures known in literature[4], as is the Zr-alkyl bond [Zr(1)-C(9)2.19(3)]. the Zr-pyrrole centroid bond length is similar, although slightly shorter than seen in **3.1** [$Zr(1)\text{-}N(1)_{centroid}$ =2.254(9)]. In the solid state at 203(2)K, the dimethylpyrrole rings are eclipsed with respect to the methyl groups and aluminum atoms which extend from the ring.

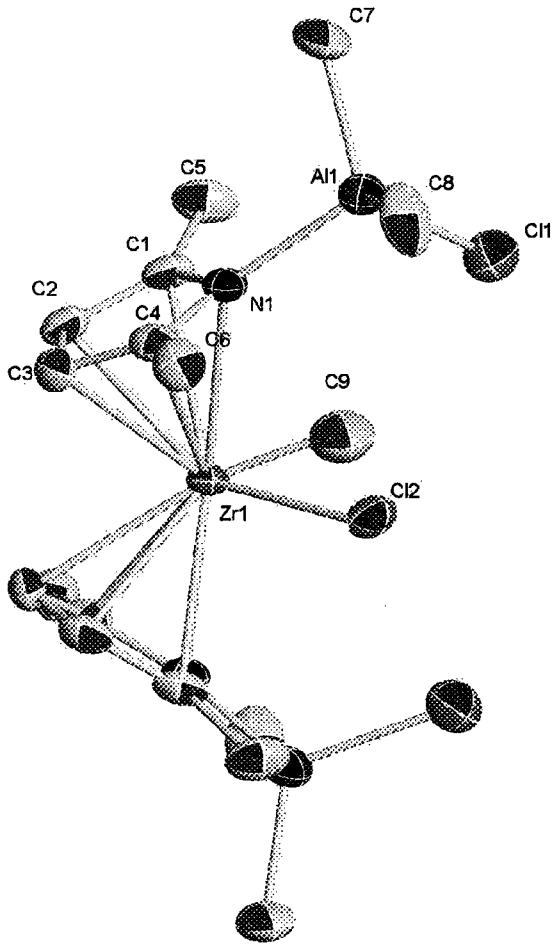


Figure 3.4: X-ray Crystal Structure of $[C_{17}H_{31}Al_2Cl_3N_2Zr]$ (**3.2**): Thermal ellipsoids were drawn at the 30% probability level. Selected Bond Distances(Å) and Angles(°): Zr(1)-$N(1)_{centroid}$ =2.254(9), Zr(1)-Cl(2) =2.418(9), Zr(1)-C(9)2.19(3), N(1)-Al(1) = 2.204(3), Al(1)-C(7) =1.965(5), Al(1)-C(8) =1.966(5), Al(1)-Cl(1) =2.1522(16), C(9)-Zr(1)-Cl(2) = 99.6(8), Zr(1)-$N(1)_{centroid}$-N(1) = 89.84(8), $N(1)_{centroid}$-Zr(1)-N(1A)-$_{centroid}$ = 125.57(9), C(7)-Al(1)-C(8) = 113.2(2), C(7)-Al(1)-Cl(1) =112.34(17), C(8)-Al(1)-Cl(1) =109.87(16).

Figure 3.5 reveals a neutral monomeric zirconium sandwich compound (**3.3**). Zirconium's coordination sphere consists of two chlorine atoms, and two π-bound dimethylpyrrole units. Each dimethylpyrrole retains at the N atom an aluminum bearing one chlorine atom and two methyl groups. The dimethylpyrrole rings adopt a bent sandwich formation as the chlorine atoms have pushed them outwards [$N(1)_{centroid}$-Zr(1)-$N(1A)_{centroid}$ = 133.45(11)]. Zr-chlorine bond lengths [Zr(1)-Cl(1) =2.387(3)] is comparable to cyclopentadienyl structures known in literature and in **3.1**. The Zr-pyrrole centroid bond length is [Zr(1)-$N1_{centroid}$ =2.261(9)]. In the solid state at 202(2)K, the dimethylpyrrole rings are eclipsed with respect to the methyl groups and aluminum atoms which extend from the ring.

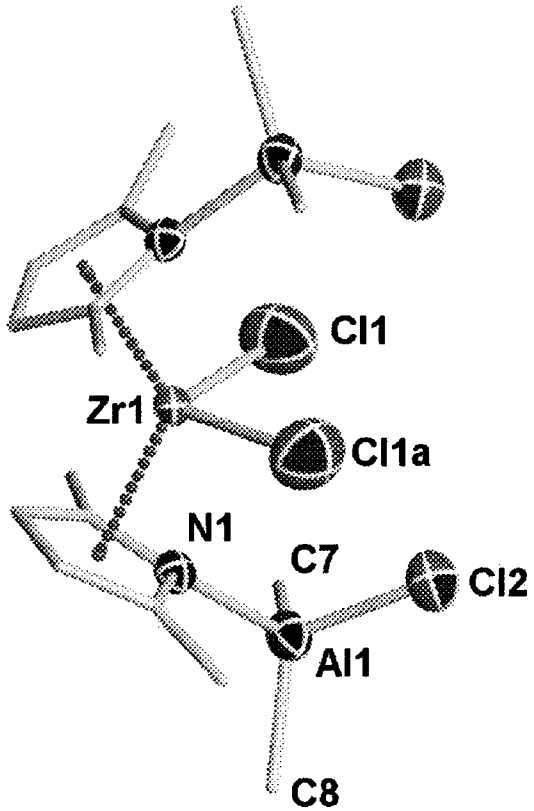


Figure 3.5: X-Ray crystal structure of [$C_{16}H_{28}Al_2Cl_4N_2Zr$] (**3.3**) Thermal ellipsoids were drawn at the 30% probability level. Selected interatomic distances (Å) and angles (°):

$Zr(1)\text{-}N(1)_{centroid}$ = 2.261(9), Zr(1)-Cl(1) = 2.387(3), N(1)-Al(1) = 2.025(5), Al(1)-C(7) = 1.958(8), Al(1)-C(8) = 1.972, Al(1)-Cl(2) = 2.168(3), $N(1)_{centroid}\text{-}Zr(1)\text{-}N(1A)_{centroid}$ = 133.45(11), Cl(1)-Zr(1)-Cl(1A) = 99.16(15), $Zr(1)\text{-}N(1)_{centroid}\text{-}N(1)$ = 86.22(11), C(7)-Al(1)-C(8) = 113.0(4), C(7)-Al(1)-Cl(2) = 112.1(2), C(8)-Al(1)-Cl(2) = 112.1(2).

Complex **3.5** is a neutral octameric cluster with the eight zirconium atoms forming a large macrocyclic structure (figure 3.6). Eight solvent molecules per molecule are present co-crystallized in the lattice. The dipyrrolide ligands do not give rise to sandwich type structures, rather they span two metals atoms with each pyrrolide ring π-bonded to one metal atom, and also σ-coordinated to a second. This created four dimetallic units which are all connected through bridging chlorine atoms. Each zirconium atom is formally in the trivalent oxidation state, attributed to four bridging chlorine atoms and one pyrrolide anion. The metal-metal distances, [Zr(1)-Zr(2) = 3.2478(15), Zr(2)-Zr(3) =3.6746(16), Zr(3)-Zr(4) =3.2135(15), Zr(5)-Zr(6) =3.1945(15), Zr(6)-Zr(7) = 3.6370(16), Zr(7)-Zr(8) =3.2161(15)] are among the shortest lengths ever observed for Zr-Zr bonding, however there is evidence for metal-metal interactions as the complex is diamagnetic. It is interesting to note that the Lewis acidic aluminum does not lock onto the nitrogen atom as previously seen in **3.1, 3.2, 3.3,** but rather connects to four of the zirconium atoms through bridging chlorines.

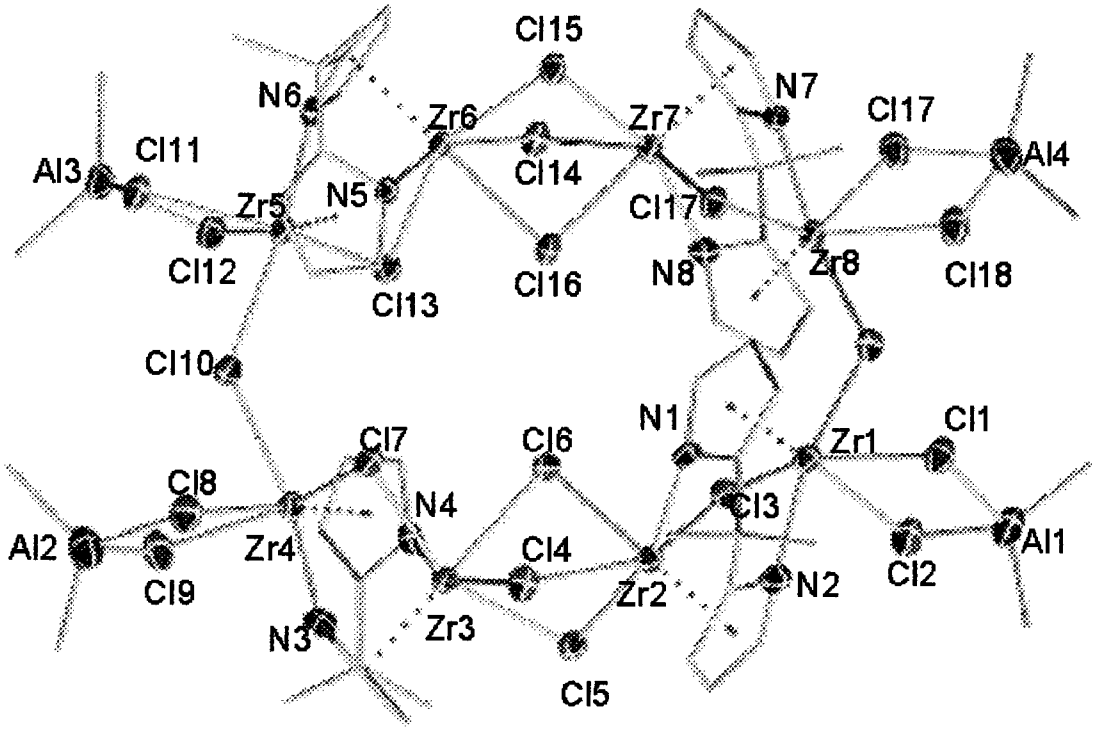


Figure 3.6: X-ray Crystal Structure of $[C_{92}H_{96}Al_4Cl_{20}N_8Zr_8]$ (**3.5**) Phenyl rings of ligand were omitted for clarity. Thermal ellipsoids were drawn at the 30% Probability level. Selected Bond Distances(Å) and Angles(°) are listed. Similar bonding environments to Zr(1) were observed for Zr(4), Zr(5), and Zr(8) and similar bonding environments to Zr(2) were observed for Zr(3), Zr(6), and Zr(7) but were omitted to prevent repetition. Zr(1)-$N(1)_{centroid}$= 2.139(8), Zr(1)-Cl(1) = 2.657(3), Zr(1)-Cl(2) = 2.722(3), Zr(1)-Cl(3) = 2.546(3), Zr(1)-N(2) = 2.320(8), Zr(1)-Cl(20) = 2.645(3), Zr(1)-Zr(2) = 3.2478(15), Al(1)-Cl(1) = 2.274(4), Al(1)-Cl(2) = 2.253(5), Al(1)-C(85) = 1.897(13), Al(1)-C(86) = 1.958(14), Zr(2)-$N(2)_{centroid}$= 2.139(8), Zr(2)-N(1) =2.239(8), Zr(2)-Cl(3) =2.587(3), Zr(2)-Cl(5) =2.640(3), Zr(2)-Cl(6) =2.643(3) =Zr(2)-Cl(4) =2.643(3), Zr(2)-Zr(3) =3.6746(16), Zr(3)-Zr(4) =3.2135(15), Zr(3)=$N(3)_{centroid}$ = 2.153(9), Zr(4)-$N(4)_{centroid}$

=2.166(11), Zr(5)-Zr(6) =3.1945(15), Zr(5)-$N(5)_{centroid}$ = 2.137(7), Zr(6)-Zr(7) = 3.6370(16), Zr(6)-$N(6)_{centroid}$ =2.165(8), Zr(7)-Zr(8) =3.2161(15), Zr(7)-$N(7)_{centroid}$ =2.163(7), Zr(8)=$N(8)_{centroid}$ =2.139(6). Zr(1)-$N(1)_{centroid}$-N(1) = 82.59, Al(1)-Cl(1)-Zr(1) = 06.82(14), Al(1)-Cl(2)-Zr(1) =95.52(13), C(85)-Al(1)-C(86) =123.2(7), Zr(1)-Cl(3)-Zr(2) =78.49(8), Zr(1)-Cl(20)-Zr(8) = 133.80(11), Zr(1)-N(1)-Zr(2) = 120.7(6), Zr(1)-N(2)-Zr(2) = 90.1(3), Zr(2)-Cl(4)-Zr(3) = 88.32(8), Zr(2)-Cl(5)-Zr(3) =88.41(8), Zr(2)-Cl(6)-Zr(3) =87.60(8).

Complex **3.7** is a neutral tetrameric cluster with the four zirconium atoms arranged in a zigzag fashion (Figure 3.7.) Four molecules of interstitial solvent per molecule are co-crystallized in the lattice. The pyrrolide ligands do not give rise to sandwich type structure but rather to dinuclear piano-stool units with the two pyrrolide anions bridged by an AlRCl residue. The two zirconium atoms within each unit are bridged by three chlorines in a face sharing bi-octahedral structure. The two zirconium centers are non-equivalent since one of the two retains an $AlRCl_3$ unit via two bridging chlorine atoms. The two identical pairs are connected through bridging chlorine atoms. Each zirconium atom is formally in the formal trivalent state given the presence of five bridging chlorine atoms per unit along with the mono-anionic aluminate dipyrrolide. The metal-metal distances between the pairing zirconium atoms, [Zr(1)-Zr(2) =3.045(2)] is the shortest ever recorded distance observed between Zr atoms. This, plus the observation of diamagnetism imply a Zr-Zr σ-bond. The Zr-pyrrole centroid bond distances are slightly shorter than previously observed [$Zr(1)\text{-}N(1)_{centroid}$ =2.220(9), $Zr(2)\text{-}N(2)_{centroid}$ =2.243(9)]

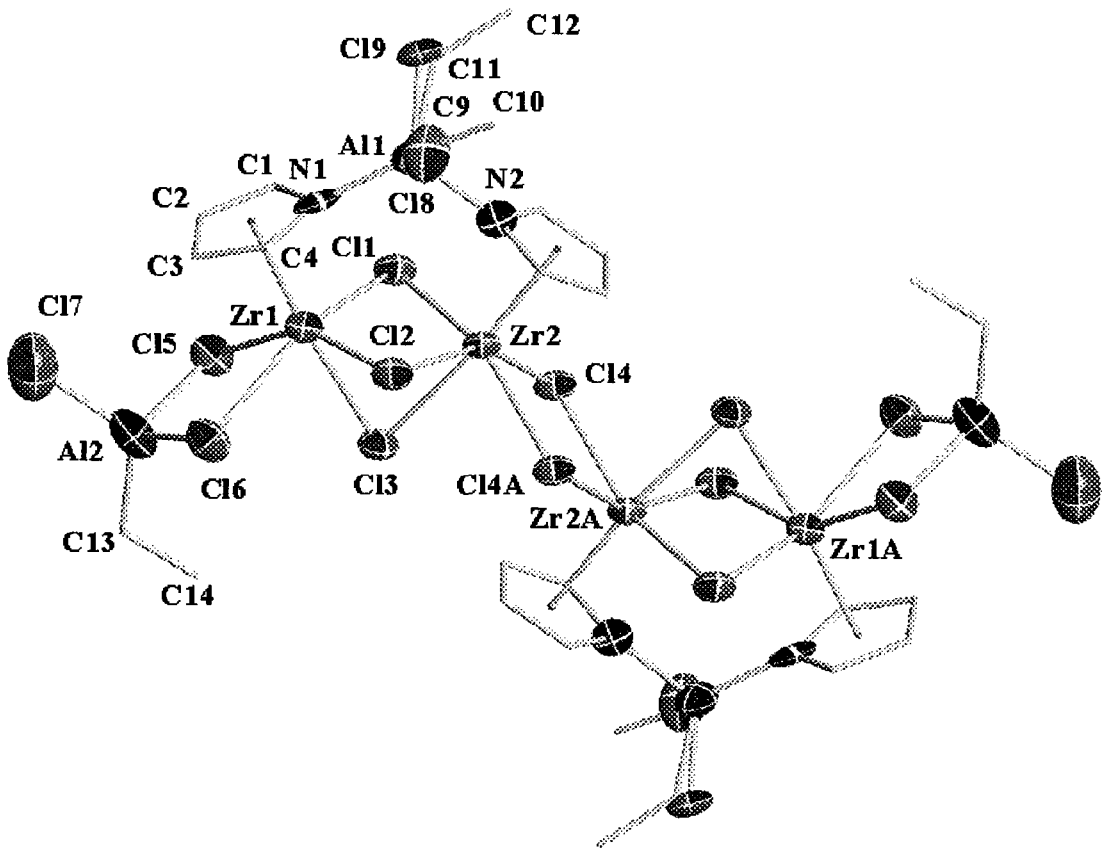


Figure 3.7: X-Ray Crystal Structure of $[C_{52}H_{68}Al_4Cl_{16}N_4Zr_4]$ **(3.7).** Thermal ellipsoids are drawn at 30% probability level. Selected Bond Distances(Å) and Angles(°): Zr(1)-$N(1)_{centroid}$ =2.220(9), Zr(1)-Zr(2) =3.045(2), Zr(1)-C(1) =2.478(12), Zr(1)-Cl(2) =2.553(4), Zr(1)-Cl(3) =2.575(3), Zr(1)-Cl(6) =2.673(4), Zr(1)-Cl(5) =2.675(4), Al(2)-C(13) =1.903(16), Al(2)-Cl(7) =2.143(7), Al(2)-Cl(5) =2.206(6) =Al(2)-Cl(6) =2.229(6), Al(1)-N(1) =1.890(12), Al(1)-N(2) =1.897(11), Zr(2)-$N(2)_{centroid}$ =2.243(9), Zr(2)-Cl(4) =2.615(3), Zr(2)-Cl(1) =2.564(4), Zr(2)-Cl(2) =2.577(4), Zr(2)-Cl(3) =2.607(3). Zr(1)-$N(1)_{centroid}$-N(1) =86.09(9), Zr(1)-Cl(1)-Zr(2) = 73.26(10), Zr(1)-Cl(2)-Zr(2) =72.82(10), Zr(1)-Cl(3)-Zr(2) =71.96(8), Al(2)-Cl(5)-Zr(1) =93.73(17), Al(2)-Cl(6)-Zr(1)

=93.27(17), Zr(2A)-Cl(4)-Zr(2) =102.27(11), Zr(2)-Cl(4A)-Zr(2A) =123.02(9), N(1)-Al(1)-N(2) =108.8(4), C(14)-C(13)-Al(2) =118.4(13), C(13)-Al(2)-Cl(7) =122.0(6), Cl(1)-Zr(1)-Cl(2) =106.17(12), Cl(1)-Zr(1)-Cl(3) =75.53(10), Cl(2)-Zr(1)-Cl(3) =75.42(10), Cl(6)-Zr(1)-Cl(5) =75.89(11), Cl(1)-Zr(2)-Cl(2) =104.75(12), Cl(1)-Zr(2)-Cl(3) =74.56(10), Cl(2)-Zr(2)-Cl(3) =74.47(11), Cl(4A)-Zr(2)-Cl(4) =77.73(11).

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Chapter IV

General Conclusions and

Insight for Future Work

Cha 2 of this thesis examined the use of the triazenide ligand system on Cr for the selectiv omerization of ethylene, specifically through the use of Cr^{I} active catalysts. T work showed that the triazenide ligand system is incapable of stabilizing movovalent is rather remvoved from the metal center under highly reducing conditions.

The vledge that amidinate ligand systems can stabilize Cr^{I} encourages future studies. Alt h the triazenide anion was unsuccessful, an investigation using other allylic type d systems may prove more successful. It ist the author's recommend that 3-center, 4-electron, monoanions are excellent candidates as ligand systems, ho r most specifically those bearing a substituent group on the central atom will have a chance at stabilization of movovalent Cr. This is due to the possibility of tuning th nd bite angle, and steric shielding of the metal center by appropriate selection of size of the substituent group. This was one clear difference between the amidinate a azenide ligand systems: the triazenide system lacked the substituent on the central a and therefore the ability to tune the bite angle and steric shielding.

In C r 3 of this thesis, several Zr compounds were prepared using the combinatio r salts, pyrrole based ligands, and alkyl aluminum reagents. This led to the isolatio everal Zr^{IV} sandwich compounds featuring monopyrrole ligands. Dipyrrole li s produced novel Zr^{III} structures, featuring the shortest known Zr-Zr contact. M f this work remained unanswered, such as the mechanism of formation of these Zr^{I} cies.

It is uthor's opinion that the combination of dipyrrole ligands, $ZrCl_4$, and AlR_3 can be ier investigated. The trivalent (and divalent) state of Zr have been known to pe n a variety of catalytic transformations, such as fixation of dinitrogen, or stereoselect olymerization of methylmethacrylate. Isolation of additional low-valent Zr structure definitely be accomplished by systematically combining different reagents of ype, and can possibly be used for other catalytic processes not investigated in this thesis. The author additionally observed very dark colours, possibly ind ve of the formation of Zr^{II}, when the more reducing $AlEt_3$ served as the alkyl alumi reagent. Exploration into all analogous types of reactions could help to answer the ions surrounding the formation of complex 3.7