Study of the Factors Affecting the Selectivity of Catalytic Ethylene Oligomerization

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Abstract

Over the past decade, advances in ethylene oligomerization have witnessed explosive growth of interest from both commercial and academic standpoint, with chromium metal invariably being the metal of preference. A common feature in this literature was the extended long debate regarding the mechanism, metal oxidation states responsible for selectivity and the role of the ligand. This thesis work embarked on the isolation and characterization of new active intermediates called "single component catalysts" (or self activating) to address two important questions: (1) how the catalyst precursors re-arrange upon activation and (2) the real oxidation state of the activated species. Four different ligands systems have been examined for this purpose.

The first part is a study on the $NP^{III}N$ ligand which can be described as a dynamic and non-spectator ligand. Upon aluminum alkyl activation, a series of single component chromium catalysts for selective ethylene oligomerization and polymerization have been isolated, fully characterized and tested. New selective single component chromium(I) catalysts have also been isolated and tested positively for ethylene trimerization. The second part includes a new series of chromium complexes based on the $NP^{V}N$ ligand. This ligands enabled to obtain the first polymer-free extremely active catalytic system. In both NPN ligand systems, a new activation pathway was discovered by using vinyl Grignard reagent [$(CH_2=CH)MgCl$] as activator and/or reducing agent.

The third part explores new modified pyrrole-chromium complexes which were found to be highly active and selective ethylene trimerization catalysts. This part was a continuation of previous work from our lab to complete the mechanistic picture of this highly successful pyrrole-

chromium catalyst independently commercialized by Phillips-Chevron and Mitsubishi. Interestingly upon aluminum alkyl treatment, the first example of a Schrock-type chromium ethylidene complex has been isolated and characterized and found to be a potent catalyst for selective ethylene trimerization. Finally, the other ligands introduced in this thesis are new systems called pyridine-SNS and Si-SNS that introduce some modification to the known commercial SNS catalyst (Sasol technology). The introduction of a pyridine ring or a silyl unit in the ligand scaffold has allowed to understand the mechanism of action of this remarkable system.

I would like to dedicate this thesis to my wife, Imane Harmouchi, and my parents for their patience and encouragement.

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Publications and Patents based on this thesis work

Publications:

[1] **Albahily, K**.; Koç, E.; Al-Baldawi, D.; Savard, D.; Gambarotta, S.; Burchell, T. J.; Duchateau, R. *Angew. Chem. Int. Ed. Engl.* **2008**, *47*, 5816.

[2] **Albahily, K**.; Al-Baldawi, D.; Gambarotta, S.; Duchateau, R.; Koç, E.; Burchell, T. J. *Organometallics* **2008**, *27*, 5708.

[3] **Albahily, K**.; Al-Baldawi, D.; Gambarotta, S.; Duchateau, R.; Koç, E.; Burchell, T. J. *Organometallics* **2008**, *27* , 5943.

[4] Licciulli, S.; Thapa, I; **Albahily, K**.; Korobkov, I.; Gambarotta, S.; Duchateau, R.; Chevalier, R.; Schuhen, K. *Angew. Chem. Int. Ed.* **2010**, *49*, 9225.

[5] Licciulli, S.; **Albahily, K**.; Fomitcheva, V.; Korobkov, I.; Gambarotta, S.; Duchateau, R. *Angew. Chem. Int. Ed.* **2011**, *50,* 2346.

[6] **Albahily, K**.; Shaikh, Y.; Sebastiao, E.; Gambarotta, S.; Korobkov, I.; Gorelsky, S. *J. Am. Chem. Soc.* **2011**, *133*, 6388.

[7] **Albahily. K**.; Fomitcheva, V.; Gambarotta, S.; Korobkov, I.; Murugesu, M.; Gorelski, S. *J. Am. Chem. Soc.* **2011**, *133*, 6380.

[8] [8]**Albahily. K**.; Fomitcheva, V.; Shaikh, Y.; Sebastiao, E.; Gambarotta, S.; Korobkov, I.; Duchateau, R. *J. Am. Chem. Soc.* (Submitted).

[9] **Albahily. K**.; Zeeshan, A.; Koç, E.; Gambarotta, S.; Korobkov, I.; Duchateau, R. *Organometallics* (Submitted).

[10] **Albahily. K**.; Shaikh, Y.; Zeeshan, A.; Korobkov, I.; Gambarotta, S.; Duchateau, R. *Organometallics* (Submitted).

[11] **Albahily. K**.; Licciulli, S.; Gambarotta, S.; Korobkov, I.; Chevalier, R.; Schuhen, K. ; Duchateau, R. *Organometallics* **2011**, *30*, 3346.

[12] **Albahily. K**.; Zeeshan, A.; Korobkov, I.; Gambarotta, S.; Korobkov, I.; Duchateau, R. *Organometallics* (Submitted).

Patents:*

[13] **Albahily, K**.; Licciulli, S, Gambarotta, S.; Duchateau, R. (Basell Polyolefin Gmbh) FR 6642 (US), **2010**.

[14] Licciulli, S, Thapa, I**.; Albahily, K.;** Gambarotta, S.; Duchateau, R. ; Schuhen, K.; Chevalier, R.; (Basell Polyolefine Gmbh). FR 6592 (US), **2010**.

[15] Licciulli, S, **Albahily, K.;** Gambarotta, S.; Duchateau, R. (Stichting Dutch Polymer Institute) DPI10.008 (EP), **2010**.

*These patents have been filed in United States and Europe.

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List of Abbreviations

Ar	aromatic group
calcd	calculated
Cy	cyclohexyl
DEAC	diethylaluminum chloride
DFT	Density Functional Theory
DMP	2,5-dimethylpyrrole
ESI	Electro Spray Ionization (Mass Spectrometry)
Et	ethyl
Et_2O	diethyl ether
GC-MS	Gas Chromatography-Mass Spectrometry
i-Bu	iso-butyl
i-Pr	iso-propyl
IR	Infrared
LAO	Linear Alpha olefins
MAO	methylaluminoxane
Me	methyl
MMAO	modified methylaluminoxane
Mw	weight-average molecular weight
m/z	mass to charge ratio
NMR	Nuclear Magnetic Resonance
PDI	polydispersity
PE	polyethylene

Ph	phenyl
PVC	poly (vinyl chloride)
R	alkyl group
S.F	Shultz-Flory distribution (random statistical distribution)
SNS	$NH(CH_2CH_2SCy)_2$
t-Bu	tert-Butyl
TEAL	triethylaluminum
THF	tetrahydrofuran
TIBA	tri-isobutylaluminum
TIBAO	tetraisobutyldialuminoxane
TMA	trimethylaluminum
Z/N	Ziegler-Natta

Chapter One

Introduction

1.1 Olefin Polymerization

With its trillion-dollar volume of annual business worldwide, polymerization and copolymerization of α-olefins are by far the most lucrative and widely used carbon-carbon bond forming reactions. The tight control that science has gained on polymer characteristics and rheology is the key to understand the large diversification of this technology and the extent of the commercial interest behind it. This has been possible only because extensive studies have been carried out on how additives and in particular co-monomers may affect the physical characteristics of the polymeric material (hardness, elasticity, durability, impact and stress resistance, etc.). As a matter of fact the current search for new polymers is the quest for new ways of incorporating in a controlled fashion different additives in the polymer chain. Linear α-olefins (LAO), in addition to their own application, remain even today the most important additives for polyolefin and polymer chemistry.

Generally speaking, a polymer is a high molecular weight compound composed of repeating structural units (monomers) linked together by covalent bonds. These large molecules are prevalent in nature and common examples include: DNA, proteins, starch, etc. Apart from their extensive occurrence in nature, polymers have endless industrial applications and to satisfy today's societal demand, synthetic polyolefins (commonly referred to as 'plastics') are continuously being developed to meet the request of a large variety of consumer products. These synthetic polymers are widely employed for their durability, versatility, and low cost. The adoption and use of synthetic polymers as a principal material in the production of nearly all

modern goods has made them indispensible to our modern society. Keeping up with the increasing demand for synthetic polymers, there has been an increasing interest for developing industrial polymerization catalysts with greater efficiency in terms of activity and selectivity. In order to fully appreciate modern advances in polymerization catalyst design, it is important to briefly examine the relatively old and yet rich history of Ziegler-Natta catalysts.

In the early 1950s, Karl Ziegler and Giulio Natta independently developed the first known catalytically active species for alkene polymerization and for which they were jointly awarded the 1963 Nobel Prize in chemistry.[1] The great simplicity of these catalytic systems based on titanium and alkyl aluminum compounds made these systems highly desirable for the commercial production of polymers since 1956. Today, the total volume of plastics, elastomers, and rubbers produced from alkenes with these catalysts worldwide exceeds 100 million metric tons.[2] On the wave of enthusiasm for the discovery of the Ziegler-Natta polymerization systems, even the field of organometallic chemistry has blossomed into one of the most active areas of research in today's science.

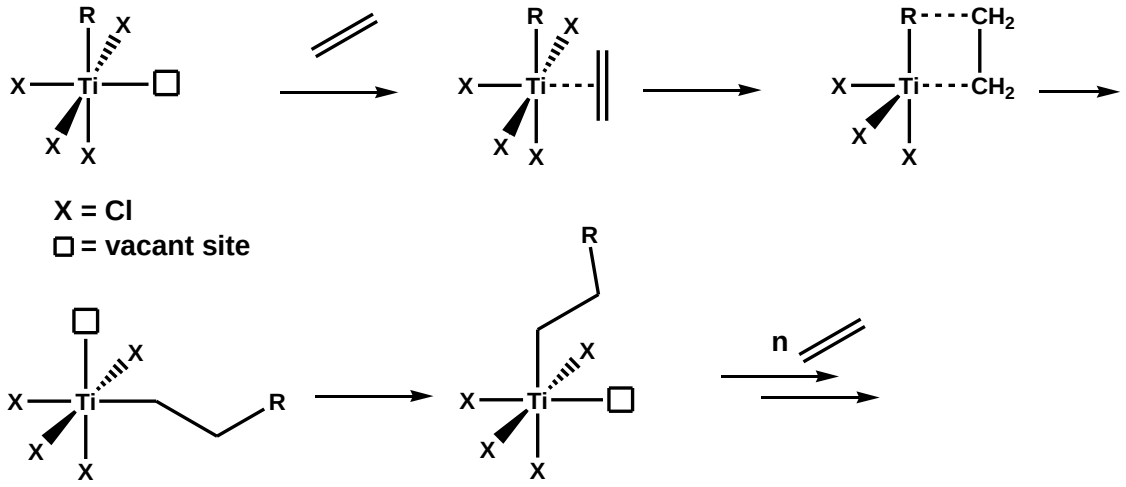
Initially, only titanium based systems were commonly referred to as Ziegler-Natta catalysts. In a second stage, the term 'Ziegler-Natta catalysts' has come to encompass vanadium based complexes, the chromium analogues as well as all the binary systems composed by a transition metal salt and alkyl aluminum. Currently, this type of polymerization catalysts still accounts for a very significant amount of commercially produced polymers.[3]

As mentioned earlier, Ziegler-Natta systems most often involve titanium or vanadium metal ions, the most common source being $TiCl_4$, $TiCl_3$, VCl_4, $VOCl_3$.[4] The most common co-catalysts are organo-aluminum compounds such as $AlMe_3$, $AlEt_3$, $Al(i\text{-}Bu)_3$, etc, and methylaluminoxane $[Al(CH_3)O]_n$.[5] Both components are essential for active polymerization catalyst to be assembled,

as neither of these component can polymerize alkenes individually. The combination of the two components triggers a series of transformations that 'primes' the system for alkene polymerization (usually *via* alkylation of the metal center to create an active site for monomer sequential insertions).[6]

The work of Cossee and Arlman has marked a milestone in understanding the Ziegler-Natta system by proposing the most widely accepted monometallic mechanism for the polymerization process (Scheme 1.1).[7] The critical step in this mechanism is the formation of the transition metal-carbon bond, as the catalytically active function. It was proposed that the active site contains a transition metal atom (with an octahedral geometry) with at least one coordination vacancy. The polymerization starts with the π-coordination of one olefin molecule at the vacant site. The next step is its insertion into the metal-alkyl bond that was previously generated by the co-catalyst during the alkylation step. The growing chain then exchanges position with the coordination vacancy in order to restore the original geometry.

Scheme 1.1



Given the satisfactory performance of the $TiCl_4$, $TiCl_3$, $VOCl_3$ and VCl_4 systems there was no real motivation for the first twenty years since discovery to develop new and possibly better performing systems. The three systems employed for commercial polymerization purposes were:

- $TiCl_4 \cdot AlEt_2Cl$ for polyethylene;
- δ- $TiCl_4 \cdot 0.33AlCl_3 \cdot AlEt_2Cl$ for crystalline polypropylene;
- $VOCl_3 \cdot Al_2Et_3Cl_3$ and $VCl_4 \cdot Al_2Et_3Cl_3$ for elastomeric ethylene-propylene co-polymer.

Subsequent to these seminal discoveries and because of the need for precisely controlling the polymer rheology (molecular weight distribution, entangling, crystallinity, etc.) spectacular breakthroughs have been made in the literature. All these discoveries may be re-conducted to different generations of Z/N catalytic systems. Namely they are the discovery of *ansa*-metallocenes,[8] their cationization,[8] metal-alkyl cationization with strong Lewis acid,[5,9] polymer tacticity control via ligand modification,[10] tandem catalysts for the control of the formation of block co-polymers,[11] and finally the discovery of heterogeneous systems,[12] including gas phase polymerization.

All these systems will not be reviewed in this thesis. It will suffice for the purpose of this introduction to mention that these milestones have altogether established the prerequisites of a performing Z-N catalyst: 1) a suitable ligand system to control catalyst solubility and polymer tacticity, 2) metal-alkyl bond as initiating function and 3) cationization and Lewis acidity to enhance the ability of the catalytic center to pre-coordinate the monomer or co-monomer.

1.2 Olefin Oligomerization

Linear α-olefins (LAO) are very important commodity chemicals and their use is central to the control of polymer rheology. These species may be conveniently prepared from ethylene by using Ziegler-Natta type of catalytic systems (oligomerization). In fact from an organic synthesis

point of view, oligomerization is a process conceptually very similar to polymerization where only a few monomeric units are being covalently bonded. As a matter of fact one might regard this reaction as a regular polymerization truncated at the very early stage. The only prerequisite for an oligomeric α-olefin to be formed is that the chain growth termination occurs through a β-H elimination step. Technically, an oligomerization is regarded as a reaction affording products in the range of four to thirty carbon atoms while a polymerization yields products that are from several thousands to millions of carbon-containing units. The range of applications of oligomers varies depending on the number of carbon atoms.

Table 1.1: Linear Alpha Olefins (LAO) applications:

LAO	Applications
C_4	Polyolefin co-monomer (LLDPE, HDPE), poly-butene-1.
C_6	Polyolefin co-monomer (LLDPE, HDPE), plasticizer alcohol, intermediate in the production of oxo alcohols, hexyl mercaptans, organo-aluminum compounds and synthetic fatty acids.
C_8	Polyolefin co-monomer (LLDPE, HDPE), plasticizer alcohol also an intermediate in the production of oxo alcohols, octyl mercaptans, amines, organo-aluminum compounds, synthetic fatty acids.
C_{10}	An intermediate in the production of epoxides, amines, oxo alcohols, synthetic lubricants, synthetic fatty acids, alkylated aromatics and synthetic lubricants, plasticizer alcohol.
C_{12}	Production of linear alkylbenzene, detergent alcohols (oxo alcohols), amines and amine oxides, mercaptans, oxo alcohols, synthetic lubricants, epoxides and synthetic fatty acids.
C_{14}	Production of linear alkylbenzene, detergent alcohols (oxo alcohols), amines and amine oxides, mercaptans, oxo alcohols, alkylated aromatics, synthetic lubricants, epoxides, synthetic fatty acids.
C_{16+}	Alpha olefin sulfonate, detergent alcohols (oxo alcohols), lubricant additives, wax lubricants.

One of the most versatile techniques to control polymer rheology is the introduction of variable amounts of α-olefins as co-monomers of the polymerization process. The size of these co-monomers profoundly affects the nature of the polymer produced. For example, α-olefins of four carbon units represent the fundamental petrochemical synthons for the most common

synthetic polymers such as PVC plasticisers, household detergents, lubricants and as co-monomers for the synthesis of linear and low density polyethylene (LDPE) (Table 1.1).[13] Therefore it comes as no surprise that research activity for finding catalytic systems for the production of high-value linear alpha olefins (LAO's) has experienced an exponential growth since the discovery in 1964 of the first catalytic oligomerization system.[14] Among the several useful LAO, 1-hexene and 1-octene occupy a very special place because of their massive employment in the polymer industry and the challenge posed by the high purity that is required for their use. In turn, this has introduced the need for developing selective tri- and tetramerization catalysts and consequently understanding the factors that may introduce high selectivity into the oligomerization cycle.

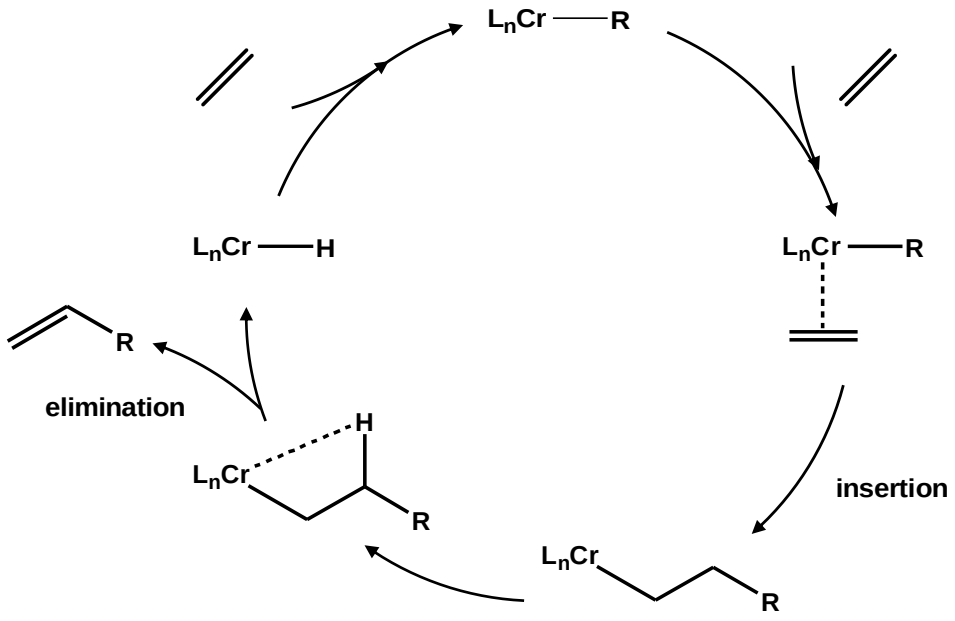
1.3 Ethylene Oligomerization Mechanistic Pathways

Of the various transition elements in different oxidation states that show catalytic activity in terms of ethylene oligomerization, trivalent chromium appears to be the most versatile species.[15] So far trivalent chromium has produced the best performing trimerization and tetramerization catalysts in terms of both activity and selectivity and accounts for over 90% of all the existing oligomerization catalysts.[16] This obviously raises questions about the reasons for this unique versatility. The answer lies on the mechanism of ethylene oligomerization.

While the chain-growth mechanism (Cossee-Arlman)[17] (Scheme 1.2) accounts very well for the general oligomerization pathway, it can hardly explain the almost complete selectivity observed in a very few trimerization systems. The chain termination process requires a β-hydrogen transfer to the metal and just steric or geometry considerations cannot convincingly explain why this event should occur with such a high selectivity at the level of the third insertion as opposed to a further expansion and more random termination process. It should be observed

that, through all the steps of the Cosse-Arlman mechanism, the metal oxidation state remains unchanged. Metal cationization, and M-R bond polarity are thus the main factors powering the catalytic cycle.

Scheme 1.2

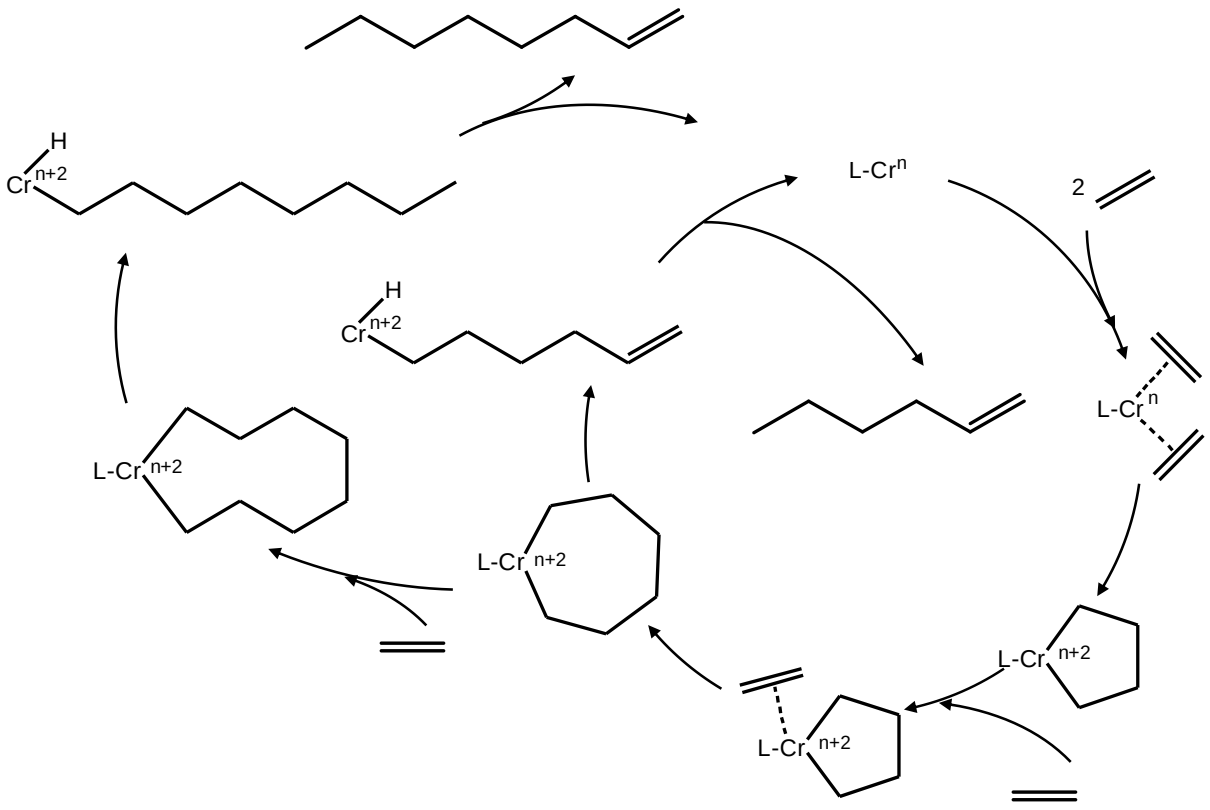


The discovery of the first example of a Pt(II) metallacycle in the early 1970s[18] had a great impact on mechanistic studies, since such organometallic functions may be envisioned as possible intermediates in selective ethylene oligomerization. Developing this concept, Manyik et al. proposed the first metallacycl-based oligomerization mechanism for the selective trimerization of ethylene, the so-called ring expansion mechanism (Scheme 1.3).[19]

The selective formation of a certain α-olefin via the metallacyclic mechanism of ethylene oligomerization involves a series of events which appear to be highly dependent on the ligand's capability to stabilize low-valent states of the metal catalyst (Scheme 1.3).[20,15c,g,h,e] In fact the mechanism is nothing more than an oxidative-coupling / reductive-elimination cycle. The

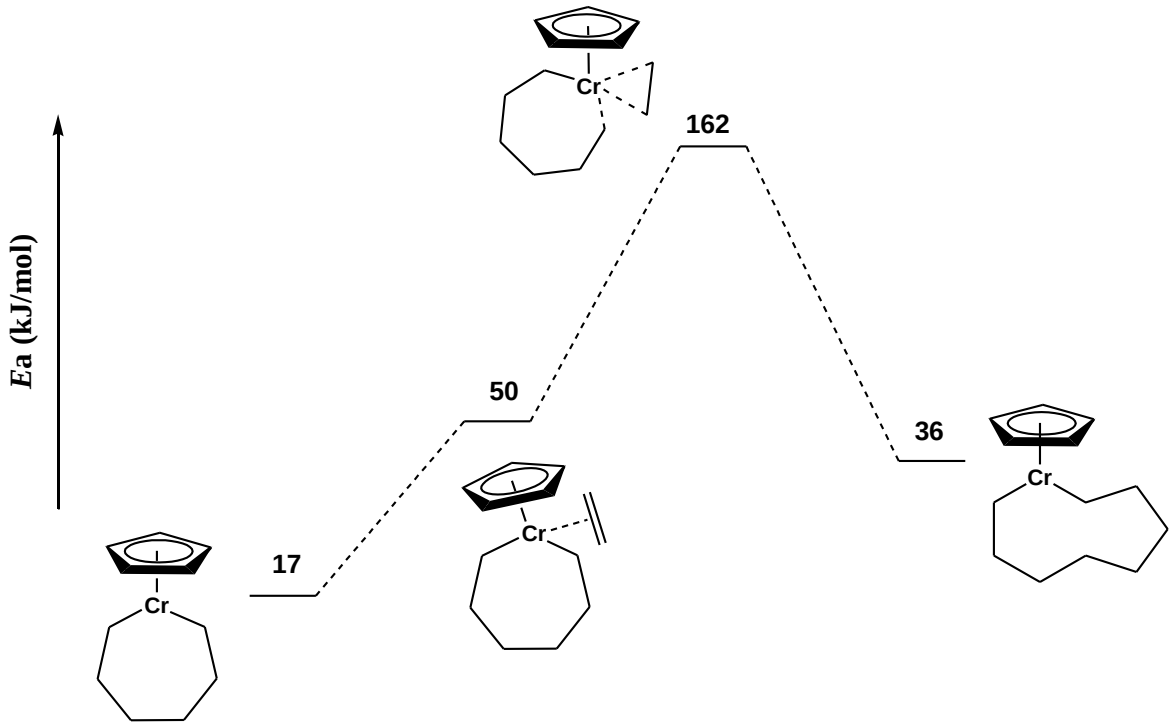
activation process simply generates the metal oxidation state appropriate to perform reductive coupling of two ethylene molecules. The metallacycle so formed may expand via subsequent insertion of ethylene until ring geometry constraints trigger the reductive elimination of α-olefin restoring the original low-valent state on the metal ready for another cycle. Every stage of the cycle (except the ring expansion) is a two-electron redox process. This mechanism is today very well accepted by workers in the field and regarded as a genuine paradigm for the selective tri- and tetramerization. The seminal work of Bercaw,[21] Gibson[22] and McGuinness[23] has demonstrated with the usage of isotope labeling experiments that indeed this mechanism may account for the trimerization.

Scheme 1.3

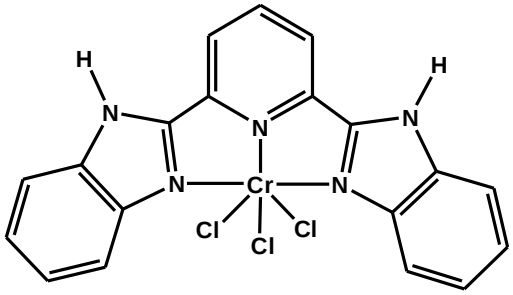


For a long time it was debated that non-selective oligomerization might also follow the same ring expansion mechanism. In this case, the difference between the activation barrier of the seven member ring expansion versus that of the reductive elimination would determine the occurrence of selective versus non-selective process (Scheme 1.4).[24]

Scheme 1.4

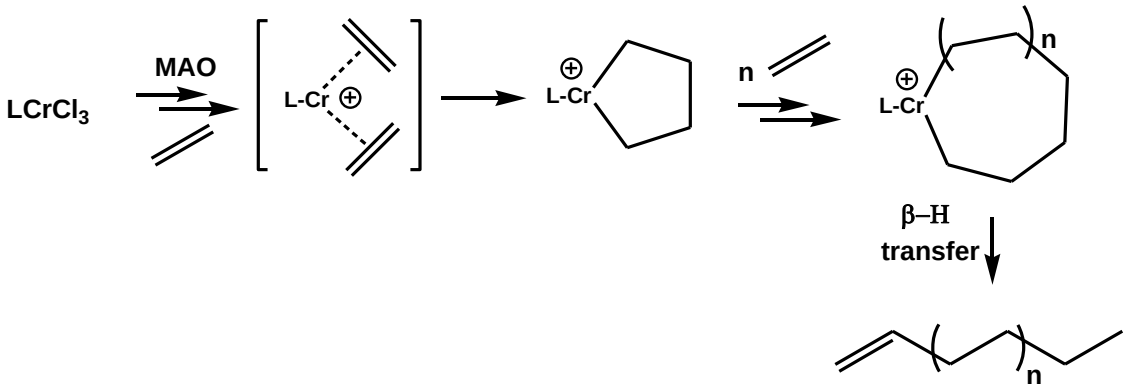


This possibility was ascertained by Gibson with his elegant experiment on the highly active oligomerization non-selective catalyst (**1.1)** (5357 g/mmol/h/bar).[25] This catalyst was tested under the same conditions using a 50:50 mixture of CH_2CH_2/CD_2CD_2. The GC analysis showed the oligomers were comprised of even numbered isotopomers (d_0, d_2, d_8, etc). This indicates that a metallacyclic mechanism is the only possible pathway for this reaction because of the absence of the H/D scrambling that would be instead observed with the Cossee-Arlman chain-growth mechanism (Scheme 1.5).[25]



(1.1)

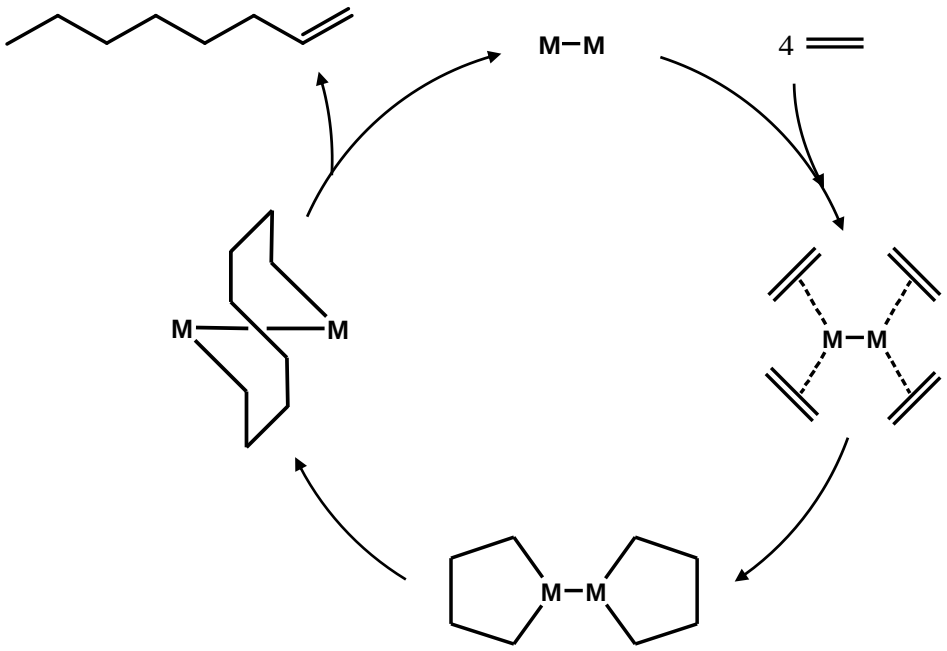
Scheme 1.5



The mechanism for formation of 1-octene deserves a special consideration. In fact, the same ring expansion mechanism has been widely assumed since the appearance in the literature of the first of the three existing tetramerization systems. In a tetramerization cycle, the elimination should occur after two events of ring expansion (ethylene insertion). A thorough study by Sasol[26] nicely explained how this mechanism could also account for the several oddities that invariably accompany the few cases of pre-eminent formation of 1-octene. Assuming that a yet-to-be-found highly selective tetramerization system would follow the ring-expansion mechanism, it is hard to envision how it would be possible to significantly prevent further expansion. While a rationale can be envisioned for a seven-member ring to collapse rather than expand, in case of further expansion towards the nine-member ring, no particular reasons can be foreseen to account for an easier reductive elimination against further expansion. Therefore it is unlikely that through a ring

expansion mechanism a highly selective tetramerization catalyst will ever be obtained. Accordingly, there are only three existing catalysts *predominantly* making 1-octene and at the beginning of this thesis work a truly selective 1-octene catalyst was yet to be discovered.

Scheme 1.6

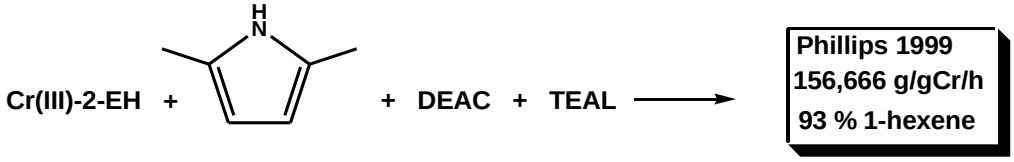


To solve this conundrum, Rosenthal has recently elaborated the proposal that for a selective tetramerization catalyst to be obtained, the mechanism should follow a "bimetallic" mechanism.[27] The idea relies on the formation of a dinuclear system where the two monovalent centers are kept by the ligand at sufficiently far distance to prevent formation of a Cr-Cr quintuple bond. Yet the intermetallic distance should be sufficiently short to enable internal reductive elimination from two independently formed metallacycles, each grown on one metal center (Scheme 1.6). This intriguing idea was recently published as concept proposal unsupported by data.[27] It should be reiterated that a selective tetramerization catalyst was yet to be found at the time of the beginning of this thesis work.

1.4 Selective Chromium Oligomerization Catalysts

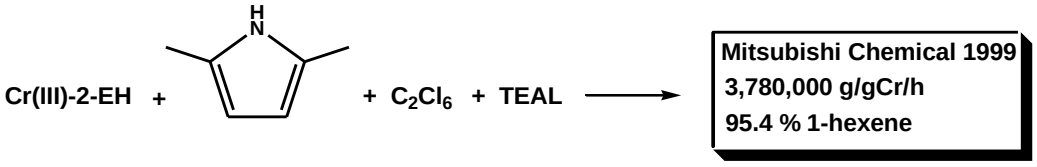
Different from the tetramerization catalysts, highly selective trimerization system do exist and are being commercially exploited.[15a,b,I] The most efficient and convenient of these catalysts is the 2,5-dimethylpyrrole (DMP) system (based on chromium) developed by the Phillips Petroleum Company (PPC).[15a] This catalyst is currently used in Qatar for the worldwide production of 1-hexene. The multi-patented recipe requires the presence of DEAC/TEAL as co-catalyst in near to stoichiometric loading. In 1994, PPC further improved the already outstanding activity (156,666 g/gCr/h) to obtain 99.85% conversion with a remarkable 93% purity of 1-hexene (Scheme 1.7).[28]

Scheme 1.7



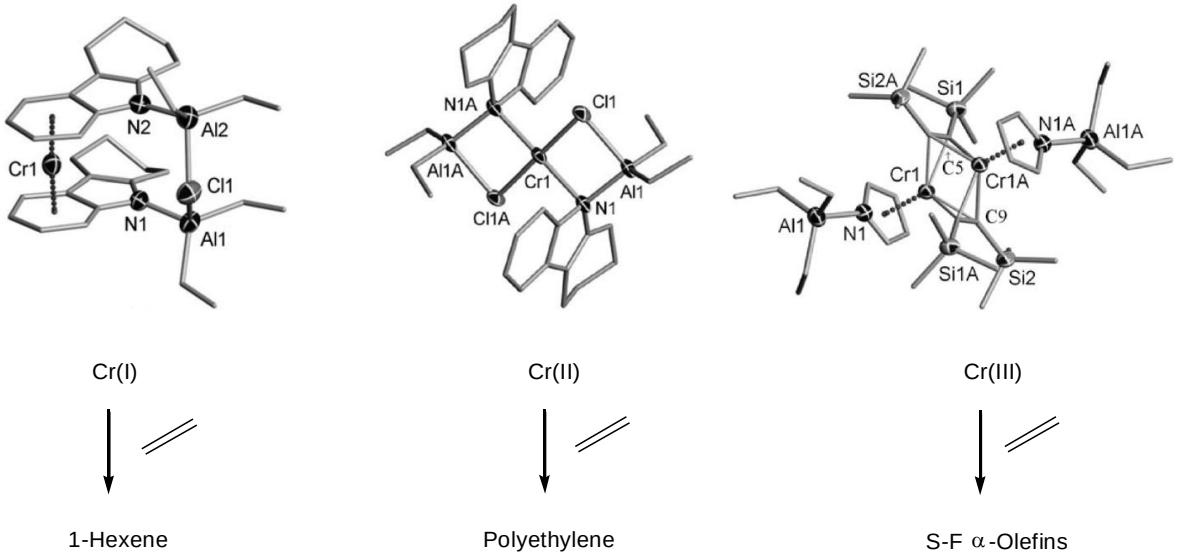
One of the most notable improvement of the Phillips system was implemented by Mitsubishi Chemical Corporation.[29] The success of this system lies in the use of a non co-ordinating Lewis acids, such as $B(C_6F_5)_3$, coupled with Cr(III) 2-EH (ethylhexanoate), DMP and TEAL (triethylaluminum), altogether being capable of boosting the activity even further.[29] A protocol was developed for conveniently preparing the catalyst *in-situ* which further improved the productivity.[30] In employing their *in-situ* protocol and combining chromium (III) 2-ethylhexanoate with 2,5-dimethylpyrrole, hexachloroethane and triethylaluminum in molar ratios of 1:6:4:40, the resulting catalyst produced 95.4% pure 1-hexene with a staggering activity of 3,780,000 g/gCr/h at 105 °C and 50 bar (Scheme 1.8).[30]

Scheme 1.8



No mechanistic information was ever provided on this important system and the nature of the catalytically active species as well as the metal oxidation state was unknown. Recent work from our labs has elucidated this important point.[31] By isolating species formed according to the Phillips recipe, it was possible to obtain mono-, di- and trivalent chromium complexes each with its own distinctive catalytic behaviour (Scheme 1.9).[31] In turn, this work has allowed for identifying a conclusive link between catalytic activity and metal oxidation state. Subsequent spectroscopic EPR work by Talsi has confirmed these findings.[32]

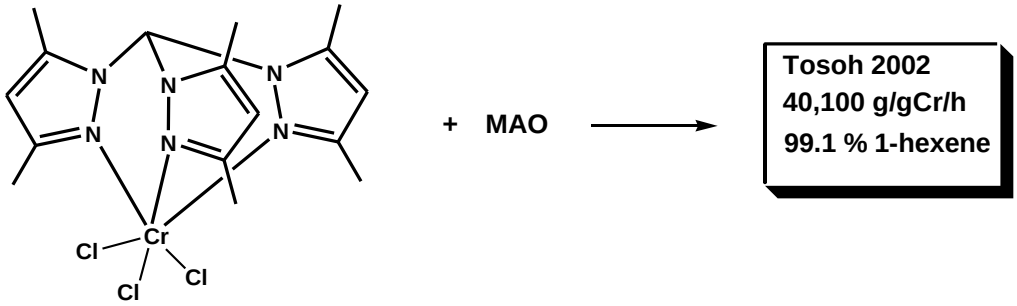
Scheme 1.9



Another remarkable catalytic system is based on tris(pyrazolyl)methane ligands. Prior to Tosoh Corporation's discovery of functional chromium complexes, tris(pyrazolyl)methane (tbz) ligands were extensively investigated with various metals, including: copper(I), silver(I),

cadmium(I), lead(II), and thallium(II).[33] Tosoh Corporation's scientists found that when coupled with activating agents such as MAO or trialkylaluminum, tris(pyrazolyl)methane (tbz) ligands afforded highly active and selective chromium catalysts.[15e] Their most effective catalyst was obtained by activating [(tbz)$CrCl_3$] with 360 molar equivalents of MAO.[15e] At 80 °C and 40 bar, the system produced 99.1% 1-hexene with an overall activity of 40,100 g/gCr/h (Scheme 1.10). The excellent stability of these complexes makes their handling far easier than in the case of the Phillips pyrrolato systems.

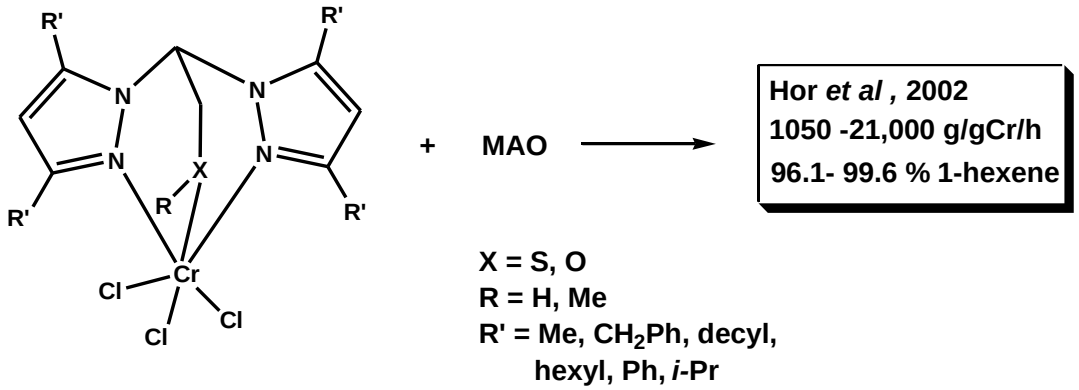
Scheme 1.10



An interesting variation of the pyrrolyl based ligands recently reported consists of heteroscorpionate pyrazolyl ligands.[34] These ligands were crafted by Hor and co-workers by placing a functionalized pendant arm on the spacer link between the pyrazolyl moieties. Moreover, the complexes formed from these ligands were robust in nature, due to the presence of coordinating ether or thioether functional groups. Their presence enables the formation of a metallabicyclic structure composed of two connected six-membered rings, and flanked by two pyrazoyl rings. The most successful complex was obtained with the ligand having a hexyl ether chain affording a selectivity of 98.9% for the C_6 fraction (99.6% 1-hexene) with an activity of 16,200 g/gCr/h. When the same reaction was carried out with 80 mL of toluene, the activity was

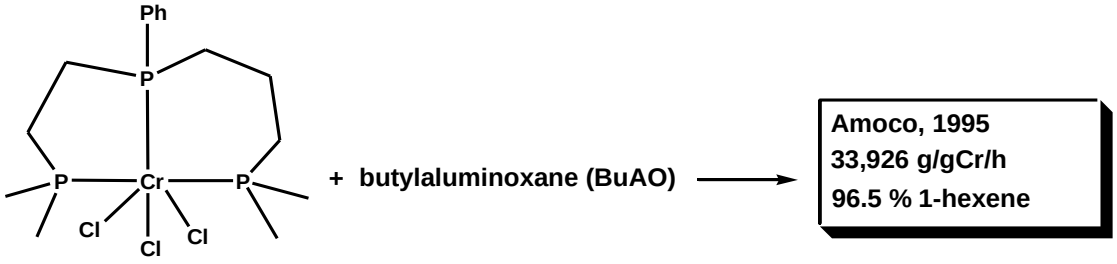
increased to 21,000 g/gCr/h, but the selectivity for the C_6 fraction decreased slightly to 96.1% 1-hexene (Scheme 1.11).[34]

Scheme 1.11



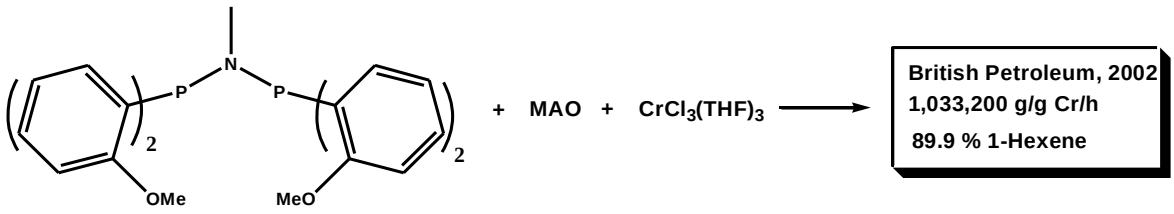
Like nitrogen-based ligands, phosphorous donor ligands have also generated quite interesting results. One of the commercial corporations investigating this class of ligands was Amoco Corporation. This work focused on polydentate phosphine based chromium complexes of general formula $R_2P(CH_2)_nP(R')(CH_2)_mPR_2$ in combination with aluminoxane as co-catalyst.[35] These ligands were found to coordinate the metal in a meridional fashion compared to the facial coordination adopted by the triazacycloalkane ligands and the tris(pyrazolyl)methane ligands. The most successful Amoco catalyst comprised an unsymmetrical ligand (2-dimethyl phosphinoethyl)(3-dimethylphosphinopropyl)phenylphosphine and butylaluminoxane (BuAO) in toluene.[35] At 80 °C and 42 bars of ethylene, this system produced 96.5% 1-hexene with an overall activity of 33,926 g/gCr/h (Scheme 1.12). The major factors preventing the commercialisation of this catalyst system are the high cost and difficulties associated with the preparation of these ligands.[35] No information about the mechanism or about the nature of the catalytically active species has ever been reported for this system.

Scheme 1.12



Given the apparent versatility of nitrogen and phosphorous based ligands, attempts were focussed at synthesising N and P hybrid ligands. A British Petroleum patent was the first to report a chromium catalyst system with diphosphazane ligands of general formula $Ar_2PN(Me)PAr_2$.[15f] The most successful system was obtained by combining $CrCl_3(THF)_3$, (2-methoxyphenyl)$_2$PN(Me)P(2-methoxyphenyl)$_2$ and 300 equivalents of MAO. This system produced 89.9% 1-hexene with an overall record activity of 1,033,200 g/gCr/h. Even further, the system displayed a surprisingly low decay rate compared to most other catalysts (Scheme 1.13).[15g]

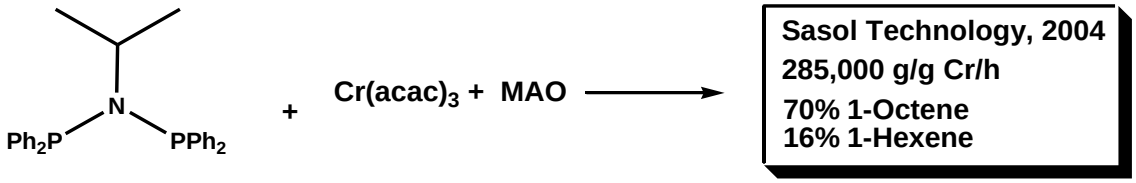
Scheme 1.13



An additional benefit is that this catalytic system can be successfully supported on silica with little or no loss in activity and selectivity. The second order dependence of the reaction rate on ethylene pressure, indicates that the classical metallacycle mechanism is being followed. Remarkably, a minor modification introduced by Sasol Technology in the ligand system

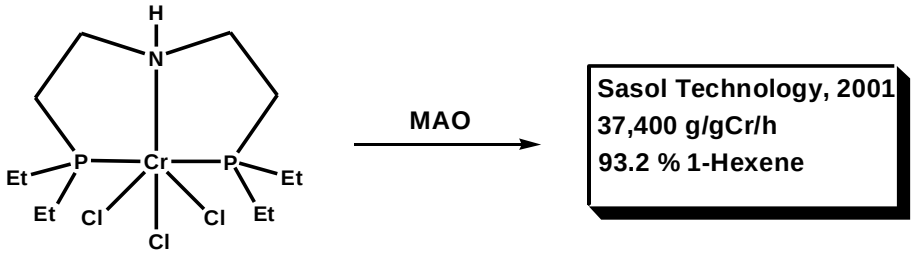
(removal of the *ortho*-substitutions from the phenyl groups) afforded the first tetramerization catalyst producing 1-octene in large excess (up to 70%) (Scheme 1.14).[15m]

Scheme 1.14



The same commercial corporation has also investigated the properties of mixed nitrogen/ phosphorous ligands, [20a,36] by using a bis-phosphinoamine ligands of the form $R_2PCH_2CH_2N(H)CH_2CH_2PR_2$ thus producing another highly performing trimerization catalyst. By analyzing a large series of systems of this type of ligand it was concluded that highly basic and sterically demanding dicyclohexylphosphino moieties decrease activity and increase PE production. Instead, basic but less sterically demanding diethylphosphino moieties increase activity and selectivity. [20a,36] The most successful system consisted of [bis-(2-diethylphosphino-ethyl)amine]$CrCl_3$ in combination with 850 equivalents of MAO as an activating agent in toluene (Scheme 1.15).[20a,36]

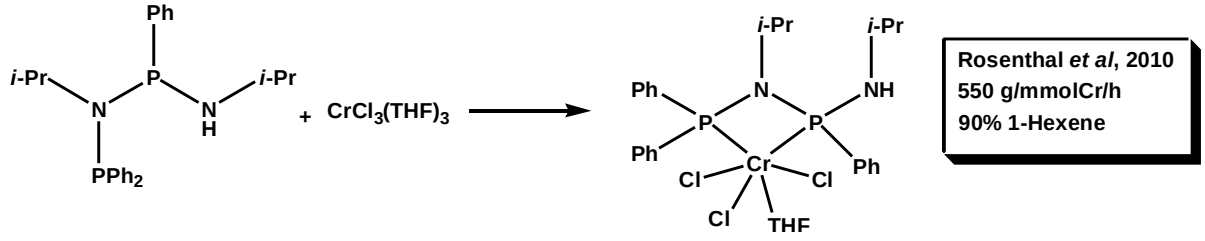
Scheme 1.15



Somewhat related to the Sasol tetramerization system, Rosenthal has reported that a phosphinamino type ligand (PNPNH), combined with $CrCl_3(THF)_3$ and activated by

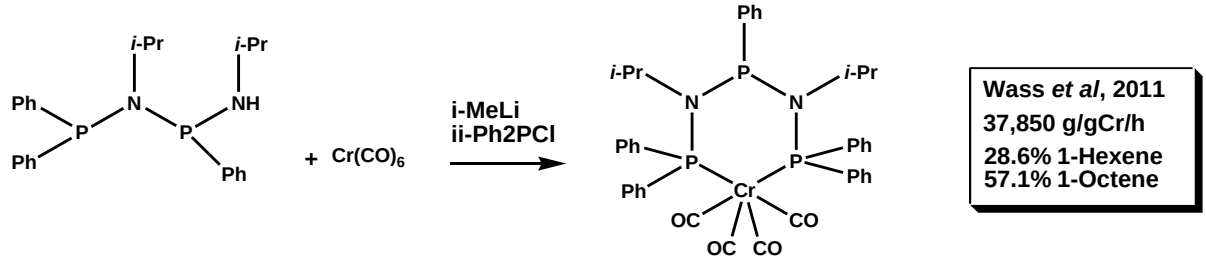
triethylaluminum can produce up to 90% of 1-hexene with overall activity of 275 g/mmolCr/h and formation of only a small amount of polyethylene (Scheme 1.16).[20d]

Scheme 1.16



One year later, Wass reported an interesting synthetic route to form the Rosenthal ligand (PNPNP) starting from (PNPNH). The new ligand could not be prepared by direct addition of Ph_2PCl to PNPNH due to close N-H···P interaction. Instead, the PNPNH ligand was complexed to $Cr(CO)_6$ then treated with MeLi and Ph_2PCl in a sort of template synthesis. The new catalyst has poor selectivity although the rarity of systems predominantly producing 1-octene makes this system automatically valuable (28% 1-hexene and 57% 1-octene, 37,850 g/gCr/h of oligomers) (Scheme 1.17).[37]

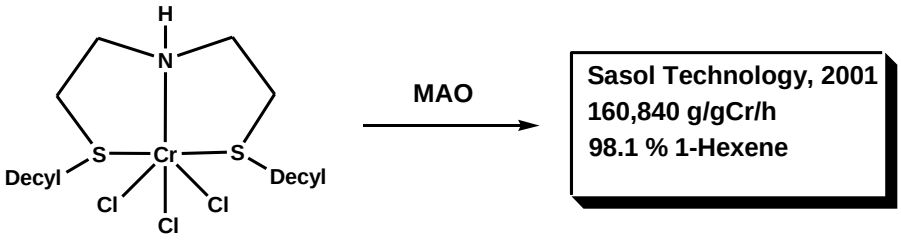
Scheme 1.17



The Sasol Technology Corporation has reported a better performing variation of the bis-phosphinoamine ligands with the bis-sulphanylamine ligands. The rationale behind thier design was that the softness of the donor nature of the phosphine pendants in the previously mentioned

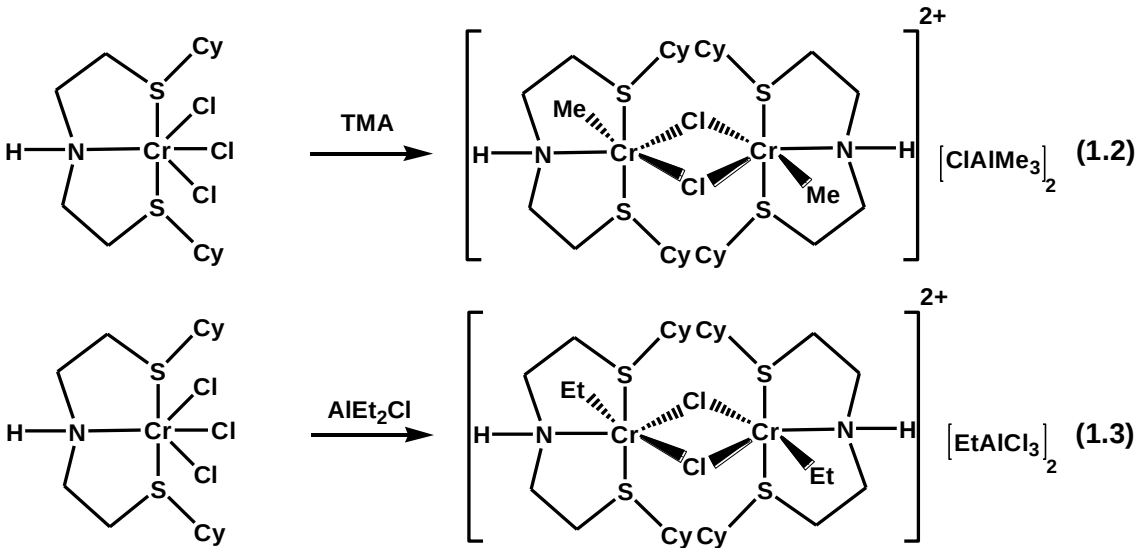
system, could in principle be replaced by other soft donors such as thioether groups.[15i] The idea proved to be correct. The [bis-(2-decylsulphanyl-ethyl)-amine]$CrCl_3$ complex when activated by 280 equivalents of MAO produced 98.1% 1-hexene with a stunning 99.9% purity (Scheme 1.18).[15h]

Scheme 1.18



Recent work from our labs has explored the organometallic chemistry of this ligand system and new interesting intermediates (**1.2**) and (**1.3**) have been isolated and fully characterized after treatment with aluminum alkyl. Such species behave as the original catalysts with very comparable selectivity and activity thus shedding some light on the reaction mechanism of these high performance catalysts (Scheme 1.19).[38]

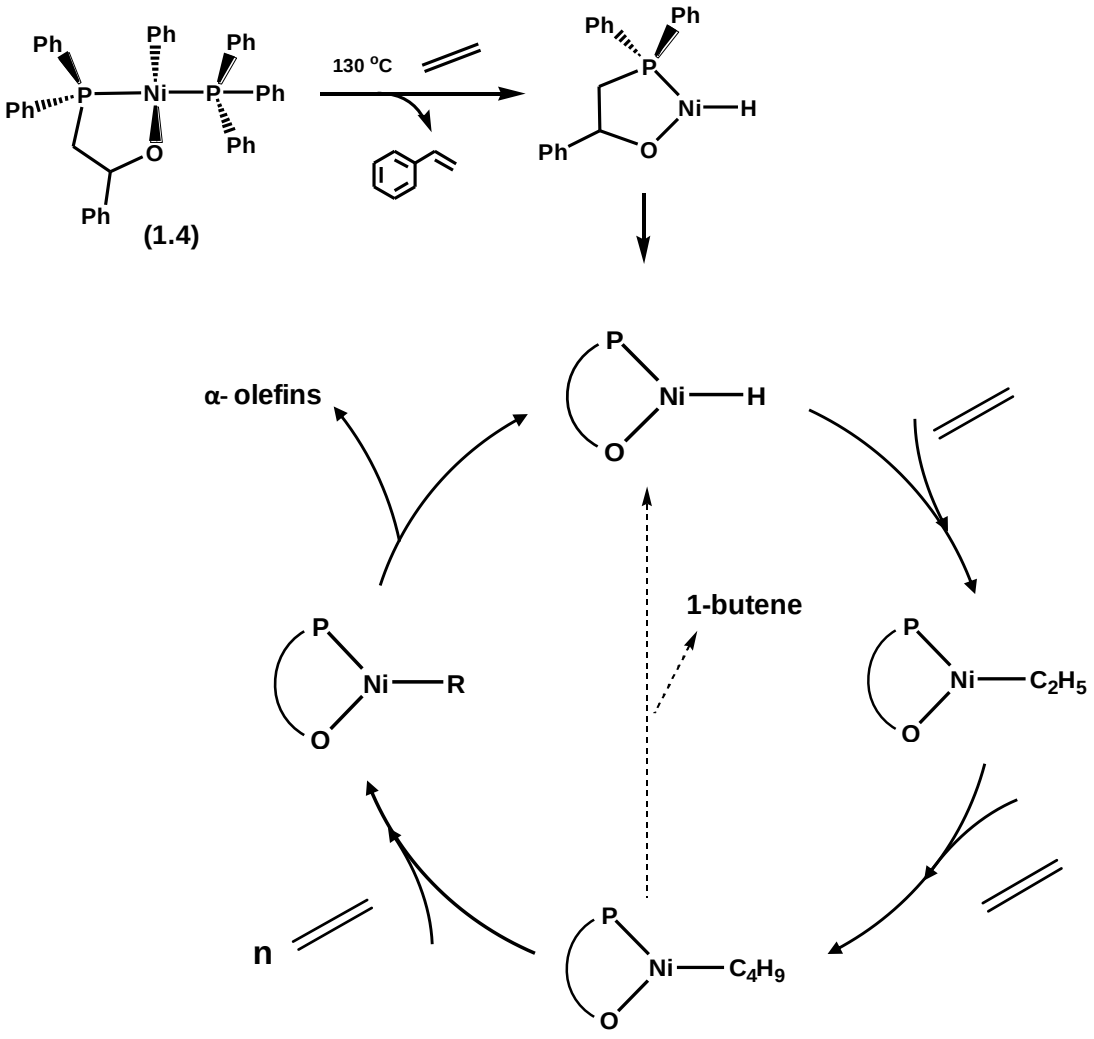
Scheme 1.19



1.5 Oligomerization Catalysts Based on Other Metals

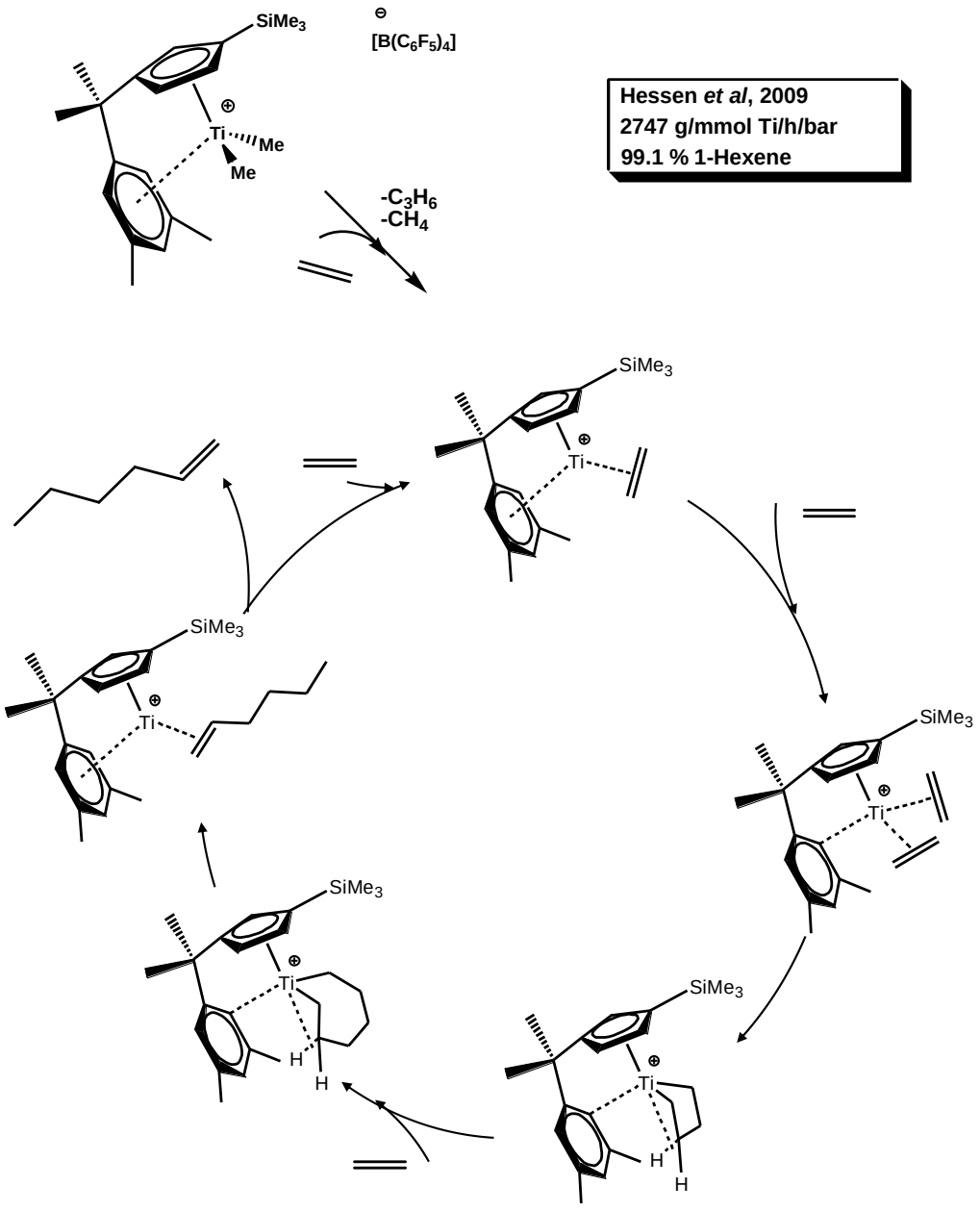
Besides chromium that accounts for more than 95% of the existing oligomerization catalysts, there are only three elements and for which interesting catalytic activity has been reported. In 1972, Keim *et al* at Shell developed a nickel complex (**1.4**) which was the first commercialized worldwide non-selective ethylene oligomerization catalyst known as Shell Higher Olefin Process (SHOP).[39] It produces 99% of linear α-olefins up to C_{30} with good activity of 6000 moles of ethylene per mol of complex.

Scheme 1.20



All marketable α-olefins have to be separated by fractional distillation. In the beginning, it was assumed that upon thermolysis, nickel hydride is produced followed by insertion of ethylene molecules into the Ni-H bond (Scheme 1.20). A few years later, this proposal was probed with *in situ* NMR studies[39b] indeed confirming the formation of the hydride intermediate which was isolated and characterized using $Ph_2PCH_2C(CF_3)_2OH$ as ligand.[40]

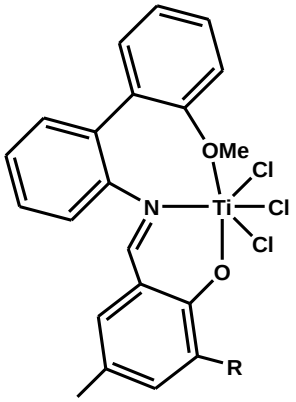
Scheme 1.21



Hessen and co-workers have developed a highly active and selective titanium complex of a hemi-labile arene-substituted cyclopentadienyl ligand {[η6-(3,5-Me_2Ph)-CMe_2-η5-($C_5H_3SiMe_3$)]$TiMe_2$}[$B(C_6F_5)_4$] (Scheme 1.21).[41] Its high activity and selectivity make this system the only one realistically competing with chromium based catalytic systems. DFT calculations carried out on this system were aimed at probing the trimerization mechanism suggesting that the same ring expansion chromacycle pathway may also be followed with the Ti(II)/Ti(IV) redox couple.[41] The intriguing idea behind this system is that the hemilability of the arene pendant connected to the Cp anions provides stability to the highly reactive divalent state and yet may readily dissociate, providing three sites for ethylene coordination on demand.

A second titanium system based on phenoxy-imine ligands with side-arm aryl-OR donors was discovered by Fujita et al.[42] It was found that the nature of the donor group contained in the side-arm significantly affects the catalytic behavior. For example, the pendant aryl-OPh donor gave very low activities and produced considerably more PE. When activated with MAO, the complex with the pendant aryl-OMe donor and adamantyl group displayed a 93.9% selectivity for C_6, also curiously producing 5.6% C_{10}. Under these conditions an outstanding overall activity of 2,720,000 g/gTi/h was obtained. When the ethylene pressure was increased slightly to 5.0 mPa, the activity increased even further to 7,140,000 g/gTi/h but with a minor loss in C_6 selectivity (92.3%) in favour to C_{10} (7.3%) (Scheme 1.22).[42] Impressively, these activities are two orders of magnitude greater than that exhibited by the Phillips catalyst under similar conditions. It is believed that the aryl-OMe group plays a crucial role in the formation and/or stabilization of the presumed Ti(II) active species expected to be capable of triggering the metallacycle mechanism.[42]

Scheme 1.22



MAO

Fujita *et al*, 2010
7,140,000 g/gTi/h
92.3 % 1-Hexene

R = Adamantyl

The second element producing worthy trimerization catalysts is tantalum. The system developed by Sen et al. has the drawback of using an expensive element but has the great advantage of an appalling simplicity.[43] The catalyst is generated by reacting $TaCl_5$ with an alkylating agent. Requiring no other reagents, these systems are commonly regarded as "ligand free". In testing varying reagents at 45 – 60 °C and 48 bar ethylene pressure, it was found that in the presence of 2 equivalents of $CH_3(CH_2)_3Li$ and PhLi both afforded the most selective catalytic systems, both with a 99% selectivity for 1-hexene and activities of 195 and 185 turnovers/Ta/h respectively (scheme 1.23). Sen suggested that reaction of $TaCl_5$ with an alkylating agent produces TaR_2Cl_3 which, upon reaction with ethylene, yields an active species believed to contain tantalum(III). This conclusion was based on previous observations about the ability of $TaCl_5$ to be reduced by alkylating agents in various stoichiometric amounts.[43]

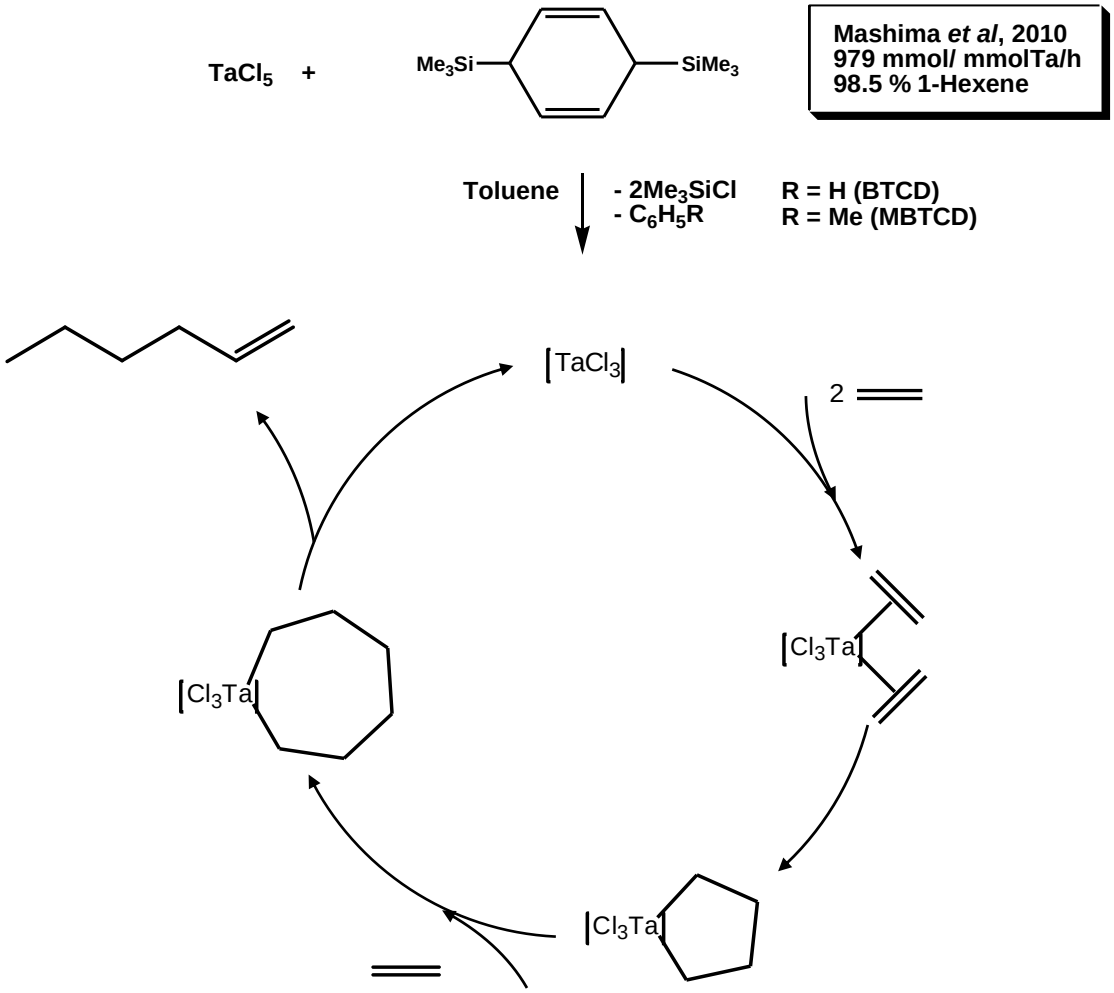
Scheme 1.23

$TaCl_5$ + *n*-BuLi or PhLi ⟶

Sen *et al*, 2001
195 and185 turnovers/Ta/h
99 % 1-Hexene

Along the same lines, Mashima et al. have been able to develop a "ligand free" tantalum system without alkylating the metal.[44] These authors were able to obtain such results by performing *in-situ* salt-free reductions of $TaCl_5$ with 3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (BTCD) or its methyl derivative (MBTCD) in the presence of ethylene. This unusual mixture produced 2 equivalents of Me_3SiCl, C_6H_5R, and an active Ta(III) species capable of trimerizing ethylene. A light excess of reducing agent provided the best catalytic activities thus suggesting that both groups, BTCD or MBTCD, might stabilize a coordinatively unsaturated Ta(III) species.

Scheme 1.24



The most selective run consisted of reacting $TaCl_5$ with MBTCD in toluene at 70 °C with 48 bar ethylene pressure yielding 98.5% 1-hexene with a moderate catalytic activity of 979 mmol/mmolTa/h (Scheme 1.24).[44] No internal olefins were formed by this system. Evidence was produced by the authors for the usual metallacycle mechanistic pathway being followed even in this case. Upon conducting Variable Temperature NMR spectroscopy experiments, the metastable tantalacyclopentane intermediate was detected and identified.

1.6 Role of the Co-Catalyst

All the catalytic systems mentioned above, whether selective or not, require an activating co-catalyst in order to produce olefins. The most commonly used is MAO (methylaluminoxane) that, for the purpose of clarifying this thesis work, requires an additional comment. Though being the most popular, the true behavior of this activating agent is not completely understood.[45] There are two roles played by MAO that can certainly be identified: alkylating agent and Lewis acid. The ability of this species to act as an alkylating agent is commonly regarded as central to the reduction of the metal center in the early stage of the activation. The second role is that of a Lewis acid. This is generally assumed to consist of alkyl abstraction, in turn affording cationization of the metal center and therefore enhancing its tendency to coordinate ethylene. Work by Hor et al. has shed more light onto the role of activating agents, and more specifically of MAO. Commercial MAO solutions are prepared through the controlled hydrolysis of $AlMe_3$. Through various testing of catalytically active [NNN] pyrazolyl Cr(III) complexes, it was found that the residual $AlMe_3$ in commercial MAO solution is a critical ingredient in both metal reduction and M-Cl activation during the early stages of activation. Such a conclusion was drawn upon examining the role of MAO once depleted of $AlMe_3$ by treatment in vacuo at 50 °C for 5 h (DMAO). By using DMAO, key intermediate species were no longer formed. Conversely, by

using pure $AlMe_3$ as activator, only very low activities were obtained indicating that MAO indeed plays an essential role in the later stages of the activation and trimerization process. Throughout all the testing performed, evidence was found for the role of $AlMe_3$ being central to adduct formation, methylation, reduction, cationization, halide abstraction, N-H deprotonation, and C-H cleavage of an unactivated arene. Contrarily, no spectroscopic or structural evidence for any MAO-stabilized adduct could be obtained despite results showing that the use of pure $AlMe_3$ as co-catalyst could not afford the same activities.[45]

1.7 Aim of the Thesis

This thesis work was originally intended to be a rather comprehensive and ambitious study aimed at clarifying the factors affecting the stability and reactivity of monovalent chromium species. The ultimate goal was gathering crucial information to assist the subsequent rational design of new and better performing oligomerization systems. Although the direct commercialization of eventual findings was not anticipated nor searched for, we have been rewarded with the discovery of commercially useful systems, now in the process of being patented by both Basell and the Dutch Polymer Institute. We have focused on a variety of ligands based on the $NP^{III}N$, $NP^{V}N$, Pyrrole, Si-SNS and Pyridine-SNS motif and used them for isolating crucial intermediates and single component catalysts. A major effort was dedicated to the characterization of intermediate active species resulting from the catalyst activation process in order to better understand the impact of the activator on the metal oxidation state and consequent repercussions on catalytic behavior. Chromium was the most obvious choice of metal.

1.7.1 Chapter 2.

Prior to this thesis work, it was reported from our lab that some chromium catalysts could switch its behaviour from oligomerization to polymerization simply by changing the activator. This observation triggers many questions about the chromium oxidation state that were responsible for both directions. Therefore, we focused on a new ligand called $NP^{III}N$ that can be described as a dynamic non-spectator because of different transformation observed after treatment of different aluminum alkyl activators. In this chapter, we describe the results of a study aiming at clarifying this important behavior. We have thus isolated five novel single-component chromium(II) oligomerization and polymerization catalysts including a rare case of a divalent chromium hydride.

1.7.2 Chapter 3.

In the oligomerization mechanistic puzzle the isolation of thoroughly characterized chromium(I) species was still missing. We believed that this species is the main one responsible for the selectivity of the oligomerization cycle. This chapter discusses a new route for the isolation of chromium(I) complexes by double vinylation of a trivalent precursor followed by reductive elimination to chromium(I)-butadiene complex. Even in this case the stabilization was provided by the anionic $NP^{III}N$ ligand. Detailed explorations of the reactivity of these new single component $NP^{III}N$-chromium(I) catalysts under different conditions are presented.

1.7.3 Chapter 4.

In many previous studies, it was proposed that chromium(II) is responsible for the non-selective ethylene oligomerization process. Therefore, in this chapter, the $NP^{III}N$ ligand system was modified further by the addition of electron donor pendant such as amine or methoxy groups in order to prevent the reduction to chromium(I) and stabilize the chromium(II) after the

aluminum alkyl treatment. We have now conclusively confirmed this point and obtained new highly active and non-selective chromium(II) oligomerization catalysts.

1.7.4 Chapter 5.

From the previous chapters, the $NP^{III}N$ framework of trivalent phosphorous has clearly indicated that this ligand frame is versatile for catalytic purposes, having allowed isolation of rare species and switchable catalytic systems. The alkylation at the P atom in turn caused retention of alkyl aluminum residues, in the end enabling the formation of single-component and switchable ethylene oligomerization and polymerization catalysts. It was argued that eliminating the possibility of alkylation at the phosphorous atom might afford a different catalytic behavior. By oxidizing the P atom to the pentavalent state ($NP^{V}N$), we have now obtained the first polymer-free highly active oligomerization system. The catalytic behavior has been extensively examined under various conditions.

1.7.5 Chapter 6.

Following the same strategies of chapters 2 and 3, herein we have isolated a chromium(I) derivative of the $NP^{V}N$ ligand system whose behavior confirms the previous observations. In this chapter we describe the reaction of $NP^{V}N$-Cr(II) complex with CH_2=CH-MgCl affording an oxidative coupling of two vinyl groups with formation of a reduced chromium complex storing additional spin density in a deprotonated butadiene residue. Its catalytic behavior as a single component selective trimerization catalyst is discussed vis a vis the charge-transfer characteristics of this particular complex.

1.7.6 Chapter 7.

This chapter discussed the deliberate alkylation of both $NP^{III}N$-Cr(II) and $NP^{V}N$-Cr(II) complexes using organo-lithium reagents such as MeLi and EtLi. We have analyzed the effect of the alkylation and oxidation of the P atom on the relative stability of the di- versus trivalent state and its effect on the preparation and catalytic behaviour of organo-chromium species. Also, it explores the role of the chlorine atom in these catalytic systems (chlorine effect) in affecting the stability of the chromium(I) intermediate and consequently the selectivity of the catalytic cycle.

1.7.7 Chapter 8.

As a follow up of previous discoveries in our lab on the Phillips pyrrolato-system, we have also further modified the pyrrole to prevent coordination of alkyl aluminum residues. These residues were invariably present in the classical Phillips system. By preventing their coordination we have isolated aluminum-free self activating catalysts that act as highly active and selective ethylene trimerization catalysts. Interestingly, we have also serendipitously discovered the first example of a Schrock-type chromium ethylidene complex, found to be a potent catalyst for selective ethylene trimerization. A mechanistic pathway has been suggested based on the isolated active intermediates and characterized by-products, which gives a much better understanding of how this catalyst selectively trimerizes ethylene to 1-hexene.

1.7.8 Chapter 9.

Previous work from our lab explored the Sasol (SNS) systems resulting in isolation of some interesting intermediates. To deepen our understanding further on the role of the unique features of this ligand in stabilizing different chromium oxidation states, we have modified the ligand by replacing the methylene carbons flanking the nitrogen atom of the SNS system by dimethyl silyl

units thus affording a modified Si-SNS system with three different substituents. These simple modifications had profound effects on the catalytic activity of the SNS system.

1.7.9 Chapter 10.

Previous work on both SNS and the Si-SNS unfortunately resulted in no isolation of a single component selective catalyst. Therefore, in this final chapter, we introduced an important modification in the ligand frame of the SNS ligand for better stabilization aimed at isolating an active intermediate that will explain the mechanism of this process. Namely, we incorporated pyridine and studied the effect of this major modification on catalytic behavior. This system has enabled the isolation of the first example of single component selective catalyst of this family of catalysts thereby providing a better and deeper understanding on the mechanism of this particular system.

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Chapter Two

Publications:

a) **Albahily, K**.; Koç, E.; Al-Baldawi, D.; Savard, D.; Gambarotta, S.; Burchell, T. J.; Duchateau, R. *Angew. Chem. Int. Ed. Engl.* **2008**, *47*, 5816.
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Chromium Catalysts Supported by a non-Spectator $NP^{III}N$ Ligand: Isolation of Single-Component Oligomerization and Polymerization Catalysts

2.1 Introduction

Ethylene oligomerization and polymerization may be regarded as belonging to the same type of C-C bond forming reaction. In fact, the highly desirable selective tri- and tetramerization processes may be simply considered as polymerizations precisely truncated at one early stage. However, it is commonly accepted that the mechanisms are completely different (oxidative addition followed by ring expansion for selective oligomerization[1] versus migratory insertion for polymerization[2]), therefore providing a conceptual distinction between the two processes. The ring-expansion mechanism implies in fact a redox process, during which, oxidative addition of the metal center to the ethylene double bond is followed by two subsequent insertions. The reductive elimination of the seven-membered ring, generated during the insertions, affords 1-hexene and restores the metal coordinative vacancy as well as the original low-valent configuration. In this event, the availability of *d* electrons seems to be a requirement for this catalytic cycle.

On the other hand, it is not obvious to which mechanism an oligomerization affording a Schultz-Flory distribution of products belongs. Furthermore, the fact that even the best chromium-based oligomerization catalysts invariably produce small amounts of PE as an undesirable side product suggests that both processes might be closely linked. Addressing these important questions cannot be dissociated from the understanding of the factors which govern the selectivity of the same catalyst towards one or the other type of transformations.

Chromium provides an ideal substrate for this research since effective catalysts for both ethylene polymerization[3] and oligomerization (including selective tri-[4] and even tetramerization)[5] have been reported for this element. Most of the homogeneous chromium-based catalytic systems reported to date invariably consist of either a di- or trivalent chromium precursor and an activator.[3] However, the understanding of these systems remains limited since even the metal's oxidation state in the catalytically active species is still debated. The nature of the transition metal is not the only important factor since the co-catalyst can also have a profound effect on the catalyst's selectivity.[6] Thus, obtaining single component catalysts by reacting a catalyst precursor with different aluminum alkyls may reveal the metal oxidation state of the catalytically active species. In turn, this may provide significant information towards the understanding of the factors which govern the C-C bond forming reaction. However, isolatable active species are relatively rare. Most well-known examples are lanthanoid single-component ethylene polymerization catalysts,[7] the borate stabilized cationic group 4 metal catalysts[7f] and borate-free transition metal single component catalysts.[8]

In this chapter, we describe the preparation and testing of new chromium-based catalyst systems supported by a non-spectator ligand. Activation with different co-catalysts gave spectacular changes in catalyst selectivity, while attempts to isolate the catalytically active

species resulted in the characterization of five unprecedented single-component oligomerization and polymerization catalysts including a rare case of a divalent chromium hydride.[9]

2.2 Experimental Part

All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried using an aluminum oxide solvent purification system. Samples for magnetic susceptibility were pre-weighed inside a drybox equipped with an analytical balance and measured on a Johnson Matthey Magnetic Susceptibility balance. Diamagnetic corrections have been applied to the calculations of the magnetic moments. Data for X-ray crystal structure determination (Table 2.1) were collected with a Bruker diffractometer equipped with a 1K Smart CCD area detector. $CrCl_2(THF)_2$ was prepared according to standard procedures. The ligands, *cis*-{(t-Bu)(H)NP[(μ-N)(t-Bu)]$_2$PN(H)(t-Bu)} and *cis*-{(2,6-diisopropylpheny)(H)NP[(μ-N)(t-Bu)]$_2$PN(H)(2,6-diisopropylphenyl)}, were prepared according to literature procedure.[10] The reagents *i*-Bu_2AlCl (Aldrich), $AlMe_3$ (Aldrich), TIBA (Aldrich), (*i*-$Bu_2Al)_2$(μ-O) and MAO (Chemtura and Aldrich) were used as received. Mass spectra were recorded on a Micromass Quattro-LC Electrospray-Triple Quadrupole Mass Spectrometer. All the experiments were done in the negative mode with toluene as the main solvent by using toluene/acetonitrile 2.5 %, Capillary voltage: 4.00-4.20 kV, Cone voltage 40 kV, and a desolvation temperature of 220 ^oC.

Preparation of [(*t*-Bu)NPN(*t*-Bu)]$_2$Cr (2.1)

A solution of *cis*-{(*t*-Bu)(H)NP[(μ-N)(*t*-Bu)]$_2$PN(H)(*t*-Bu)} (0.348 g, 1.0 mmol) in THF (20 mL) was treated with *n*-BuLi (0.84 mL, 2.1 mmol, 2.5 M in hexanes) at 0 ^oC. The mixture was allowed to stir at room temperature for 18 h. The resulting solution was added to a suspension of $CrCl_2(THF)_2$ (0.268 g, 1.0 mmol) in THF (10 mL). The reaction mixture was stirred at room

temperature overnight. The solvent was evaporated *in vacuo* and the residue redissolved in toluene. The resulting suspension was centrifuged and the solution was stored at -30 ^{o}C. Brown crystals of **2.1** separated over two days and were filtered, washed with cold hexanes (10 mL) and dried *in vacuo* to give analytical pure **2.1** (0.294 g, 74%). [μ_{eff} = 4.98 μ_B]. ESI-MS (rel. int.) *m/z* = 397.0 ([M-H]$^-$, 42), 341.1 ([M-C_4H_9]$^-$, 98), 324.0 ([M-C_4H_9-NH_3]$^-$, 100). El. Anal. Calcd (Found) for $C_{16}H_{36}CrN_4P_2$: C 48.23 (48.25), H 9.11 (9.17), N 14.06 (13.91).

Preparation of {[(*t*-Bu)NP(Me)N(*t*-Bu)]AlMe$_2$}Cr{[(*t*-Bu)NP(Me)(AlMe$_3$)N(*t*-Bu)]AlMe(μ-Me)} (2.2)

A solution of **2.1** (0.398 g, 1.0 mmol) in toluene (20 mL) was treated with trimethyl aluminum (0.288 g, 4.0 mmol) at room temperature and stirred for 10 minutes. The solvent was removed *in vacuo* and then hexane (5 mL) was added. Storing the resulting solution at -30 ^{o}C for 3 days afforded small purple crystals of **2.2** which were filtered and washed with cold hexanes and dried *in vacuo* (0.386 g, 63%). [μ_{eff} = 4.97 μ_B]. ESI-MS (rel. int.) *m/z* = 613.9 ([M-H]$^-$, 48), 703.2 (multiple signals, [M+toluene-H]$^-$, 100) (experiments with toluene-d^8 gave the expected isotopic pattern), 571.0 ([M-C_3H_7]$^-$, 88). El. Anal. Calcd (Found) for $C_{25}H_{63}Al_3CrN_4P_2$: C 48.93 (48.77), H 10.18 (9.98), N 9.13 (9.15).

Preparation of {[(*t*-Bu)NP(*i*-Bu)N(*t*-Bu)]AlCl(*i*-Bu)}Cr(μ-Cl)$_2$Al(*i*-Bu)$_2$ (2.3)

A solution of **2.1** (0.398 g, 1.0 mmol) in toluene (20 mL) was treated with diisobutylaluminum chloride (0.704 g, 4.0 mmol) at room temperature and allowed to stir for 10 minutes. The solvent was removed by vacuum and then hexanes were added. The solution was stored in a -30 ^{o}C freezer for 3 days. The resulting product was filtered and washed with cold hexanes and dried *in vacuo* to give **2.3** as blue crystals (0.282 g, 46%). [μ_{eff} = 5.24μ_B]. ESI-MS (rel. int.) *m/z* = 613.8 (multiple signals, [M-H]$^-$, 20), 690.0 (multiple signals, [M+toluene-CH_2]$^-$,

28) (experiments with toluene-d^8 gave the expected isotopic pattern), 577.0 ([M-Cl]$^-$, 100). El. Anal. Calcd (Found) for $C_{24}H_{54}Al_2Cl_3CrN_2P$: C 46.95 (46.68), H 8.87 (8.71), N 4.56 (4.63).

Preparation of [(Ar)NPN(*t*-Bu)]$_2$Cr (2.4)

A solution of *cis*-{(2,6-diisopropylphenyl)(H)NP[(μ-N)(*t*-Bu)]$_2$PN(H)(2,6-diisopropylphenyl} (0.556 g, 1.0 mmol) in THF (20 mL) was treated with *n*-BuLi (0.84 mL, 2.1 mmol, 2.5 M in hexanes) at 0 ºC. The mixture was allowed to stir at room temperature for 20 h. The resulting solution was added to a suspension of $CrCl_2(THF)_2$ (0.268 g, 1.0 mmol) in THF (10 mL). The reaction mixture was stirred at room temperature overnight. The solvent was evaporated *in vacuo* and the residue redissolved in toluene. The resulting suspension was centrifuged and the solution was stored at -30 ^{o}C. Brown crystals separated over four days and were filtered, washed with cold hexanes (10 mL) and dried *in vacuo* to give analytically pure **2.4** (0.355 g, 59%). [μ_{eff} = 4.96 μ_B]. Anal. Calcd. (Found) for $C_{32}H_{52}CrN_4P_2$: C 63.35 (63.28), H 8.64 (8.59); N 9.23 (9.19).

Preparation of {[(Ar)NP(Me)N(*t*-Bu)]AlMe$_2$}Cr{[(Ar)NP(Me)(AlMe$_3$)N(*t*-Bu)]AlMe(μ-Me)} (2.5)

A solution of **2.4** (0.606 g, 1.0 mmol) in toluene (5 mL) was treated with trimethyl aluminum (0.288 g, 4.0 mmol) at room temperature and stirred for 10 minutes. Storing the resulting solution at -30 ºC for 5 days afforded small purple crystals of **2.5** which were filtered and washed with cold hexanes (5 mL) and dried *in vacuo* (0.455 g, 55%). [μ_{eff} = 4.98 μ_B]. Anal. Calcd (Found) for $C_{41}H_{78}Al_3CrN_4P_2$: C 59.91 (59.87), H 9.57 (9.55), N 6.82 (6.78).

Preparation of {μ-[(*t*-Bu)NP(*i*-Bu)N(*t*-Bu)]Al(*i*-Bu)$_2$}$_2$Cr (2.6)

Neat Al(*i*-Bu)$_3$ (0.79 g, 4.0 mmol) was added at -30 ^{o}C to a solution of [(*t*-Bu)NPN(*t*-Bu)]$_2$Cr (**2.1**) (0.83 g, 2.1 mmol) in toluene (10 mL) and allowed to stir for 15 minutes at room temperature. The solvent was removed *in vacuo* and the residue redissolved in hexane. Crystals of **2.6** separated from the resulting solution upon standing at -30 ^{o}C for 3 days. The brown crystals were filtered and washed with cold hexanes (10 mL) and dried *in vacuo* (0.96 g, 57%). [μ_{eff} = 4.74 μ_B]. El. Anal. Calcd. (found) for $C_{40}H_{90}Al_2CrN_4P_2$: C 60.43(60.41), H 11.41(11.39), N 7.05(7.00).

Preparation of {[μ-{(*i*-Bu)P[N(*t*-Bu)]$_2$}Al(*i*-Bu)$_2$]Cr(μ-H)}$_2$ (2.7)

Neat Al(*i*-Bu)$_3$ (3.96 g, 20.0 mmol) was added at -30 ^{o}C to a solution of [(*t*-Bu)NPN(*t*-Bu)]$_2$Cr (**2.1**) (0.80 g, 2.0 mmol) in toluene (10 mL) and allowed to stir for 15 minutes at room temperature. The solvent and the excess of Al(*i*-Bu)$_3$ was removed *in vacuo* and the resulting solid residue redissolved in hexane. The solution was stored in a -30 ^{o}C freezer for 3 days. Red-purple crystals of **2.7** separated which were filtered, washed with cold hexanes (10 mL) and dried *in vacuo* (0.75 g, 90%). [μ_{eff} = 1.63 μ_B]. El. Anal. Calcd. (found) for $C_{40}H_{92}Al_2Cr_2N_4P_2$: C 56.58(56.55), H 10.92(10.88), N 6.60(6.54).

2.3 X-ray Data

Table 2.1. Crystal Data and Structure Analysis Results of Complexes **2.1**-**2.7**.

	2.1	**2.2**	**2.3**
Formula	$C_{16}H_{36}CrN_4P_2$	$C_{25}H_{63}Al_3CrN_4P_2$	$C_{24}H_{54}Al_2Cl_3CrN_2P$
Mw	398.43	614.67	613.97
space group	Orthorhombic, Pccn	Triclinic, P-1	Orthorhombic, P2(1)2(1)2(1)
***a* (Å)**	16.166(4)	9.3177(13)	8.6978(14)
***b* (Å)**	11.929(3)	11.7323(16)	16.930(3)
***c* (Å)**	11.814(3)	17.301(2)	23.134(4)
α, (deg)	90	90.963(2)	90
β, (deg)	90	95.876(2)	90
γ, (deg)	90	94.465(2)	90
***V* (Å^3)**	2278.1(11)	1875.0(4)	3406.6(10)
Z	4	2	4
Radiation	0.71073	0.71073	0.71073
***T* (K)**	200(2)	200(2)	200(2)
D_{calcd} (g cm^{-3})	1.162	1.087	1.197
μ_{calcd} (mm^{-1})	0.647	0.479	0.685
***F*$_{000}$**	856	766	1312
***R*, *Rw*^{2a}**	0.0446, 0.1054	0.0568, 0.1327	0.0275, 0. 0622
GoF	1.118	0.993	1.041

	2.4	**2.5**	**2.6**	**2.7**
Formula	$C_{32}H_{52}CrN_4P_2$	$C_{41}H_{78}Al_3CrN_4P_2$	$C_{40}H_{90}Al_2CrN_4P_2$	$C_{40}H_{92}Al_2Cr_2N_4P_2$
Mw	606.72	821.95	795.06	849.08
space group	Monoclinic, P2(1)/n	Monoclinic, P2(1)/c	Monoclinic, P2(1)/n	Triclinic, P-1
***a* (Å)**	9.201(9)	18.9199(16)	12.604(3)	9.702(4)
***b* (Å)**	21.91(2)	14.7620(12)	13.740(3)	10.454(4)
***c* (Å)**	9.597(9)	18.1352(15)	14.445(4)	14.135(8)
α, (deg)	90	90	90	107.554(6)
β, (deg)	113.947(11)	102.7670(10)	97.494(4)	95.139(9)
γ, (deg)	90	90	90	101.520(6)
***V* (Å^3)**	1768(3)	4939.9(7)	2480.2(11)	1322.0(11)
Z	2	4	2	1
Radiation	0.71073	0.71073	0.71073	0.71073
***T* (K)**	203(2)	201(2)	202(2)	202(2)
D_{calcd} (g cm^{-3})	1.140	1.105	1.065	1.066
μ_{calcd} (mm^{-1})	0.439	0.379	0.359	0.532
***F*$_{000}$**	652	1780	876	464
***R*, *Rw*^{2a}**	0.0559, 0.1350	0.0648, 0.1383	0.0537, 0.1292	0.0679, 0.1809
GoF	1.039	1.069	1.055	1.021

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

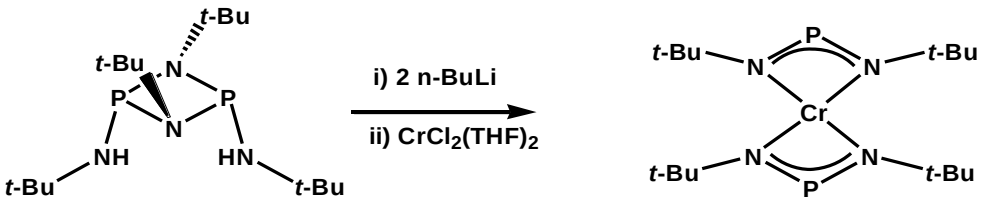
2.4 Results and Discussions

2.4.1 New Chromium Catalyst Switches from non-Selective Ethylene Oligomerization to Trimerization and Polymerization: Isolation of Single-Component Chromium Polymerization Catalysts

In this part, we describe the preparation and testing of a chromium-based catalytic system supported by a non-spectator ligand. Activation with different co-catalysts gave spectacular changes in catalyst selectivity while attempts to isolate the catalytically active species resulted in the characterization of two unprecedented single component polymerization catalysts.

The work of Wass, Overett and Bercaw has clearly demonstrated the potential of the combination of nitrogen and phosphorous donor atoms in a three-atom array for selective trimerization[4f,g,j,k] and tetramerization catalysts.[5] Our previous mechanistic studies on selective trimerization has led us to believe that a stable cationic organo Cr(III) might be the key to selectivity for the oligomerization process.[11a] These two arguments prompted us to use the established $[(t\text{-Bu})NPN(t\text{-Bu})]_2^{2-}$ dianion,[10,12] since the particular geometry of the cage, as defined by the ligand four-member P_2N_2 ring, with the two additional N donor atoms was assumed to be unsuited to accommodate the square planar geometry of d^4 Cr(II).

Scheme 2.1



(2.1)

The reaction of the dianion, under the form of dilithium salt, with $CrCl_2(THF)_2$ produced the divalent, distorted square-planar $[(t\text{-Bu})NPN(t\text{-Bu})]_2Cr$ (**2.1**) (Figure 2.1). In this species the

dianion was cleaved into two [(*t*-Bu)NPN(*t*-Bu)]$^-$ mono-anions, a transformation occasionally observed only with main group elements[12f,g,h] (Scheme 2.1).

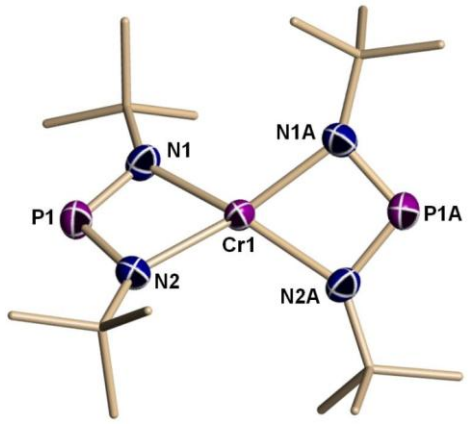


Figure 2.1. Partial thermal ellipsoid plot of **2.1** with ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (°): Cr(1)-N(1) = 2.098(3), Cr(1)-N(2) = 2.103(3), N(1)-Cr(1)-N(2) = 70.50(10), N(1)-Cr(1)-N(1a) = 158.10(16), N(1)-Cr(1)-N(2a) = 114.08(11).

When activated with MAO, **2.1** yielded a statistical distribution of ethylene oligomers (including waxes) but with an unprecedented activity. It proved difficult to control the reaction temperature with catalyst concentrations as low as 5 μmol. The catalyst was found to be thermally robust as catalytic tests with higher catalyst loading easily reached and maintained temperatures above 110 ^{o}C for prolonged periods of time. The activity gradually increases with an increasing Al:Cr ratio but did not affect the product distribution. Interestingly, the selectivity of **2.1** was completely determined by the nature of the activator (Table 2.2). While MAO resulted in oligomerization of ethylene, activation with (i-$Bu_2Al)_2$(μ-O) gave low molecular weight polyethylene with a similarly high activity as when activated with MAO. Notably, small amounts of a mixture of exclusively 1-hexene and 1-octene (ave. ratio = 85:15) were formed as side product. In an attempt to track the origin of the oligomerization, it was argued that possibly i-Bu_3Al present in (i-$Bu_2Al)_2$(μ-O) was responsible for the oligomers. In fact upon activation with Al(i-Bu)$_3$, complex **2.1** indeed gave 1-hexene with excellent selectivity (>99.9 by GC). Although

the activity was substantially less, while comparing to the activity when activated with MAO, it is still similar to that of the other existing selective catalysts.[11,13]

This intriguing diversity of catalytic behavior as a function of the activator clearly indicates that different catalytically active species are generated from the reaction of **2.1** with the alkyl aluminum reagent. Therefore, we embarked on attempts to isolate such species by carrying out the reaction of **2.1** with various aluminum alkyls. In all cases, the reactions were surprisingly clean and produced crystalline or microcrystalline materials. In the particular cases when **2.1** was reacted with $AlMe_3$ and *i*-Bu_2AlCl, was it possible to reveal the structures by single crystal X-ray diffraction. Both complexes {[(*t*-Bu)NP(Me)N(*t*-Bu)]$AlMe_2$}Cr{[(*t*-Bu)NP(Me)($AlMe_3$)N(*t*-Bu)]AlMe(μ-Me)} (**2.2)** and {[(*t*-Bu)NP(*i*-Bu)N(*t*-Bu)]AlCl(*i*-Bu)}Cr(μ-$Cl)_2Al(i$-$Bu)_2$ (**2.3**) contain chromium in the divalent state (Scheme 2.2).

Table 2.2. Ethylene oligomerization and polymerization by 2.1-2.3 as single component catalysts or in combination with different cocatalysts.

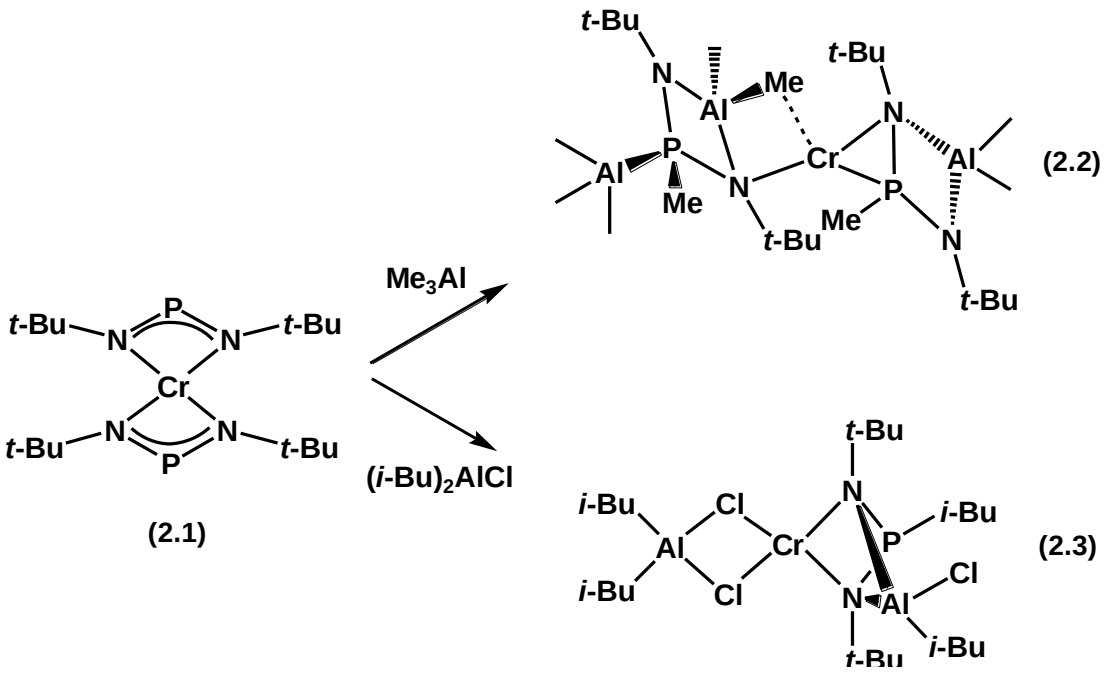
#	Cat. #	[cat] µmol	Cocat.	Al:Cr	PE g	M_n g·mol^{-1}	PDI	Oligom. mL	Activity g·mmol^{-1}·h^{-1}	C_6 %	C_8 %	C_{10} %	C_{12} %	C_{14} %	C_{16} %	α
1	**2.1**	5	MAO	2000	0.9	310[b]	1.4	59	23600	45.2	29.7	11.0	6.6	3.8	2.1	0.58
2	**2.1**	5	MAO	1000	0.9	420[b]	1.3	16	6400	40.0	23.9	15.4	9.1	5.3	2.8	0.61
3	**2.1**[a]	5	MAO	1000	trace	-		12	4800	41.5	25.1	15.8	9.0	4.8	2.5	0.57
4	**2.1**	5	MAO	500	3.4	440[b]	1.4	1	400	44.1	23.2	12.1	7.9	4.9	4.4	0.62
5	**2.1**	5	Al(*i*-Bu)$_3$	1000	1.5	400[b]	1.3	2	800	>99.9	-	-	-	-	-	-
6	**2.1**	5	Al(*i*-Bu)$_3$	500	trace	-		1	400	>99.9	-	-	-	-	-	-
7	**2.1**	1	(*i*-$Bu_2Al)_2$(µ-O)	1000	16.4	34940	3.7	2	32800	82.5	17.5	-	-	-	-	-
8	**2.1**	1	(*i*-$Bu_2Al)_2$(µ-O)	500	12.2	12760	3.0	2	24400	85.0	15.0	-	-	-	-	-
9	**2.2**	10	-	-	11.2	37990	3.2	0	2240	-	-	-	-	-	-	-
10	**2.2**	5	MAO	2000	0.2	490[b]	1.3	47	18800	45.3	26.1	14.2	8.3	4.7	2.1	0.57
11	**2.2**	5	MAO	1000	0.1	500[b]	1.2	45	18000	39.2	26.0	15.3	9.8	6.3	3.4	0.64
12	**2.2**	5	Al(*i*-Bu)$_3$	1000	1.4			0	560	-	-	-	-	-	-	-
13	**2.3**	10	-	-	16.5	26780	2.8	0	3300	-	-	-	-	-	-	-
14	**2.3**	5	MAO	2000	1.2	450[b]	1.3	85	34000	35.2	26.3	15.8	11.5	7.1	4.1	0.67
15	**2.3**	5	MAO	1000	0.7	410[b]	1.2	69	27600	36.7	26.5	15.9	10.6	6.5	3.8	0.64
16	**2.3**	5	Al(*i*-Bu)$_3$	1000	3.6	11420	4.3	0	920	-	-	-	-	-	-	-

Standard conditions: T = 50 °C, 100 mL of toluene, 35 bar of ethylene, 30 min reaction time; [a] 5 bar; [b] waxes.

In spite of their different appearance, the two reactions have in fact followed a similar trend, in the sense that the P atom has been alkylated in both cases. Also the resulting [(*t*-Bu)NP(R)N(*t*-Bu)] dianion uses the two N donor atoms to bridge the chromium metal to an AlX_2 [X = Me

(**2.2**); Cl, *i*-Bu (**2.3**)] residue eventually affording an $\{RP[N(t\text{-}Bu)]_2AlX_2\}^-$ anion. The difference between the two complexes is that **2.3** contains one $\{RP[N(t\text{-}Bu)]_2AlX_2\}^-$ ligand with chromium bonded to a second $Al(i\text{-}Bu)_2$ residue via two bridging chlorides, while complex **2.2** contains two $\{RP[N(t\text{-}Bu)]_2AlX_2\}^-$ ligand systems. The second ligand in **2.2** has the alkylated phosphorous atom coordinating an additional $AlMe_3$, which prevents it from binding to chromium like the other does. Consequently, one of the two aluminum methyl groups occupies the fourth coordination site of the distorted square planar chromium atom (Figures 2.2).

Scheme 2.2



Since the anionic charge of the $[RPN(t\text{-}Bu)_2AlX_2]^-$ ligand is located at the aluminum center that, at least for Al(3), is situated relatively far away from the chromium center, the structure can be regarded as containing a formally dicationic chromium stabilized by two anionic $\{RP[N(t\text{-}Bu)]_2AlX_2\}^-$ ligands. Interestingly, such a structure resembles the earlier reported divalent chromium tetramerization catalyst precursor $\{[CyN(PPh_2)_2]_2Cr\text{-}ClAlMe_3\}^+$ where a formally

cationic chromium is stabilized by one Me_3AlCl^- fragment and two diphosphinoamine ligands.[13] Different from this complex which required a co-catalyst before any catalytic activity may be observed, **2.2** is a single-component catalyst. Simple exposure of **2.2** to ethylene (35 bar, 50 ^oC) yielded polyethylene with moderate activity. Upon treatment of **2.2** with MAO, again a radical switch in selectivity towards a statistical distribution of ethylene oligomers (including some waxes) was observed with a similarly phenomenal activity as found for the **2.1**/MAO system. Surprisingly, attempts of activating both **2.1** and **2.2** with excess of $AlMe_3$ in fact reached the opposite effect of totally deactivating the system.

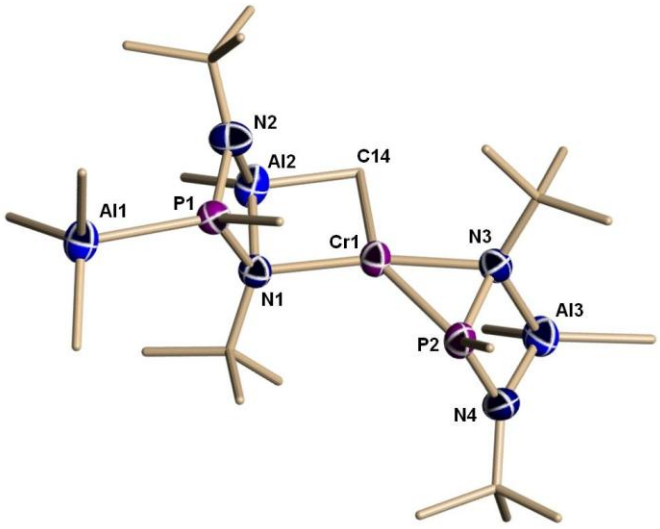


Figure 2.2. Partial thermal ellipsoid plot of **2.2** with ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (°): Cr(1)-N(1) = 2.135(3), Cr(1)-N(3) = 2.136(3), Cr(1)-C(14) = 2.344(5), Cr(1)-P(2) = 2.3505(12), N(1)-Al(2) = 1.940(3), N(2)-Al(2) = 1.839(3), Al(2)-C(14) = 2.025(5), P(1)-N(1) = 1.736(3), P(1)-N(2) = 1.667(3), Al(1)-P(1) = 2.5549(15), Al(3)-N(3) = 1.993(3), Al(3)-N(4) = 1.876(4), P(2)-N(3) = 1.710(3), P(2)-N(4) = 1.648(4) ; N(1)-Cr(1)-N(3) = 167.32(12), N(1)-Cr(1)-C(14) = 89.40(14), N(3)-Cr(1)-C(14) =103.24(14), N(1)-Cr(1)-P(2) = 122.95(9), N(3)-Cr(1)-P(2) = 44.50(9), C(14)-Cr(1)-P(2) = 145.67(12), Al(2)-C(14)-Cr(1) = 78.08(16).

Complex **2.3** also acts as a single component ethylene polymerization catalyst with similar activity as for **2.2**. Different from **2.2**, there are no free coordination sites around chromium in

2.3, nor are Cr-C bonds present which could possibly act as polymerization initiators (Figure 2.3). In analogy with **2.2**, attempts to activate **2.1** and **2.3** with excess *i*-Bu_2AlCl did not produce any catalytic transformation. Treatment of **2.3** with MAO instead afforded an ethylene oligomerization catalyst even more active than **2.1** with a nearly constant activity over the period of at least 30 minutes. The most probable explanation for the single–component activity of **2.3** is migration of an alkyl from the Al-R residue leading to "{*i*-BuP[N(*t*-Bu)]$_2$Al(*i*-Bu)Cl}Cr(*i*-Bu)" that again can be regarded as an ionic structure containing a cationic chromium alkyl. Alkyl shuttling from the alkylated P atom is also another possibility which cannot be ruled out at this stage. Since **2.2**, **2.3** and (*i*-$Bu_2Al)_2$(μ-O)–activated **2.1** yield similar molecular weight polymers, it is probable that closely related active species are being generated in the three systems.

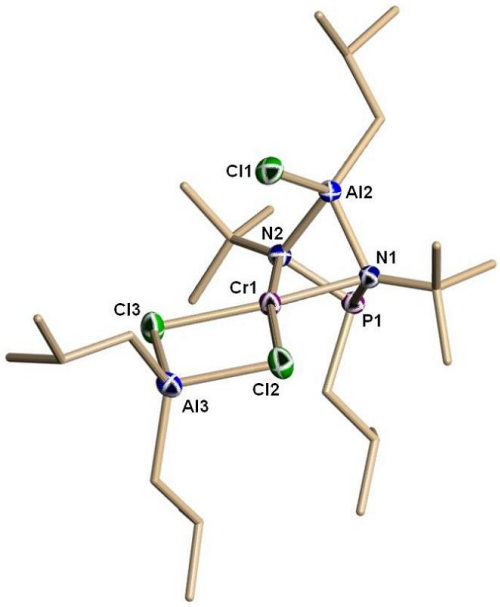
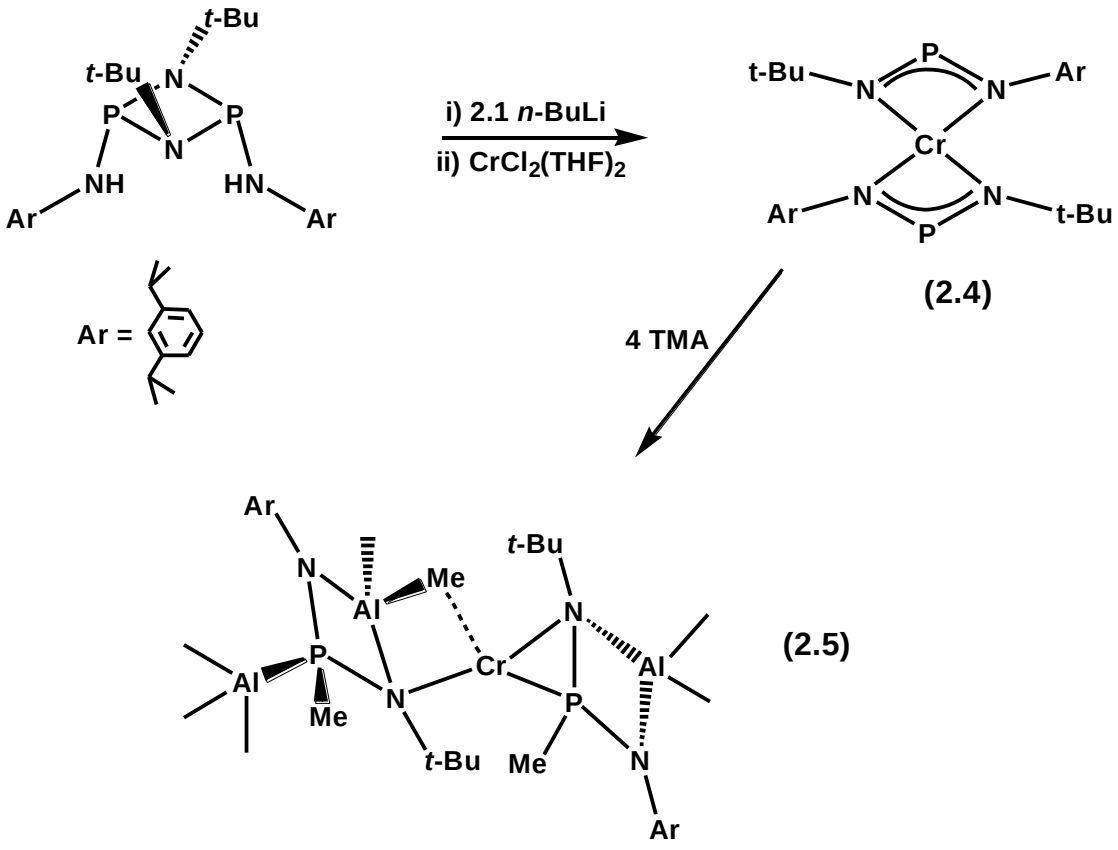


Figure 2.3. Partial thermal ellipsoid plot of **2.3** with ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (°): Cr(1)-N(2) = 2.1256(12); Cr(1)-N(1) = 2.1305(13); Cr(1)-Cl(3) = 2.4041(5); Cr(1)-Cl(2) = 2.4063(5); Al(3)-Cl(3) = 2.2764(7); Al(3)-Cl(2) = 2.2765(7); Al(2)-N(1) = 1.9209(13); Al(2)-N(2) = 1.9283(13); Al(2)-C(13) = 1.9370(16); P(1)-N(1) = 1.7651(14); P(1)-N(2) = 1.7730(14); N(2)-Cr(1)-N(1) = 65.26(5); N(2)-Cr(1)-Cl(3) = 104.24(4); N(1)-Cr(1)-Cl(3) = 169.42(4); N(2)-Cr(1)-Cl(2) = 169.26(4); N(1)-Cr(1)-Cl(2) = 104.67(4); Cl(3)-Cr(1)-Cl(2) = 85.713(17); Cl(3)-Al(3)-Cl(2) = 91.88(2); N(1)-Al(2)-N(2) = 73.20(6); N(1)-P(1)-N(2) = 80.88(6).

2.4.2 Switchable Single-Component Chromium Trimerization Catalyst

The reaction of $[(Ar)N(H)PN(t\text{-}Bu)]_2$ with *n*-BuLi followed by reaction with $CrCl_2(THF)_2$ afforded the divalent $[(Ar)NPN(t\text{-}Bu)]_2Cr$ (**2.4**) where the ligand system underwent a dimer to monomer dissociation generating two (Ar)NPN(*t*-Bu) monoanions (Scheme 2.3). The affinity of divalent chromium for square-planar ligand fields as dictated by the d^4 electronic configuration is most probably the driving force behind this unusual behavior. The structure of **2.4** is very similar to the divalent $[(t\text{-}Bu)NPN(t\text{-}Bu)]_2Cr$ (**2.1**) and does not show any relevant feature other than a divalent chromium center in much expected square-planar environment defined by the four nitrogen atoms of the two NPN anions (Figure 2.4).

Scheme 2.3



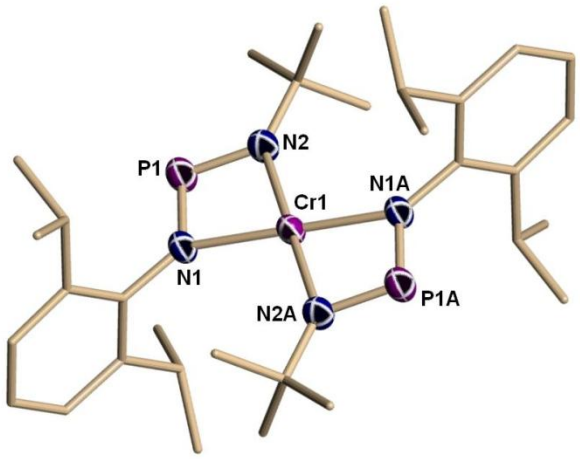


Figure 2.4. Partial thermal ellipsoid plot of **2.4** with ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (°): Cr(1)-N(1) = 2.114(3), Cr(1)-N(2) = 2.086(3), N(1)-P(1) = 1.628(3), N(2)-P(1) = 1.612(3), N(1)-Cr(1)-N(2) = 71.02(13), N(1)-Cr(1)-N(2a) = 108.98(13), N(2)-Cr(2a)-N(1a) = 179.998(1).

Following our interest for the behavior of chromium complexes with aluminum alkyls,[6,11a,13,14,] we reacted **2.4** with a diverse series of alanes using several different stoichiometric ratios. Whereas the reaction of the [(*t*-Bu)NPN(*t*-Bu)]$_2$Cr system with several alanes afforded crystalline products, to this end, only treatment of **2.4** with 4 equivalent of Al(CH$_3$)$_3$ gave material in good yield that could be characterized by X-ray single crystal diffraction and was found to be the novel {[(Ar)NP(Me)N(*t*-Bu)]AlMe$_2$}Cr{[(Ar)NP(Me)(AlMe$_3$)N(*t*-Bu)]AlMe(μ-Me)} (**2.5**) (Scheme 2.3). A similar product was also obtained when [(*t*-Bu)NPN(*t*-Bu)]$_2$Cr was treated with AlMe$_3$. The primary role of the alane activators appears to have been the alkylation of the P atom. The resulting (Ar)NP(R)N(*t*-Bu) dianion binds to the AlMe$_2$ residue via the two N donor atoms forming an {MeP[N(*t*-Bu)][N(Ar)]AlMe$_2$}$^-$ anion that is attached to the chromium metal via a nitrogen and a phosphorus atom (Figure 2.5). In the second ligand in **2.5** the alkylated phosphorus atom coordinates to an additional AlMe$_3$, which prevents it from binding to chromium. As a result, one

of the two aluminum methyl groups of the $AlMe_2$ residue occupies the fourth coordination site of the distorted square planar chromium atom.

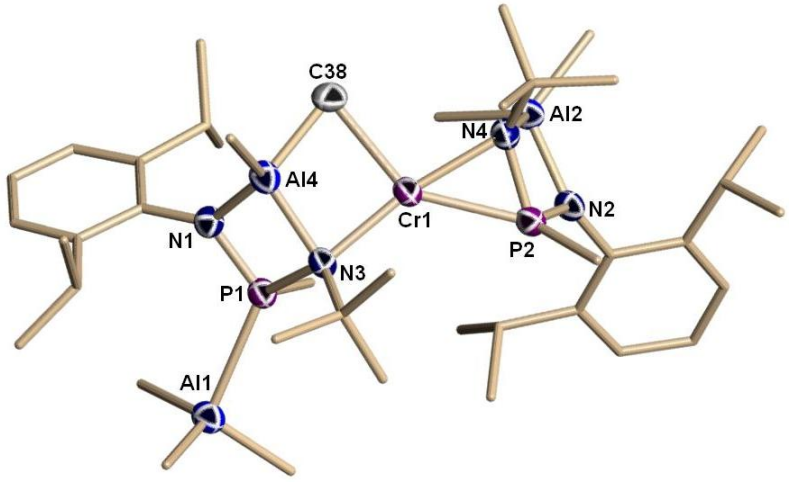


Figure 2.5. Partial thermal ellipsoid plot of **2.5** with ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (°): Cr(1)-N(3) = 2.144(4), Cr(1)-N(4) = 2.125(4), Cr(1)-C(38) = 2.289(6), Cr(1)-P(2) = 2.4035(16), N(4)-Al(2) = 2.026(4), N(2)-Al(2) = 1.899(4), Cr(1)-Al(4) = 2.8098(18), Al(2)-P(2) = 2.627(2), P(2)-N(2) = 1.659(4), P(2)-N(4) = 1.717(4), Al(4)-P(1) = 2.634(2), Al(4)-N(3) = 1.951(4), Al(4)-N(1) = 1.845(4), P(1)-N(3) = 1.746(4), P(1)-N(1) = 1.674(4), Cr(1)...Al(4) = 2.8098(18), N(4)-Cr(1)-N(3) = 165.94(16), N(4)-Cr(1)-C(38) = 98.89(19), N(3)-Cr(1)-C(38) = 90.15(19), N(4)-Cr(1)-P(2) = 44.03(11), N(3)-Cr(1)-P(2) = 127.78(12), C(38)-Cr(1)-P(2) = 142.07(16), Al(4)-C(38)-Cr(1) = 79.9(2).

Complex **2.5** is a single component trimerization catalyst exclusively producing 1-hexene (Table 2.3). Its activity is of the same order of magnitude as that of other selective systems recently reported such as the Sasol's [SNS]$CrCl_3$ system.[4h] The selectivity also depends on temperature. Namely, at 80 ºC 1-hexene is no longer produced and polymer is formed instead. A similar behavior was observed by de Wet-Roos and coworkers for the Sasol PNP-type tetramerization catalyst system.[15] At room temperature, the catalytic activity drops and the activity is marginal. Reaction times up to 10 hours at typical reaction temperature (50 ºC) did not improve the productivity of 1-hexene indicating rapid catalyst deactivation (in less than 30 minutes). Interestingly, the analogue of **2.5** with only nitrogen–*t*-Bu substituents, {[MeP{N(*t*-

Bu)}$_2$]AlMe$_2$}Cr{[MeP(AlMe$_3$){N(*t*-Bu)}$_2$]AlMe(μ-Me)} (**2.2**), afforded polyethylene already at 50 ºC. This is assumed to be due to a lower stabilizing ability of *t*-Bu substituents versus aryl substituents. Upon addition of aluminum-based co-catalysts, the selectivity of complex **2.5** shows a dramatic switch. In the case of treatment with MAO, a statistical distribution of oligomers with an enormous increment of activity was observed.[9,16] Upon activation with [(*t*-Bu)$_2$Al]$_2$O the catalyst selectivity switches to ethylene polymerization instead. With Al(*i*-Bu)$_3$ as co-catalyst, no oligomers and only a small amount of polymer is formed. The switch of catalytic behavior from selective to non-selective oligomerization is intriguing given that the ligand and the initiating alkyl function (methyl) are the same for the two processes in this case. The fact that at elevated temperature **2.5** becomes an ethylene polymerization catalyst indicates that it is rather facile to switch between the two different processes.

Table 2.3. Oligomerization and polymerization results for complex **2.5** with and without cocatalysts.[a]

Catalyst	Cat µ-mol	Cocat.	Al:Cr	PE (g)	Oligom. (g)	Activity g/mmolCr/h	C_6 %	C_8 %	C_{10} %	C_{12} %	C_{14} %	C_{16} %	C_{18} %	α
2.5	10	-	-	-	3	600	99.9	-	-	-	-	-	-	
2.5[b]	10	-	-	-	0.5	100	99.9	-	-	-	-	-	-	
2.5[c]	10	-	-	3.9	-	780	-	-	-	-	-	-	-	
2.5	10	MAO	2000	0.4	85	17000	39.0	27.6	15.7	8.7	4.8	2.9	1.4	0.55
2.5	10	[(*t*-Bu)$_2$Al]$_2$O	1000	10.5[d]	2	400	9.9	-	-	-	-	-	-	
2.5	10	Al(*t*-Bu)$_3$	1000	1.2	-	240	-	-	-	-	-	-	-	
(SNS)CrCl$_3$	10	MAO	1000	0.2	7	1400	≥98	2	-	-	-	-	-	
(SNS)CrCl$_3$	10	MAO	300	0.4	6	1200	≥98	2	-	-	-	-	-	

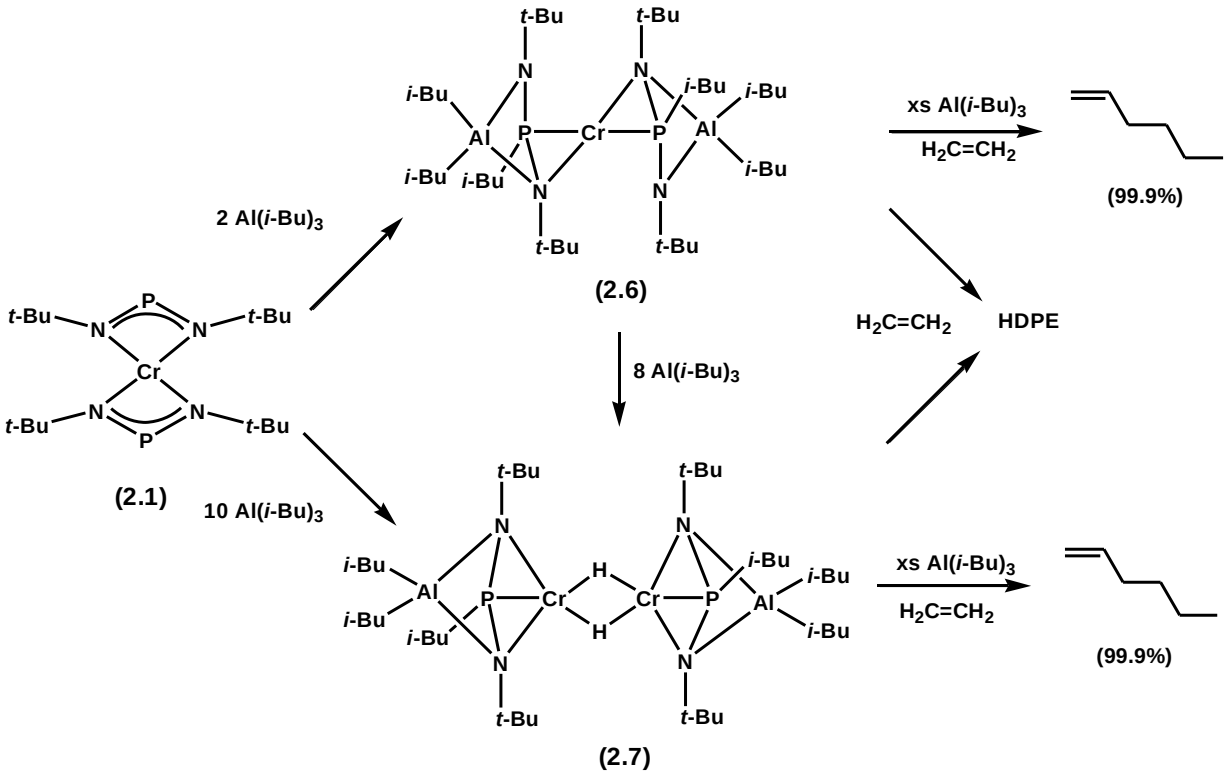
[a)] Conditions: 100 mL of toluene, 35 bar of ethylene, reaction temperature 50 °C, reaction time 30 min; [b)] Reaction temperature 25 °C, [c)] Reaction temperature 80 °C; [d)] The SEC of the polyethylene shows a bimodal distribution with an M_w for the main peak at $1.3 \cdot 10^6$ g·mol^{-1} and the M_w for the smaller peak at 12,000 g·mol^{-1}.

Explaining or simply rationalizing this intriguing behavior is not an easy task at this early stage. We speculate that the difference of reactivity (trimerization, oligomerization and polymerization) as a function of the presence/absence and nature of the alane is to be ascribed to three different species.

2.4.3 Isolation of a Chromium-Hydride Single-Component Ethylene Polymerization Catalyst

In section (2.4.1) we described that [(*t*-Bu)NPN(*t*-Bu)]$_2$Cr (**2.1**) affords 1-hexene upon activation with Al(*i*-Bu)$_3$ alongside with small amount of polymer. In an attempt to isolate this trimerization catalyst, we have reacted **2.1** on preparative scale with two equivalents of Al(*i*-Bu)$_3$ in toluene. The reaction afforded the new paramagnetic species {μ-[(*t*-Bu)NP(*i*-Bu)N(*t*-Bu)]Al(*i*-Bu)$_2$}$_2$Cr (**2.6**) as dark brown crystals [μ_{eff} = 4.74 μ_{BM}] (Scheme 2.4).

Scheme 2.4



The crystal structure of **2.6** (Figure 2.6) revealed the connectivity as consisting of a divalent chromium atom in a square planar coordination environment. Both NPN ligands have undergone the same addition of a (*i*-Bu) and Al(*i*-Bu)$_2$ residues across the N=P formal double bond. As a result, the P atom is alkylated, the ligand acquired a second negative charge, and the Al(*i*-Bu)$_2$ cationic residue is retained through coordination to the two N atoms.

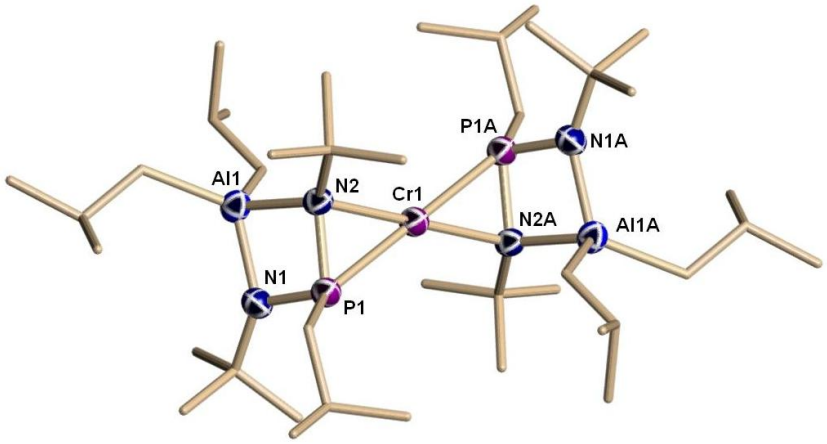


Figure 2.6. Partial thermal ellipsoid plot of **2.6** with ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (°): Cr(1)-N(2) = 2.129(3), Cr(1)-P(1) = 2.3989(10), Cr(1)-N(2a) = 2.129(3), N(1)-Al(1) = 1.898(3), N(2)-Al(1) = 1.988(3), P(1)-Cr(1)-P(1a) = 180.0, N(2)-Cr(1)-N(2a) = 180.0, P(1)-Cr(1)-N(2) = 44.51(7).

Treatment of **2.6** with eight equivalents of Al(*i*-Bu)$_3$ or a convenient one-pot synthesis via reaction of **2.1** with ten equivalents afforded the dinuclear hydride bridged {[μ-{(*i*-Bu)P[N(*t*-Bu)]$_2$}Al(*i*-Bu)$_2$]Cr(μ-H)}$_2$ (**2.7**) as dark-purple crystals (Figure 2.7). Complex **2.7** is paramagnetic [μ_{eff} = 1.63 μ_{BM}] with a magnetic moment that would be expected on the basis of the presence of a fairly short Cr-Cr distance [Cr(1)..Cr(1a) = 2.6142 Å] and two bridging hydrides.[17] The ^{1}H-NMR spectrum showed only broad and overlapping features in the range -30 to 30 ppm which could not be conclusively assigned (Figure 2.8).

The salient features of the crystal structure of **2.7** are the replacement of one alkylated ligand system by one hydride, which bridges an identical unit by forming a Cr_2H_2 core. Different from **2.6** the ligand adopted a "tridentate" facial-type of bonding mode in the sense that both nitrogen and phosphorus coordinate the chromium center. This is of course in the event that we consider the short Cr-P contact [Cr-P = 2.6178(15)] as a genuine bond. Depending on this, the coordination geometry can be considered as either square planar or distorted square-pyramidal. This difference is most likely the result of the release of steric compression and increased Lewis

acidity of the metal as arising from the loss of one ligand system. The position of the two bridging hydrogen atoms was yielded by the difference Fourier maps. The intermetallic distance is consistent with that observed in the other very few existing divalent chromium hydrides.[17]

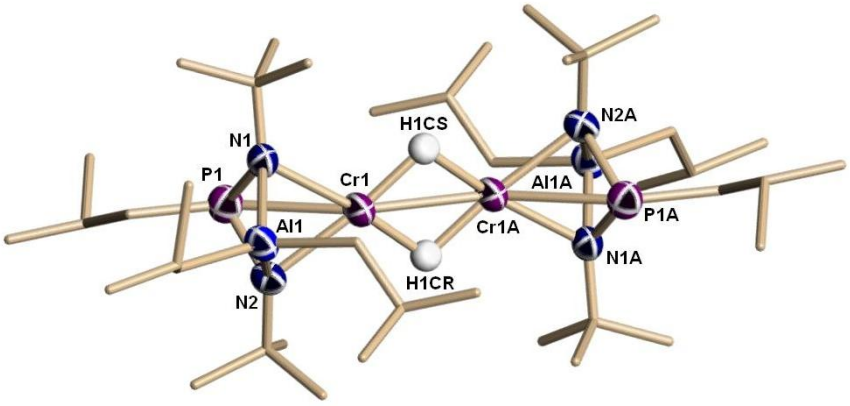


Figure 2.7. Partial thermal ellipsoid plot of **2.7** with ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (°): Cr(1)...Cr(1a) = 2.6142(16), Cr(1)-N(1) = 2.156(3), Cr(1)-N(2) = 2.141(3), Cr(1)-P(1) = 2.6178(15), N(1)-Al(1) = 1.953(3), N(2)-Al(1) = 1.956(3), N(1)-Cr(1)-N(2) = 65.20(11), N(1)-Cr(1)-P(1) = 41.88(8), N(2)-Cr(1)-P(1) = 42.27(8).

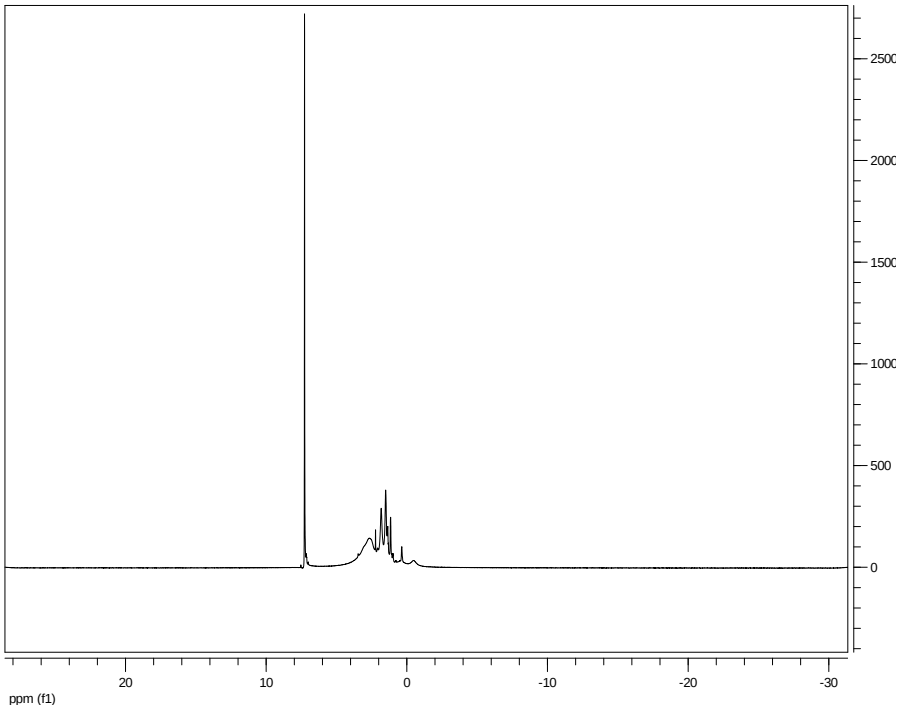


Figure 2.8. ^{1}H-NMR spectrum of complex **2.7**.

Given the structure of **2.7**, it is reasonable to propose that the role of the excess Al(*i*-Bu)$_3$ during its formation from either **2.1** or **2.6** is twofold: 1) abstracting one ligand system and 2) producing an unstable *i*-Bu-Cr group which, upon *β*-H elimination reaction, generates the hydride. Conversely, other possibilities such as isobutene elimination of (*i*-Bu)$_3$Al affording (*i*-Bu)$_2$Al(μ-H)$_2$Al(*i*-Bu)$_2$ as a possible source of hydride cannot be conclusively ruled out. However, attempts to more directly obtain **2.7** via reaction of **2.1** with (*i*-Bu)$_2$Al(μ-H)$_2$Al(*i*-Bu)$_2$, afforded complete decomposition to metallic chromium. Well-characterized chromium hydrides are rare.[17] Divalent chromium hydrides are exclusively limited to one cubane structure of the Cp*Cr moiety,[17b-d] one dinuclear structure with a Cr_2H_2 core similar to **2.7**,[17f] two cases of the NacNac ligand system,[17g,h] and two terminally bonded phosphine complexes.[17a,i-j] In the present case, it is the first time that a chromium-hydride is actually active as single-component polymerization catalyst (Table 2.4). The single component catalytic behavior of **2.7** can be easily explained by assuming dimer-to-monomer dissociation, ethylene coordination and insertion into the Cr-H bond. It is interesting to observe that the complex contains Cr in its divalent state. Thus, assuming that reaction with ethylene does not result in an oxidation of the metal center, neutral, divalent chromium is responsible for ethylene polymerization.

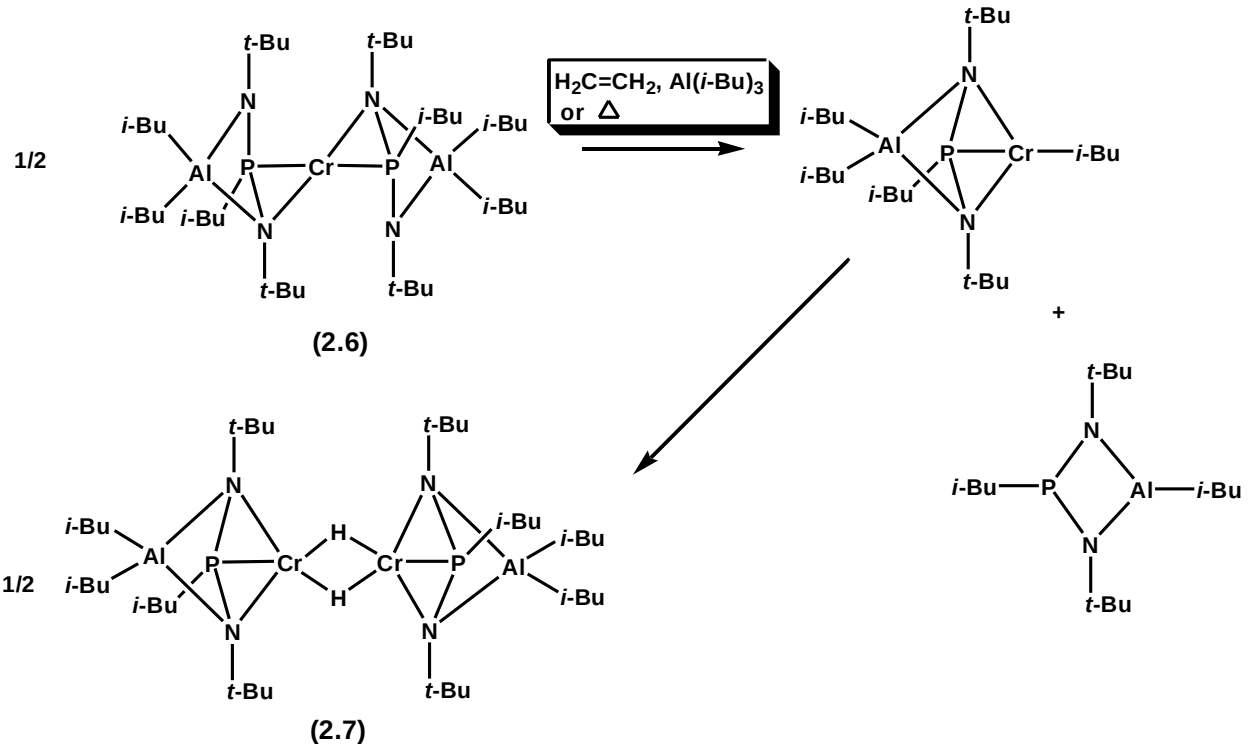
Table 2.4. Oligomerization and polymerization results for complex **2.1**-**2.7** with and without co-catalysts.[a]

Catalyst	TIBA (equiv.)	Activity[c]	PE (g)	1-hexene (mL)	Mw, g/mol	PDI
2.1	500	415[b]	trace	4	-	-
2.1	1000	801[b]	1.5	8	-	-
2.6	-	820[c]	8.2	-	1,300,000	3.2
2.6	500	402[b]	0.5	4	-	-
2.6	1000	807[b]	0.2	8	-	-
2.7	-	1450[c]	14.5	2	1,400,000	3.0
2.7	500	399[b]	2.0	4	-	-
2.7	1000	800[b]	0.8	8	-	-

[a)] Conditions: 20 μmoles, 50 °C, 35 bar, 30 min. [b)] mL(C_6)/mmol(Cr)/h. [c)] g(PE)/mmol(Cr)/h.

Complex **2.6,** which does not have a pre-formed Cr-C bond, is also active as a single-component polymerization catalyst. The single-component character of **2.6** is most likely due to a spontaneous conversion of **2.6** into **2.7** under the polymerization conditions (Scheme 2.5) given that both **2.6** and **2.7** produce polyethylene with basically identical activities, molecular weights and polydispersities. It is tempting to speculate that a similar formation of chromium hydrides might be responsible for the ubiquitous presence of polyethylene in variable amounts during the oligomerization processes. The catalytic activity of the single-component **2.7** is of the same order of magnitude as the most active chromium catalyst precursors.[18]

Scheme 2.5



Upon activation with a large excess of Al(*i*-Bu)$_3$, both **2.6** and **2.7** show a switching of selectivity from ethylene polymerization to selective trimerization. Given that also complex **2.1** affords a selective ethylene trimerization catalyst upon treatment with an excess of Al(*i*-Bu)$_3$, it

is reasonable to assume that the same active species is generated regardless which of the three complexes has been used as a precursor. This is also reiterated by the nearly identical catalytic activity observed for the three species. It is most unfortunate that the actually active trimerization catalyst has so far escaped crystallographic characterization. At this stage we can only reiterate that it is the *large excess* of Al(*i*-Bu)$_3$ that triggers this further transformation towards the selective trimerization catalyst. Oxidation to the trivalent state via a disproportionation,[11a] similar to the case of the Sasol "SNS" catalyst is certainly a possibility. Alternatively, the formation of a coordinatively unsaturated Cr(I) species {μ-[(*t*-Bu)NP(*i*-Bu)N(*t*-Bu)]Al(*i*-Bu)$_2$}Cr, possibly under the formation of a toluene complex,[19] is another realistic possibility.

2.5 Conclusions

The unexpected behavior of the initially intended [(*t*-Bu)NPN(*t*-Bu)]$_2^{2-}$ ligand system gave access to a non-spectator [(*t*-Bu)NPN(*t*-Bu)]$^-$ anion, which readily reacts with aluminum alkyls. The resulting {RP[N(*t*-Bu)]$_2$AlX$_2$}$^-$ anions affords thermally stable chromium single-component catalysts. This desirable behavior is to be ascribed to two characteristics of the {RP[N(*t*-Bu)]$_2$AlX$_2$}$^-$ mono-anion: a) it has the potential to transfer an alkyl to chromium (either from P or from the Al residue), evidently affording robust chromium alkyl species and b) it establishes a structure where the Lewis acidity of the aluminum residue enhances the chromium positive charge. Complexes **2.2** and **2.3** can reasonably be regarded as representative of the fate of **2.1** in the early stage of its activation. The intriguing selective trimerization as obtained upon activation of **2.1, 2.6** and **2.7** with large excess of Al(*i*-Bu)$_3$ remains unexplained at this stage.

We have also reported a single-component catalyst (**2.5**) selectively producing 1-hexene with good activity. It is interesting to observe that this species contains chromium in its divalent state as it is unlikely that the divalent state enables the selective trimerization process.[7c,13,14]

Finally, the isolation of the divalent chromium hydrides (**2.7**) that act as a single component polymerization catalyst gave a great clue about the polymerization source (side product) in most of the oligomerization catalyst systems. In the next chapter, we will describe the isolation and characterization of chromium(I) derivative of this ligand system and its behaviour vis-à-vis the catalytic performance.

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Chapter Three

Publications:

Albahily, K.; Shaikh, Y.; Sebastiao, E.; Gambarotta, S.; Korobkov, I.; Gorelsky, S. *J. Am. Chem. Soc.* **2011**, *133*, 6388.

Vinyl Oxidative Coupling as a Synthetic Route to Catalytically Active Monovalent Chromium

3.1 Introduction

There is a sharp resurgence of interest in the recent literature for the preparation, characterization and reactivity of monovalent chromium complexes. This interest may be understood in view of the tremendous reactivity of these species capable of forming dinitrogen,[1] inverted sandwich,[2] and the so-called quintuple bonded complexes.[3] There is also a keen industrial interest focused on these complexes since the monovalent state of chromium has been linked to the occurrence of selectivity in the ethylene oligomerization catalytic cycle.[4,5a,b] Nonetheless, low valent chromium and its highly coveted monovalent state remain scarce. This is in spite of the existence of a fairly large family of chemically inert carbonyl/arene monovalent derivatives that may be obtained through partial oxidation of readily-available zerovalent starting materials.[5] Only recently an effective strategy has been developed to extract the strongly stabilizing carbonyls from the metal coordination sphere thus enhancing reactivity and catalytic behavior.[5a,b,d]

The utilization of ligands with electron storage capability is a well-consolidated technique to prepare reduced species (low-valent synthons).[6] In other words, it has been possible to prepare

complexes with a formal low-valent appearance, in reality possessing higher-valent metals coupled to radical anionic forms of the ligands.[7] Despite the fact that the low-valent appearance is deceptive, the high reactivity expected for genuine low-valent species is remarkably preserved. Chromium falls within this same line of behavior[7s] since this strategy has allowed observing a rare case of dinitrogen fixation as well as partial protonation and cleavage.[1b]

In this chapter, we have explored a synthetic pathway to monovalent chromium alternative to the traditional reductions with alkali metal, hydrides or alkyl aluminum. In fact, one of the problems to be faced in reaching the monovalent state, especially during catalytic cycles, is the chromium's redox dynamism. In other words, the mono-, di- and trivalent states readily inter-convert, even in the presence of a reducing agent,[4c,8] via disproportionation triggered by intermediate dimeric aggregations. Therefore, all ligand's features, such as steric hindrance and electron storage capability, which might be capable of preventing clusterification or minimally stabilize the monovalent state, may be the key to the preparation of monovalent chromium complexes or synthons. Furthermore, due to the generally good stability of chromium's divalent state, it is important to develop two-electron reduction pathways of trivalent precursors capable of bypassing divalent intermediates. A particularly illustrative example is provided by the *in situ* formation of monovalent complexes during the catalytic cycles for selective ethylene tri- and tetramerization. Catalyst activation in those cases relies on the double alkylation of the trivalent center followed by two-electron reductive elimination.[2c]

Given this background, we have now probed the possibility of performing a two-electron reduction of trivalent chromium via Stille-type oxidative coupling of two vinyl functions in line with the behavior of the platinoid metal systems.[9] This methodology stems from the basic idea that a butadiene unit, generated by the oxidative coupling of the two vinyls, could sufficiently

stabilize the monovalent state. Of course there was always the possibility that due to a large extent of back-bonding the oxidation state might be increased and the oligomerization behavior quenched. Keeping in consideration all these possibilities, we attempted the double vinylation of a trivalent chromium complex formed with an anionic ligand system based on the $NP^{III}N$ framework. The preceding work in chapter two has clearly indicated that this $NP^{III}N$ ligand is versatile for catalytic systems, having allowed isolation of rare intermediate species and studying switchable catalytic behavior.[8c,10] Furthermore, there have been a few instances where we have observed that activation with most reducing alkylaluminum activators, such as Al(*i*-Bu)$_3$, resulted in selective trimerization.[8c] This clearly indicates that the monovalent state may be reached and sufficiently stabilized with this ligand.

3.2 Experimental Part

All reactions were carried out under dry nitrogen atmosphere. Solvents were dried using an aluminum oxide solvent purification system. Samples for magnetic susceptibility were pre-weighed inside a dry-box equipped with an analytical balance and measured on a Johnson Matthey Magnetic Susceptibility balance. Elemental analyses were carried out with a Perkin-Elmer 2400 CHN analyzer. Data for X-ray crystal structure determination (Table 3.1) were obtained with a Bruker diffractometer equipped with a 1K Smart CCD area detector. Methylaluminoxane (MAO, 10% in toluene) was purchased from Aldrich. The ligand *cis*-{(*t*-Bu)N(H)P[μ-N(*t*-Bu)]$_2$PN(H)(*t*-Bu)} was prepared according to a published procedure.[11]

Preparation of *cis*-{(*t*-Bu)NP[μ-N(*t*-Bu)]$_2$PN(*t*-Bu)}[Li(THF)])CrCl$_2$ (3.1)

A solution *cis*-{(*t*-Bu)N(H)P[μ-N(*t*-Bu)]$_2$PN(H)(*t*-Bu)} (0.348 g, 1.0 mmol) in THF (10 mL) was treated with *n*-BuLi (0.84 mL, 2.1 mmol, 2.5 M in hexanes). The mixture was allowed to stir

at room temperature for 18 h. The resulting solution was added to a suspension of $CrCl_3(THF)_3$ (0.375 g, 1.0 mmol) in THF (5 mL). Stirring was continued at room temperature for 4 h forming a brown solution. The resulting solution was analyzed by mass spectroscopy: ESI-MS *m/z* = 548.16 $([M+H]^+$.

Preparation of (*cis*-{(*t*-Bu)NP[μ-N(*t*-Bu)]$_2$PN(*t*-Bu)}CrCl)$_2$ (3.2)

A solution of (*t*-Bu)(H)NP[(μ-N)(*t*-Bu)]$_2$PN(H)(*t*-Bu) (0.240 g, 0.69 mmol) in THF (10 mL) was treated with *n*-BuLi (0.55 mL, 1.38 mmol, 2.5 M in hexanes) and stirred over a 24 h period at room temperature. Solid $CrCl_3(THF)_3$ (0.258 g, 0.69 mmol) was added and the resulting mixture was stirred over 24 h at room temperature. The solvent was then removed *in vacuo* and replaced with hexane (5 mL). The green solution that resulted was centrifuged and the supernatant stored at -30 ^oC for four days affording deep-green long prisms of **3.2** (0.191 g, 0.220 mmol 64%) μ_{eff} = 3.88 μ_B. Crystals spontaneously loose lattice hexane and samples needed to be pumped *in vacuo* prior to analytical characterization. El. Anal. Calcd. (found) for $C_{32}H_{72}Cl_2Cr_2N_8P_4$: C 44.29 (44.14), H 8.36 (8.31), N 12.91 (12.88). ESI-MS *m/z* = 867.08 $([M+H]^+$.

Preparation of (*cis*-{(*t*-Bu)NP[μ-N(*t*-Bu)]$_2$PN(*t*-Bu)}[Li(THF)])Cr(*cis*-η^4-butadiene) (3.3)

A solution of (*t*-Bu)(H)NP[(μ-N)(*t*-Bu)]$_2$PN(H)(*t*-Bu) (0.348 g, 1.0 mmol) in THF (10 mL) was treated with *n*-BuLi (0.84 mL, 2.1 mmol, 2.5 M in hexanes). The mixture was allowed to stir at room temperature for 20 h. The resulting solution was added to a suspension of $CrCl_3(THF)_3$ (0.375 g, 1 mmol) in THF (5 mL). Stirring was continued at room temperature for 2 h. After cooling to -30 ^oC, a solution of vinylmagnesium chloride (1.28 mL, 1.6 M in THF) was introduced via syringe and the mixture stirred for 18 h at room temperature. The solvent was removed *in vacuo* and hexane (10 mL) was added. The suspension was centrifuged and, after

concentration of the supernatant to 4 mL, stored at -30 ^{o}C for four days. The resulting crystalline product was filtered, washed with cold hexanes (10 mL) and dried *in vacuo* affording **3.3** (0.212 g, 0.40 mmol, 40 %) as a brown crystalline solid. μ_{eff} = 3.81 μ_B. El. Anal. Calcd. (found) for $C_{24}H_{50}CrLiN_4OP_2$: C 54.23 (54.24), H 9.48 (9.46), N 10.54 (10.53). ESI-MS *m/z* = 532.58 $[M+H]^+$.

Preparation of [(*t*-Bu)N-P-N(*t*-Bu)]Cr(*cis*-η^4-butadiene)PMe_3 (3.4).

A solution of **3.3** (0.150 g, 0.28 mmol) in hexane (3 mL) was treated with PMe_3 (0.016 g, 0.28 mmol) and stirred for 2 days. The resultant dark red-green solution was centrifuged and slow evaporation of the supernatant yielded dark red-green crystals of **3.4** (0.031 g, 0.087 mmol, 31%). μ_{eff} = 3.86 μ_B. El. Anal. Calcd. (found) for $C_{15}H_{33}CrN_2P_2$: C 50.70 (50.71), H 9.36 (9.38), N 7.88 (7.89). ESI-MS *m/z* = 356.51$[M+H]^+$.

Isolation of *cis*-{(*t*-Bu)NP[μ-N(*t*-Bu)]$_2$PN(*t*-Bu)}[Li(THF)]$_2$ (3.5)

The insoluble material obtained from the centrifugation of the reaction mixture above was washed using cold hexanes (5 mL) then dissolved in diethyl ether (2 mL) and stored at -30 ^{o}C for 4 days where it afforded colorless crystals of **3.5** (0.042 g,0.083 mmol, 59 %). ^{1}H-NMR (C_6D_6, 300 MHz, 300 K) δ 1.32 (q, 8H), THF (OCH_2CH_2)), 1.48 (s, 18H, C(C*H*)$_3$), 1.55 (s, 18H, C(C*H*)$_3$), 3.67 (t, 8H, THF (OCH_2CH_2)). ^{31}P{^{1}H}-NMR (C_6D_6, 300 MHz, 300 K) 160.3 (S). El. Anal. Calcd. (found) for $C_{24}H_{52}Li_2N_4O_2P_2$: C 57.13 (57.28), H 10.39 (10.42), N 11.10 (11.07).

3.3 Computational Details

DFT calculations were performed using the Gaussian 09 package[12] using the PBE[13] functional and the TZVP[14] basis set. Tight SCF convergence criteria were used for all calculations. Harmonic frequency calculations were performed on the optimized structures to

establish the nature of stationary points. The converged wave functions were tested to confirm that they correspond to the ground-state surface. All calculations for the analysis of the electronic structure, including the generation of initial wave functions, Mulliken population analysis[15] and the calculation of Mayer bond order indices,[16] natural population analysis (NPA)[17]-derived spin densities and populations of fragment orbitals[18] were performed using the AOMix software package.[19]

3.4 X-Ray Data

Table 3.1. Crystal Data and Structure Analysis Results of Complexes **3.2-3.5**.

	3.2	**3.3**	**3.4**	**3.5**
formula	$C_{32}H_{72}Cl_2Cr_2N_8P_4(hexane)_{0.8}$	$C_{24}H_{50}CrLiN_4OP_2$	$C_{15}H_{33}CrN_2P_2$	$C_{24}H_{52}Li_2N_4O_2P_2$
Mw	936.69	531.56	355.37	504.52
space group	Monoclinic, C2/m	Monoclinic, P2(1)/c	Orthorhombic,	Monoclinic,
***a* (Å)**	24.9305(9)	16.3492(8)	13.5057(6)	10.635(5)
***b* (Å)**	11.2301(4)	9.8141(5)	16.7235(8)	15.822(7)
***c* (Å)**	9.7869(4)	19.5718(10)	8.9182(4)	19.350(8)
α	90	90	90	90
β	109.799(2)	110.647(3)	90	105.545(7)
γ	90	90	90	90
***V* (Å^3)**	2578.08(17)	2938.6(3)	2014.29(16)	3137(2)
Z	2	4	4	4
radiation	0.71073	0.71073	0.71073	0.71073
***T* (K)**	200(2)	200(2)	200(2)	201(2) K
D_{calcd} (g cm$^-$	1.207	1.201	1.172	1.068
μ_{calcd} (mm^{-1})	0.682	0.520	0.721	0.163
***F*$_{000}$**	1004	1148	764	1104
***R*, *Rw*^{2a}**	0.0717, 0.1849	0.0524, 0.1238	0.0741, 0.1053	0.0521,0.1287
GoF	1.031	1.029	1.086	1.024

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

3.5 Results and Discussion

The Cr(III) complex starting material was prepared via direct reaction of the deprotonated form of *cis*-{(*t*-Bu)N(H)P[μ-N(*t*-Bu)]$_2$PN(H)(*t*-Bu)}with $CrCl_3(THF)_3$. The reaction afforded a new species believed to be the trivalent *cis*-{(*t*-Bu)NP[μ-N(*t*-Bu)]$_2$PN(*t*-Bu)}[Li(THF)])$CrCl_2$ (**3.1**) (Scheme 3.1). Complex **3.1** cannot be isolated and normally characterized, since it visibly changes color when its THF solutions are evaporated to dryness and the residue recrystallized from hexane, or more simply precipitation with non-solvent was attempted. Its structure is therefore proposed on the basis of the ESI-MS of the reaction solutions and its chemical behavior as highlighted in Scheme 3.1. In fact, recrystallization from hexane of the dried residues was accompanied by separation of LiCl affording a new crystalline compound formulated as trivalent (*cis*-{(*t*-Bu)NP[μ-N(*t*-Bu)]$_2$PN(*t*-Bu)}$CrCl)_2$ (**3.2**) on the basis of its crystal structure (Figure 3.1) and analytical data.

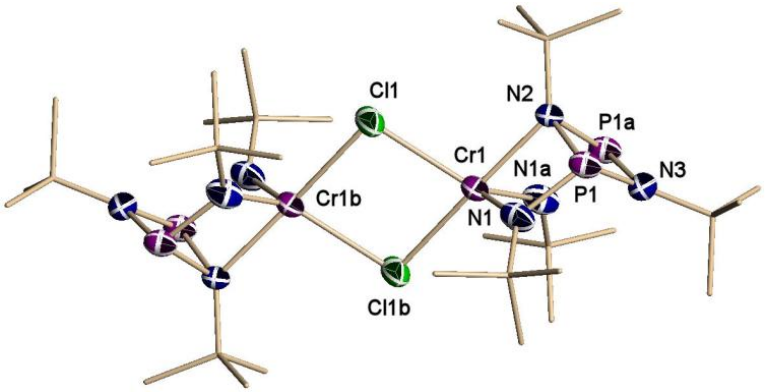
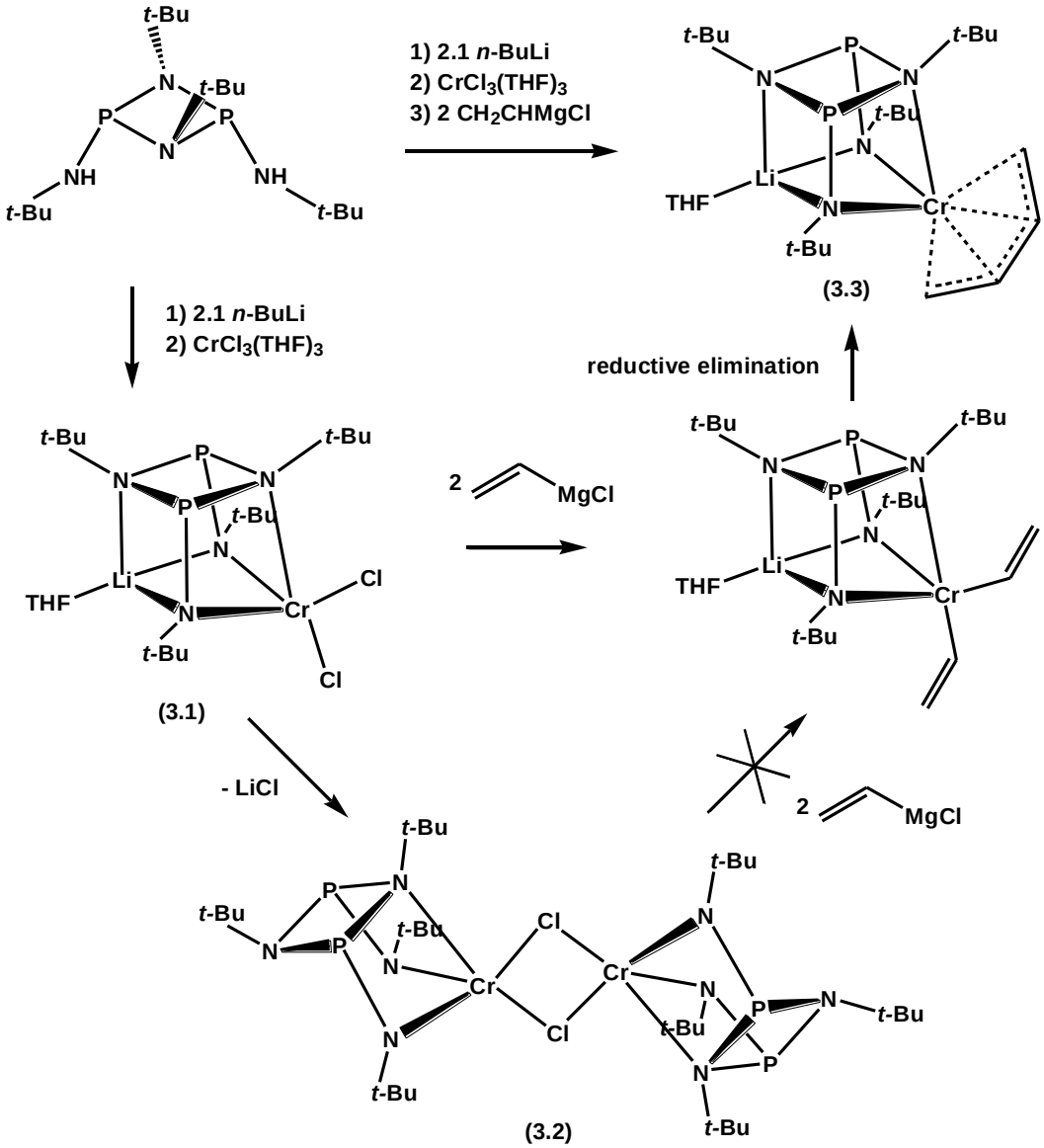


Figure 3.1. Drawing of **3.2** with thermal ellipsoids drawn at the 50% probability level.

The structure of **3.2** shows a symmetry generated dimer with the two metal centers, each bearing a N_2P_2 dianion, bridged by two chlorine atoms in a Cr_2Cl_2 planar core [Cr(1)-Cl(1) = 2.4094(17)Å, Cr(1)-Cl(1B) = 2.4559(19)Å]. The ligand bonds chromium by using three of the ligand's four nitrogen atoms [Cr(1)-N(1) = 1.938(3)Å, Cr(1)-N(2) = 2.071(4)Å] and adopts with

chromium an open-cuboid type of structure. The coordination geometry of the metal center may be described in terms of distorted trigonal bipyramidal with one bridging chlorine and one nitrogen atom occupying the apical positions [N(2A)-Cr(1)-Cl(1) = 169.38(5)°]. The second bridging chlorine and other two nitrogen donor atoms define the equatorial plane [N(1)-Cr(1)-N(2) = 75.22(10)°, Cl(1)-Cr(1)-Cl(1B) = 78.06(7)°, N(2)-Cr(1)-Cl(1) = 101.47(11)°, N(1A)-Cr(1)-N(1) = 108.56(19)°, N(1)-Cr(1)-Cl(1) = 112.81(10)°, N(1A)-Cr(1)-Cl(1) = 134.62(11)°].

Scheme 3.1



Further support for the structural proposal of **3.1** is given by the result of its subsequent reaction with vinyl Grignard. Treatment of a THF solution of *in situ* generated **3.1** with two equivalents of CH_2=CHMgCl afforded (*cis*-{(*t*-Bu)NP[μ-N(*t*-Bu)]$_2$PN(*t*-Bu)}[Li(THF)])Cr(*cis*-η^4-butadiene) (**3.3**) that is the fifth case of a chromium butadiene compound.[20] Even in this case, the structure was elucidated by X-ray diffraction methods showing a monomeric species with the ligand in the same cuboid arrangement proposed for **3.1** (Figure 3.2). The retention of lithium in **3.3** indirectly confirms that the same core structure is likely to be present in **3.1**.

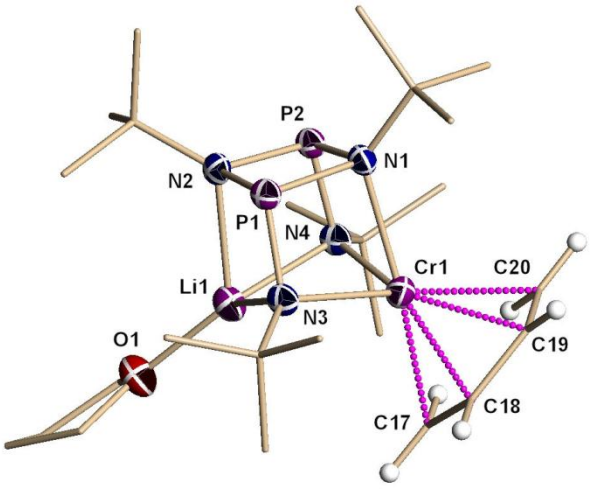


Figure 3.2. Drawing of **3.3** with thermal ellipsoids drawn at the 50% probability level.

The structure consists of a chromium atom bonded to one NPN ligand and π-coordinated to one butadiene unit [Cr(1)-C(19) = 2.186(3)Å, Cr(1)-C(20) = 2.204(4)Å, Cr(1)-C(17) = 2.160(3)Å, Cr(1)-C(18) = 2.158(4)Å] in *cis* conformation [C(17)-C(18) = 1.444(5)Å, C(18)-C(19) = 1.402(5)Å, C(19)-C(20) = 1.375(6)Å, C(18)-C(19)-C(20) = 117.6(4)^o, C(19)-C(18)-C(17) = 118.3(4)^o]. One THF-solvated lithium atom also bonded to the ligand completes the structure [Li(1)-O(1) = 1.947(5)Å, Li(1)-N(3) = 2.116(5)Å, Li(1)-N(4) = 2.126(5)Å, Li(1)-N(2) = 2.196(5)Å]. The NPN ligand adopts with both Li and Cr a cuboid type of structure with the

two metals located *trans* to each other on one of the cube distorted faces [Li(1)-N(3)-Cr(1) = 80.62(15)°, Cr(1)-N(4)-Li(1) = 81.39(15)°] Each metal is bonded to three of the four nitrogen atoms [Cr(1)-N(4) = 2.125(2)Å, Cr(1)-N(3) = 2.167(2)Å, Cr(1)-N(1) = 2.198(2)Å]. The overall coordination around chromium is distorted pseudo-tetrahedral [N(4)-Cr(1)-N(3) = 92.71(8)°, N(4)-Cr(1)-N(1) = 72.57(8)°, N(3)-Cr(1)-N(1) = 72.43(8)°] considering one coordination site as occupied by the centroid of the π-bonded butadiene unit. All the hydrogen atoms of the coordinated butadiene were located at their expected positions and the angles of the planar C units were as expected for the sp^2 carbon atoms. However, the C-C distances display a curious asymmetry. One of the two C-C terminal positions is shorter [C(19)-C(20) = 1.375(6)Å] than the other [C(17)-C(18) = 1.444(5)Å] that is instead in the normal range for a π-coordinated butadiene. However, the thermal parameters of the carbon atoms forming the short distance are somewhat large showing elongation of the ellipsoids on the C-C vector. This is a possible indication of some minor disorder that could not be modeled by splitting the occupancy. It is therefore conceivable that the short C-C distance may be nothing less than a crystallographic artifact. Furthermore, the asymmetry of bond distances does not significantly affect the Cr-C distances, that are all in the expected range [Cr(1)-C(17) = 2.160(3)Å, Cr(1)-C(18) = 2.158(4)Å , Cr(1)-C(19) = 2.186(3)Å, Cr(1)-C(20) = 2.204(4)Å]. Also the angles subtended at the internal carbon atoms are as expected for sp^2 hybrids.

The room temperature magnetic moment of **3.3** (μ_{eff} = 3.71μ_{MB}) is in agreement with either high-spin Cr(III) or intermediate-spin Cr(I) electronic configuration with three unpaired electrons. To conclusively clarify the electronic structure of the complex, DFT calculations were undertaken using the atomic coordinates obtained from the crystal structure as a starting geometry. Geometry optimization calculations at the spin-unrestricted PBE level on the full

structure of **3.3** yielded geometrical parameters in excellent agreement with the X-ray values (Figure 3.3). The calculated C-C distances of the butadiene ligand were [C(17)-C(18) = 1.442Å, C(18)-C(19) = 1.404Å, and C(19)-C(20) = 1.432Å]. These values are in the predictable range for butadiene complexes showing a fairly symmetrical bonding mode. DFT calculation predicted a more standard symmetrical bonding mode between the Cr ion and the butadiene ligand. The mismatch between calculated and experimental C(19)-C(20) distance reiterates that the unusually short experimental value is more likely an artifact of the large thermal parameters of these two particular C atoms. The predicted Cr-C distances [Cr(1)-C(17) = 2.164Å, Cr(1)-C(18) = 2.191Å, Cr(1)-C(19) = 2.211Å, Cr(1)-C(20) = 2.206Å] were in excellent agreement with the observed values [Cr(1)-C(17) = 2.160(3)Å, Cr(1)-C(18) = 2.158(4)Å, Cr(1)-C(19) = 2.186(3)Å, Cr(1)-C(20) = 2.204(4)Å]. Among the several possible spin states (S = 1/2, S = 3/2, and S = 5/2) that have been used for calculation, the state with three unpaired electrons (S = 3/2) yielded the lowest energy and the best agreement between calculated and observed structural parameters, thus lending credibility to the formulation.

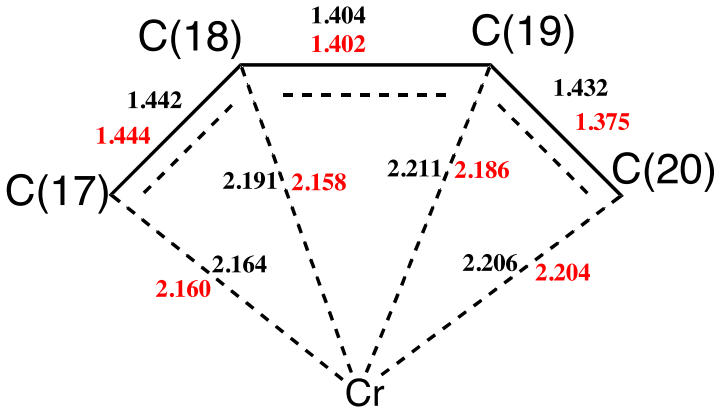


Figure 3.3. Calculated and experimental bond distances for the Cr-butadiene moiety in black and red, respectively.

The calculated Mayer bond orders for the C-C bonds of the butadiene ligand are 1.11, 1.35, and 1.16 for C(17)-C(18), C(18)-C(19), and C(19)-C(20) bonds, respectively. The net NPA-derived charge and spin density on the butadiene ligand is -0.20 a.u. and -0.18 a.u., respectively. The three unpaired electrons responsible for the observed magnetism were located in three singly occupied molecular orbitals with 62-68% Cr 3*d* character, resulting in the spin density of 3.07 for the Cr atom (Figure 3.4). The NPA-derived atomic charge of the Cr atom (+0.15 a.u.) and NPA-derived populations of the valence orbitals of the Cr atom, $3d^{4.02}$ $4s^{0.11}$ $4p^{0.30}$ for α-spin orbitals and $3d^{1.00}$ $4s^{0.10}$ $4p^{0.27}$ for β-spin orbitals, are consistent with the Cr(I) description (d^5 electron configuration). Thus, the complex should be considered as containing an intermediate-spin Cr(I) ion.

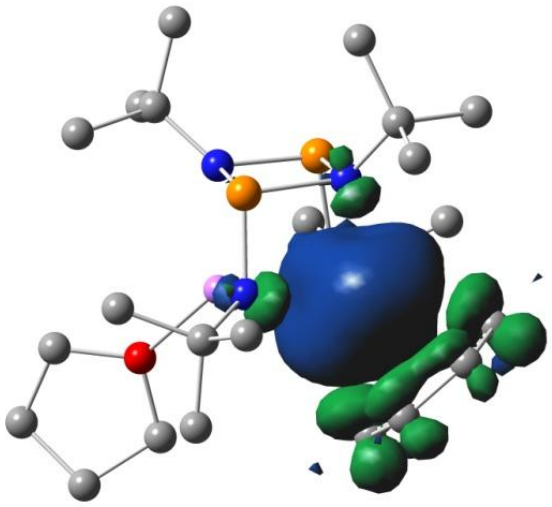
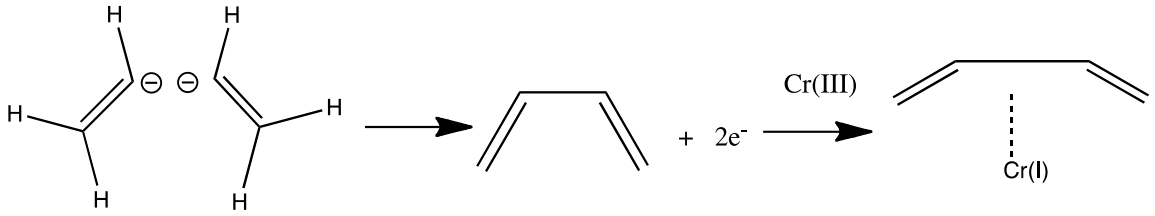


Figure 3.4. Spin density distribution for the ground electronic state of **3.3** (at PBE/TZVP level). H atoms are not shown for clarity.

The formation of the butadiene residue and the two-electron reduction of the metal center is likely to proceed via double vinylation followed by oxidative C-C bond formation (Stille coupling). The trivalent metal center is the recipient of the two electrons necessary to afford the

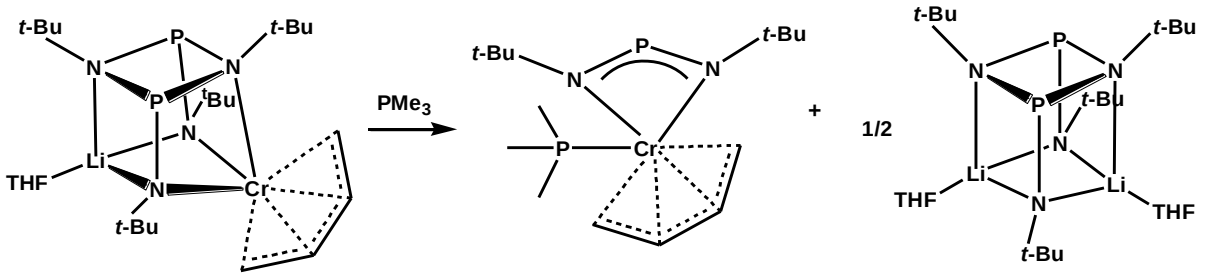
final monovalent chromium complex (Scheme 3.2). This type of coupling, established for the platinoid elements,[9] has never been observed before for an early metal.

Scheme 3.2



Different from all our previous observations in chapter two,[10] the ligand system has retained its original square-planar dimeric core[20] rather than forming the chelating NPN mono-anion, invariably observed in the divalent chromium structures.[10] In an attempt to probe both ligand stability and possible lability of butadiene coordination we have treated complex **3.3** with a strongly coordinating ligand such as Me_3P. The reaction was carried out in hexane where it gave instant color change. Two new species could be isolated from the resulting solution via fractional crystallization (Scheme 3.3). The first complex appeared to be [(*t*-Bu)N-P-N(*t*-Bu)]Cr(*cis*-η^4-butadiene)PMe_3 (**3.4**) as indicated by X-ray crystallography.

Scheme 3.3



(3.3) **(3.4)** **(3.5)**

The structure (Figure 3.5) consists of a distorted pseudo-tetrahedral chromium atom [N(2)-Cr(1)-N(1) = 70.76(15)°, N(2)-Cr(1)-P(2) = 98.78(8)°, N(1)-Cr(1)-P(2) = 98.78(8)°] with one of the coordination sites occupied by the centroid of the π-coordinated butadiene [C(7)-C(8) = 1.404(6)Å, C(8)-C(8A) = 1.373(8)Å, Cr(1)-C(8) = 2.156(3)Å, Cr(1)-C(7) = 2.185(4)Å]. The remaining three coordination sites are occupied by the phosphorus atom of Me_3P [Cr(1)-P(2) = 2.4348(14)Å] and two nitrogen atoms of the monomeric NPN ligand unit [Cr(1)-N(1) = 2.080(3)Å].

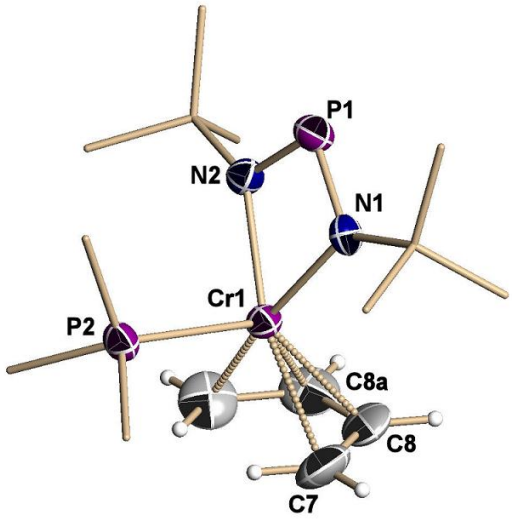


Figure 3.5. Drawing of **3.4** with thermal ellipsoids drawn at the 50% probability level.

The coordination of Me_3P during the formation of **3.4** has resulted in cleavage of the dimeric cuboid form of the ligand and consequent expulsion of a formal monomeric NPN-Li(THF) unit. The robust coordination of phosphine has been clearly the determining factor for the ligand to adopt the monomeric form but not to dissociate butadiene. Accordingly, the second species obtained from the reaction mixture was the lithiated form of the ligand *cis*-{(*t*-Bu)NP[μ-N(*t*-Bu)]$_2$PN(*t*-Bu)}[Li(THF)]$_2$ (**3.5**) where the dimeric core was re-established (Figure 3.6).

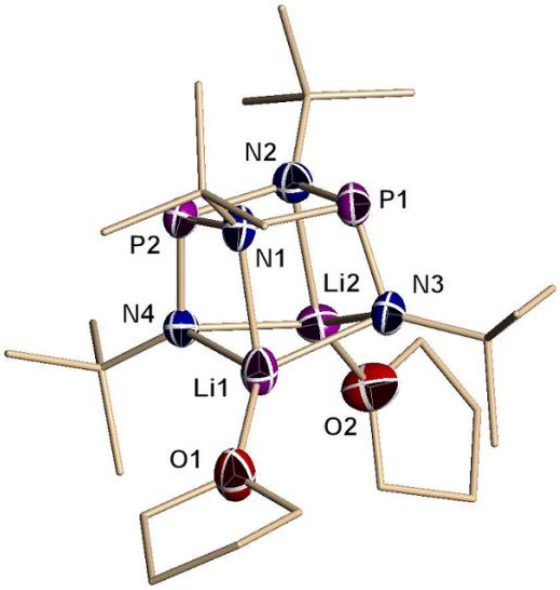


Figure 3.6. Drawing of **3.5** with thermal ellipsoids drawn at the 50% probability level.

The structure consists of the same cuboid type of structure observed above and with the two lithium atoms, each solvated by one molecule of THF located on the two opposite corners of on square face of the distorted cube [Li(1)-N(4) = 2.070(5)Å, Li(1)-N(3) = 2.085(5)Å, Li(1)-N(1) = 2.119(6)Å, Li(1)-N(4)-Li(2) = 75.63(18)°, N(4)-Li(1)-N(1) = 76.59(18)°].

The theoretical calculation performed on the geometrical parameters of **3.3** clearly indicated that the chromium center is present in its monovalent state. Accordingly, solutions of **3.3** in methylcyclohexane, when exposed to 35 bar of ethylene, acted as a self-activating catalytic system of moderate activity producing highly pure 1-hexene and no polymer (Table 3.2). The reaction also required a rather high temperature and gave only moderate activity. This was rather expected since the initial dissociation of a relatively robust ligand such as butadiene may indeed require a substantial amount of thermal energy. Attempts to activate the complex by using classical alkyl aluminum activators only led to decomposition with the exception of MAO. In that case, the catalytic activity increased sharply with a switch to a Schulz-Flory distribution of

polymer-free α-olefins. In turn, this indicates that the alkyl aluminum activator has triggered a disproportionation towards the divalent state.

Table 3.2. Oligomerization Results.

Cat	Co-Catalyst	Al:Cr	Temp (^{o}C)	Alkenes (mL)	PE (g)	Activity (g/mmolCr/h)	C_4 (mol%)	C_6 (mol%)	C_8 (mol%)	C_{10}-C_{16} (mol%)
3.2[a]	MAO	300	60	96	10	2580	3	26	28	43
3.2[a]	MAO	1000	60	104	0	2430	2	22	28	48
3.2[b]	MAO	1000	60	24	24	1360	1	14	27	58
3.2[b]	MAO[c]	1000	60	6	48	1740	0	99	traces	0
3.2[b]	MAO[c]	300	60	12	52	2010	0	99	traces	0
3.2[b]	MMAO	300	60	8	32	1255	0	99	traces	0
3.3[b]	-	-	60	0	0	0	0	0	0	0
3.3[b]	-	-	110	2	0	47	0	95	3	2
3.3[a]	MAO	500	60	91	0	2125	7	33	24	36
3.4[b]	-	-	110	3	0	63	99	0	0	0
3.4[a]	MAO	500	60	28	1	690	6	24	26	44

Conditions: loading 30 µmol of complex, 35 bar of ethylene, reaction time 60 min; [a)] 100 mL of toluene °C, [b)] 100 mL of methylcyclohexane, [c)] Me_3Al free MAO.

Complex **3.2** also displayed and interesting behavior since, depending on the reaction conditions, switched catalytic performance from polymerization to polymer-free oligomerization was observed. In both cases the activities were very high. The choice of the solvent (toluene *versus* methylcyclohexane) had the most visible effect since polymer-free oligomerization was replaced by good-activity polymerization. Polymer formation could be further increased when TMA-free MAO was used as activator.

The butadiene containing **3.4** also is a self-activating catalyst producing, however, only 1-butene and not even traces of heavier oligomers or polymer. Selectivity in the formation of 1-butene is commonly observed with nickel based catalysts but to the best of our knowledge it has been observed only twice in chromium chemistry.[21] The high selectivity of the present case implies that the presence of coordinated phosphine inhibits the metallacycle ring expansion

necessary for the formation of 1-hexene[22] in favor of a reductive elimination. Similar to **3.3**, the activation with MAO switched the catalytic behavior to a S-F distribution of oligomers.

3.6 Conclusions

In conclusion, we have herein reported the double vinylation of a Cr(III) complex affording a genuine monovalent butadiene derivative, catalytically active. In spite of the robustness of the coordination of the butadiene unit, as apparent from the result of the reaction with phosphine, this complex acts as a single component selective trimerization catalyst. Should it be possible to labilize the coordination of butadiene by acting on either the substituents on the C_4 backbone or the nature of this coordinatively versatile ligand, it will be possible to increase the catalytic activity. We find intriguing that complex **3.4** acts as a single-component dimerization catalyst, implying that phosphine coordination may inhibit metallacycle ring expansion but not its initial formation. In the following chapter the $NP^{III}N$ ligand system was further modified by adding pendants containing additional donor atoms such as amine or methoxy groups. This was to stabilize the chromium divalent state for conclusively linking this oxidation state to the non-selective oligomerization process.

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Chapter Four

Publication:

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New Iminophosphonamide Chromium (II) Complexes as Polymer-Free Highly Active Ethylene Oligomerization Catalysts

4.1 Introduction

Chromium plays a very important role in polyolefin chemistry since it provides some of the best performing catalysts for commercial ethylene polymerization,[1] non-selective oligomerization[2] and selective tri-[3] and tetramerization.[4] Therefore, its derivatives are ideal substrates for studying the relationship between catalytic behavior, ligand features and metal oxidation state. The recent isolation of a catalytically active species that act as a selective ethylene trimerization system serves as a conclusive link between the selectivity of a chromium based trimerization process and monovalent oxidation.[5] While this information may be of use for targeting the preparation of new and better performing catalysts, chromium still poses a major challenge because of its redox dynamism. In other words, the three catalytically active oxidation states (III, II and I) may be readily interconverted by the activators via reduction[5c,6] and disproportionation.[5b] Since each oxidation state has its own distinctive catalytic behavior,[5] chromium catalysts producing mixtures of polymers and oligomers, occasionally enriched with 1-hexene or 1-octene, are often encountered.[7]

While targeting selective oligomerization catalysts, it is thereby of primary importance that the ligand system be capable of preventing disproportionation to the zero- and divalent states,

respectively responsible for deactivation and unselective oligomerization. Since the trivalent state is normally used for conveniently feeding the metal into the catalytic cycle, [1-4] it is equally important to reach the monovalent state via two-electron reductions bypassing divalent intermediates.[5c] While this is not easily feasible when using alkyl aluminum as reductants, an alternative possibility consists of the destabilization of divalent intermediates through unfavorable ligand fields. For example, tridentate ligands unable to accommodate the square-planar and square-pyramidal geometries normally demanded by the d^4 electronic configuration of Cr(II) might be able to destabilize the undesirable divalent state in favor of the selective monovalent state.

In chapter one, we discovered a Cr-based catalytic system of a non-innocent (*t*-Bu)NPN(*t*-Bu) ligand that, depending on the activator, switched selectivity from ethylene polymerization to non-selective oligomerization and even to selective trimerization. The switchability of this catalytic system in turn speaks for the ability of this ligand to irreversibly reach certain oxidation states and to prevent disproportionation reactions. To improve our understanding of this versatile ligand system, we have now attempted to assess its ability to affect the stability of the chromium divalent state depending on denticity, and steric effects. Herein, we report the results of our further studies on this system where a few variations of the ligand scaffold have been examined in relation to the catalytic behavior of these complexes.

4.2 Experimental Part

All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried using an aluminum oxide solvent purification system. The liquid product mixtures were analyzed by using a CP 9000 gas chromatograph (GC) equipped with a 30 mL × 0.32 mm id, capillary CP volamine column and a FID detector. All single-point experiments were performed in duplicate. The yield

was determined by ^{1}H-NMR spectroscopy (Varian Mercury 400 MHz spectrometer). Samples for magnetic susceptibility were pre-weighed inside a dry box equipped with an analytical balance and measured on a Johnson Matthey Magnetic Susceptibility balance. Elemental analysis was carried out with a Perkin-Elmer 2400 CHN analyzer. Data for X-ray crystal structure determination (Table 4.1) were obtained with a Bruker diffractometer equipped with a 1K Smart CCD area detector. The ligand precursor *cis*-ClP[(μ-N)(*t*-Bu)]$_2$PCl was prepared according to a published procedure.[8] Al(*i*-Bu)$_3$ (Strem), MAO (10% wt, ALDRICH), Al(Et)$_3$ (Strem) and TIBAO (10% wt, ALDRICH) were used a received.

Preparation of [(*t*-Bu)NPNH(2-MeOPh)]$_2$ (4.a):

2-methoxyaniline (7.16 g, 58.16 mmol) and Et$_3$N (11.9 g, 116.40 mmol) were added to a stirred solution of *cis*-ClP[(μ-N)(*t*-Bu)]$_2$PCl (8.0 g, 29.10 mmol) in THF (100 mL). The reaction mixture was refluxed for 1 day. After filtration, all the volatile compounds were removed by vacuum and hexane (25 mL) was added to the residue. The solution was stored at -30 ^{o}C for 3 days and after filtration and removal of the solvent the product was obtained as white crystals (11.2 g, 24.97 mmol, 86%) ^{1}H-NMR ($CDCl_3$, 300 MHz, 300K) δ 1.28 (s, 18H, C(*CH$_3$*)$_3$) 3.86 (s, 6H, O*CH$_3$*) 5.65 (s, 2H, *NH*) 6.8-7.0 (m, 4H, *Ph*), 7.48-7.6 (m, 4H, *Ph*). ^{13}C-NMR ($CDCl_3$, 300 MHz, 300K) δ 30.95 (C(*CH$_3$*)$_3$) 50.47 (*C*(CH$_3$)$_3$) 55.55 (O*CH$_3$*). 110.39, 119.78, 120.88, 133.22, 147.90 (*Ph*). ^{31}P{^{1}H}-NMR ($CDCl_3$, 300 MHz, 300K) δ 97.93 (s). MS (EI) *m/z* $(M)^{+}$ = 448.22. El. Anal. Calcd. (found) for $C_{22}H_{34}N_4O_2P_2$: C 58.92 (58.84), H 7.64 (7.58), N 12.49 (12.47).

Preparation of {(*t*-Bu)NPNH[CH$_2$CH$_2$N(*i*-Pr)$_2$)]}$_2$ (4.b)

2-(diisopropylamino)ethylamine (14.68 g, 101.70 mmol) and Et$_3$N (20.80 g, 203.50 mmol) were added to a stirred solution of *cis*-ClP[(μ-N)(*t*-Bu)]$_2$PCl (14 g, 50.89 mmol) in THF (100 mL). The reaction mixture was refluxed for 1 day. After filtration all volatile compounds were

removed in vacuo and the product was obtained as light yellow oil-wax (22.6 g, 46.05 mmol, 91%). ^{1}H-NMR ($CDCl_3$, 300 MHz, 300 K) δ 0.975 (d, *j* = 6.6Hz, 24H, CH(CH_3)$_2$) 1.24 (s, 18H, C(CH_3)$_3$) 2.44 (t, *j* = 6.9 Hz 4H, NHCH$_2$$CH_2$N(*i*-Pr)$_2$) 2.8-3.1 (m, 4H, CH(CH$_3$)$_2$) 2.9 (m, 4H, NHCH_2CH$_2$N(*i*-Pr)$_2$). ^{13}C-NMR ($CDCl_3$, 300 MHz, 300K) δ 20.90 (CH(CH_3)$_2$) 30.98 (C(CH_3)$_3$) 39.16 (NHCH$_2$$CH_2$N(*i*-Pr)$_2$) 46.62 ($CH$(CH$_3$)$_2$) 47.90 (NH$CH_2CH_2$N(*i*-Pr)$_2$) 50.9 ($C$(CH$_3$)$_3$). ^{31}P{^{1}H}-NMR ($CDCl_3$, 300 MHz, 300K) δ 90.32 (s). MS (ESI) *m/z* $(M+H)^+$ = 491.29. El. Anal. Calcd. (found) for $C_{24}H_{56}N_6P_2$: C 58.75 (58.70), H 11.50 (11.52), N 17.13 (17.15).

Preparation of {[(*t*-Bu)NPN(2-MeOPh)]$_2$Cr}$_2$ (4.1a):

n-BuLi (0.84 mL, 2.10 mmol , 2.5 M in hexanes) was added to a solution of **4.a** (0.45 g, 1.00 mmol) in THF (5 mL) at 0 ^{o}C. The resulting mixture was stirred at room temperature for 18 h and the resulting solution added to a suspension of $CrCl_2(THF)_2$ (0.27 g, 1.00 mmol) in THF (5 mL). The reaction was allowed to stir at room temperature overnight. The solvent was removed *in vacuo* and the residue re-dissolved in toluene (10 mL). The solution was centrifuged and the supernatant reduced to 3 mL and stored at -30 ^{o}C for 5 days. The resulting green crystals of **4.1a** were filtered, washed with cold hexanes (10 mL) and dried *in vacuo* (0.40 g, 0.40 mmol, 80%). μ_{eff} = 4.97 μ_B. El. Anal. Calcd. (found) for $C_{44}H_{64}Cr_2N_8O_4P_4$: C 53.01 (53.11), H 6.47 (6.51), N 11.24 (11.31).

Preparation [(*t*-Bu)NPN(2-MeOPh)]$_2$CrCl (4.2a)

n-BuLi (0.84 mL, 2.10 mmol, 2.5 M in hexanes) was added to a solution of **4.a** (0.45 g, 1.00 mmol) in THF (5 mL) at 0 ^{o}C and the resulting mixture was stirred at room temperature for 18 h. The resulting solution was added to a suspension of $CrCl_3(THF)_3$ (0.37 g, 1.00 mmol) in THF (5 mL). The reaction was allowed to stir at room temperature overnight. The solvent was removed *in vacuo* and the residue re-dissolved in toluene (10 mL). The solution was centrifuged and the

resulting supernatant concentrated to about 3 mL and then stored at -30 ^{o}C for 5 days. The resulting green crystals of **4.2a** were filtered and washed with cold hexanes (10 mL) and dried *in vacuo* (0.20 g, 0.37 mmol, 37%). μ_{eff} = 3.89 μ_B. El. Anal. Calcd. (found) for $C_{22}H_{32}ClCrN_4O_2P_2$: C 49.49 (49.45), H 6.04 (6.01), N 10.49 (10.40).

Preparation of [{(*t*-Bu)NPN[CH_2CH_2N(*i*-Pr)$_2$)]}$_2$CrCl]$_2$ (4.1b)

n-BuLi (0.84 mL, 2.10 mmol, 2.5 M in hexanes) was added to a solution of **4.b** (0.49 g, 1.00 mmol) in THF (5 mL) at 0 ^{o}C and the resulting mixture was stirred at room temperature for 18 h. The solution was added to a suspension of $CrCl_2(THF)_2$ (0.536 g, 2.00 mmol) in THF (5 mL). The reaction mixture was stirred at room temperature overnight. The solvent was removed *in vacuo* and diethylether (5 mL) was added. The solution was centrifuged and the volume of the resulting solution reduced to about 3 mL and stored at -30 ^{o}C for 3 days. The resulting green crystals of **4.1b** were filtered, washed with cold hexanes (10 mL) and dried *in vacuo* (0.46 g, 0.74 mmol, 74%). μ_{eff} = 4.01 μ_B. El. Anal. Calcd. (found) for $C_{24}H_{54}Cl_2Cr_2N_6P_2$: C 43.44 (43.40), H 8.20 (8.18), N 12.66 (12.61).

4.3 X-ray Data

Table 4.1. Crystal Data and Structure Analysis Results of Complexes **4.1a, 4.2a** and **4.1b**.

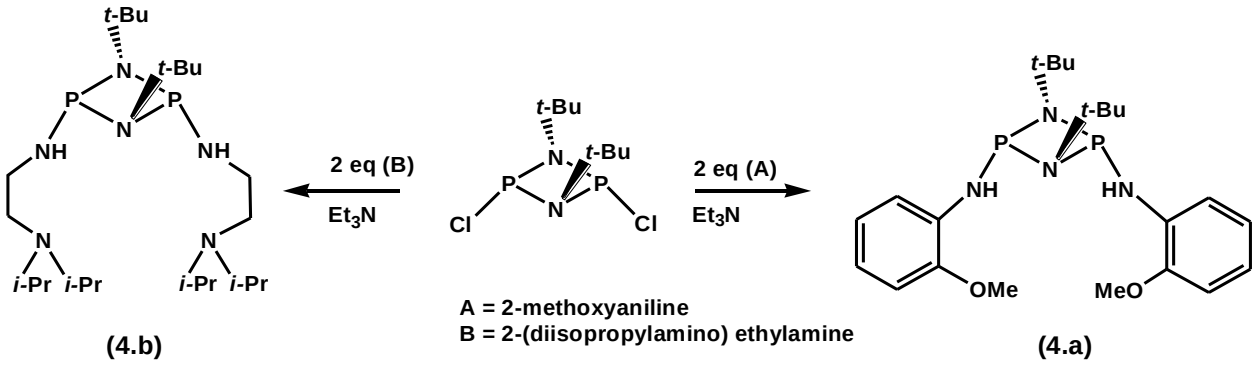
	4.1a	**4.2a**	**4.1b**
formula	$C_{47.50}H_{68}Cr_2N_8O_4P_4$	$C_{49}H_{75}Cl_2Cr_2N_8O_{4.50}P_4$	$C_{25}H_{56.50}Cl_2Cr_2N_6O_{0.25}P_2$
Mw	1042.98	1146.95	682.10
space group	P-1	P-1	P2(1)/c
***a* (Å)**	11.1140(8)	10.426(3)	16.680(3)
***b* (Å)**	13.2931(10)	15.044(5)	16.182(3)
***c* (Å)**	18.0547(14)	19.059(6)	26.027(5)
***α*, (deg)**	80.2940(10)	87.161(5)	90
***β*, (deg)**	78.8410(10)	77.551(5)	92.078(2)
***γ*, (deg)**	79.5040(10)	86.551(5)	90
***V* (Å^3)**	2548.5(3)	2911.8(16)	7020(2)
Z	2	2	8
radiation	0.71073	0.71073	0.71073
***T* (K)**	200(2)	201(2)	201(2)
D_{calcd} (g cm^{-3})	1.359	1.308	1.291
μ_{calcd} (mm^{-1})	0.602	0.623	0.887
***F*$_{000}$**	1098	1206	2900
***R*, *Rw*^{2a}**	0.0527, 0.1073	0.0685, 0.1448	0.0665, 0.1603
GoF	1.040	0.958	1.057

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

4.4 Discussion and results

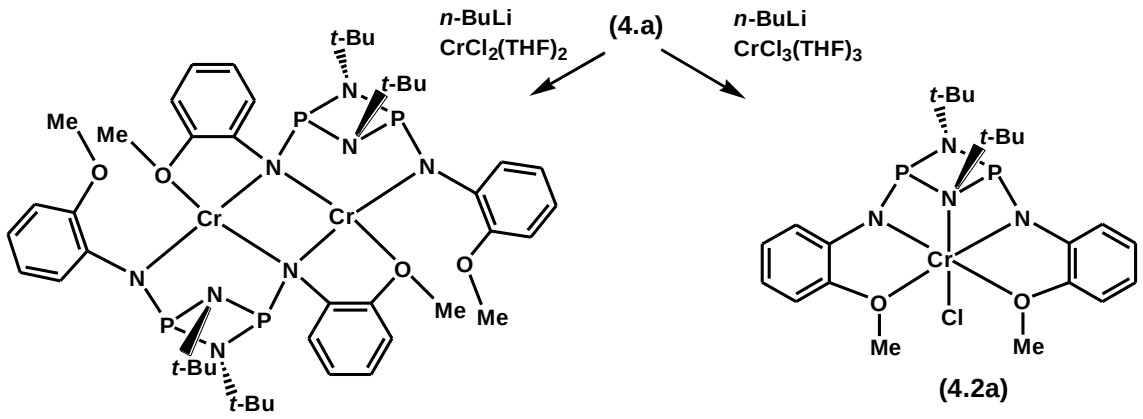
The two ligands used for this work [(*t*-Bu)NPNH(2-MeOPh)]$_2$ (**4.a**) and {(*t*-Bu)NPNH[$CH_2CH_2N(i\text{-}Pr)_2$)]}$_2$ (**4.b**) were prepared via reaction of *cis*-ClP[(μ-N)(*t*-Bu)]$_2$PCl with 2-methoxyaniline or (i-Pr)$_2$N$CH_2CH_2NH_2$ respectively (Scheme 4.1). The reactions of both $CrCl_2(THF)_2$ and $CrCl_3(THF)_3$ with doubly deprotonated form of **4.a** were carried out at room temperature and in THF affording the corresponding {[(*t*-Bu)NPN(2-MeOPh)]$_2$Cr}$_2$ (**4.1a**) and [(*t*-Bu)NPN(2-MeOPh)]$_2$CrCl (**4.2a**) respectively (Scheme 4.2).

Scheme 4.1



The structures of the two compounds have been elucidated by X-ray analysis. Complex **4.1a** is a symmetry generated dimer with two dianionic ligands surrounding the dimetallic unit with each metal in a distorted square planar coordination environment [N(4)-Cr(1)-N(3) = 96.33(11)°, N(4)-Cr(1)-N(3)A = 168.74(12)°, N(3)-Cr(1)-N(3)A = 88.71(11)°, N(4)-Cr(1)-O(1)A = 95.83(10)°, N(3)-Cr(1)-O(1)A = 155.48(11)°, N(3)A-Cr(1)-O(1)A = 75.94(10)°] (Figure 4.1).

Scheme 4.2



Each ligand adopted a curious bridging bonding mode. The ligand P_2N_2 square core is capping the chromium center with none of the four atoms reaching a bonding contact with the metal [Cr(1)..N(1) = 3.579 Å ; Cr(1)..N(2) = 2.572 Å]. Instead the two nitrogen atoms of the two "arms" are both bonding the same chromium atom [Cr(1)-N(4) = 2.056(3) Å, Cr(1)-N(3) =

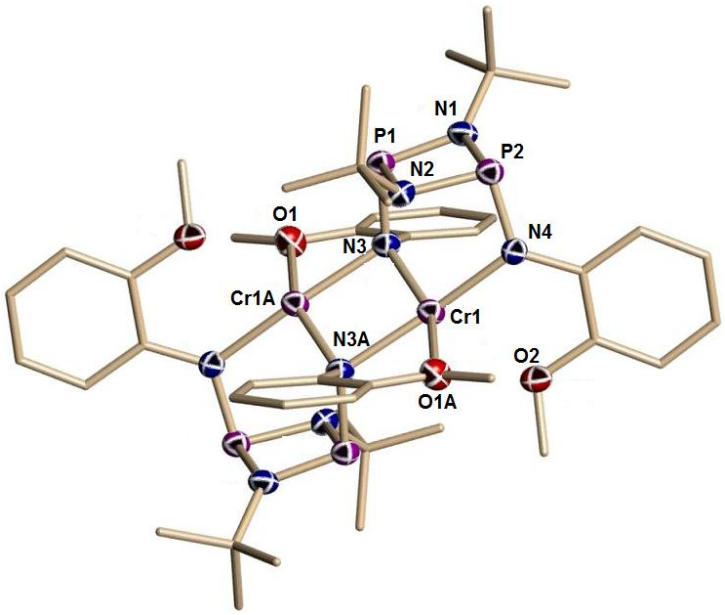


Figure 4.1. Thermal ellipsoid plot of **4.1a** with ellipsoids drawn at 50% probability.

2.098(3) Å]. One of the two nitrogen also bridges the second metal center [N(3)-Cr(1)A = 2.118(3) Å]. The methoxy group of the phenyl group attached to the bridging nitrogen also bonds the second chromium center [O(1)-Cr(1)A = 2.208(2) Å]. The second OMe group of the same ligand is not forming a bonding contact but it is located on an equatorial vertex of an ideal trigonal bipyramid centered on the chromium atom [Cr(1)-O(2) = 2.450 Å].

The structure of **4.2a** shows a monomeric complex with the chromium atom in a distorted octahedral geometry (Figure 4.2) [O(1)-Cr(1)-N(3) = 149.93(18)°; N(3)-Cr(1)-Cl(1) = 104.09(14)°; N(1)-Cr(1)-N(3) = 73.3(2)°] The coordination octahedron is defined by the two *ortho* located oxygen atoms [Cr(1)-O(1) = 2.098(4) Å, Cr(1)-O(2) = 2.156(4) Å] of the two ligand's methoxy groups, one terminally bonded Cl atom [Cr(1)-Cl(1) = 2.326(2)Å] and three of the four nitrogen donor atom of the ligand system facially oriented [Cr(1)-N(1) = 1.912(5) Å, Cr(1)-N(2) = 1.987(5) Å, Cr(1)-N(3) = 2.111(5) Å]. The fourth N atom not engaged in bonding interaction with the metal center adopted a trigonal planar geometry [C(19)-N(4)-P(2) = 128.5(5)°, C(19)-N(4)-P(1) = 128.1(5)°, P(2)-N(4)-P(1) = 101.6(3)°].

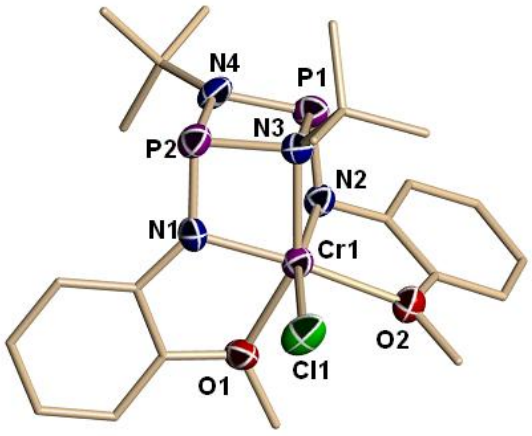
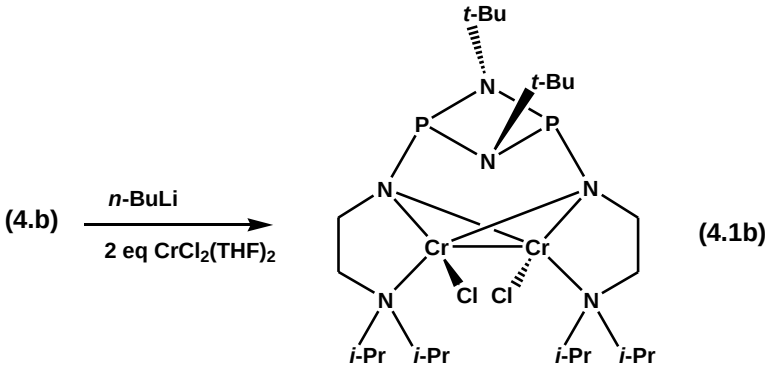


Figure 4.2. Thermal ellipsoid plot of **4.2a** with ellipsoids drawn at 50% probability.

Scheme 4.3



The reaction of the ligand **4.b** with $CrCl_2(THF)_2$ also afforded a dinuclear complex [{(*t*-Bu)NPN[$CH_2CH_2N(i\text{-}Pr)_2$)]}$_2$CrCl]$_2$ (**4.1b**) where one sole ligand wrapped the dimetallic unit (Scheme 4.3). A chlorine atom was also retained by each of the two chromium atoms. Since unreacted chromium salt was invariably present in the reaction mixture even under prolonged reflux, it was decided to carry the reaction with the appropriate stoichiometry as yielded by the formula elucidated by X-ray analysis.

The structure of **4.1b** (Figure 4.3) shows the N_2P_2 core of the ligand symmetrically capping the dimetallic unit without bonding contact between any of the donor atoms and the metal centers. Each of the two ligand's "arms" N atoms instead bridges the two metal centers [Cr(1)-N(5) = 2.081(4) Å, Cr(1)-N(3) = 2.114(4) Å, Cr(2)-N(3) = 2.071(4) Å, Cr(2)-N(5) = 2.144(5) Å] forming an intermetallic distance [Cr(1)-Cr(2) = 2.6354(13) Å] as expected for a folded Cr_2N_2 core. The aliphatic amino-pendant attached to each of the two arm's nitrogen atom wrap each of the two metal centers [Cr(1)-N(6) = 2.232(5) Å, Cr(2)-N(4) = 2.245(5) Å] which, with a terminally bonded chlorine atom [Cr(1)-Cl(1) = 2.3208(17) Å, Cr(2)-Cl(2) = 2.3241(17) Å] on the fourth coordination site, achieves a distorted square planar geometry [N(3)-Cr(1)-N(6) = 161.76(18)º, N(5)-Cr(1)-Cl(1) = 179.73(14)º, N(3)-Cr(1)-Cl(1) = 95.23(12)º]. Attempts to form the trivalent analogue only afforded oily material of dubious catalytic behavior with low activity.

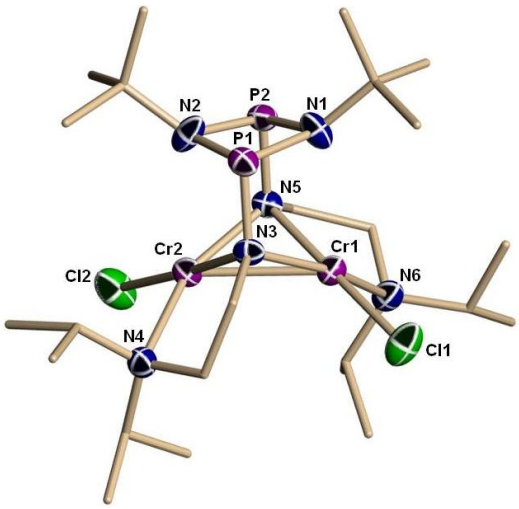


Figure 4.3. Thermal ellipsoid plot of **4.1b** with ellipsoids drawn at 50% probability.

The three complexes described above have all been tested for ethylene oligomerization under standard Ziegler-Natta conditions and with the help of a few activators (Table 4.2). MAO seems to be the only effective activator in all cases driving the reactivity towards S-F distributions of oligomers. The activities were in general quite high for the two divalent complexes **4.1a** and **4.1b** and, even more interestingly, the production of LAO was *not* accompanied by the usual formation of waxes or polymer. Therefore the two catalysts may in principle be used for commercial application purposes. Other activators gave no catalytic activity with the only exception of TIBAO that in the case of **4.1a** gave substantial amount of polymer along with a mixture of 1-hexene and 1-octene. No such behavior was observed for **4.1b**.

The lack of selectivity of **4.1a** and **4.1b** speaks for the stability of the divalent state in these two complexes unlikely to undergo any further reduction towards the monovalent state. The presence in the case of the most reducing TIBAO of small amount of 1-hexene and 1-octene in the mixture, along with a large amount of polymer, indicates that perhaps some reduction occurs but not to an extent required to produce an interesting catalytic system. Surprisingly, complex

4.2a is catalytically inert therefore suggesting that no reduction towards the divalent state occurs with this ligand system.

Table 4.2. Ethylene oligomerization results.[a]

Cat	Cocat.	Al:Cr	PE g	Oligo. mL	Activity g/mmolCr/h	C_6 %	C_8 %	C_{10} %	C_{12-18} %
4.1a	MAO	500	0	33	9,240	25	23	18	34
4.1a	MAO	1000	0	71	19,900	23	22	17	38
4.1a	TIBA	500	0	0	0	0	0	0	0
4.1a	TEAL	20	0	0	0	0	0	0	0
4.1a	TIBAO	500	5.1	3	2,900	52	41	7	0
4.2a	MAO	1000	0	0	0	0	0	0	0
4.1b	MAO	500	0	24	6,700	32	26	16	26
4.1b	MAO	1000	0	56	15,700	30	25	18	27
4.1b	TIBAO	500	0	0	0	0	0	0	0
4.1b	TIBA	2000	0	0	0	0	0	0	0

[a)] Conditions 100 mL of toluene, 35 bar ethylene, reaction time 30 minutes, reaction temperature 70 °C ; Catalyst loading 5 µmol **.**

4.5 Conclusions

In conclusion, we have herein reported divalent chromium catalyst precursors that are producing a statistical mixture of oligomers with high activity. High activity and lack of PE formation is what makes these complexes potentially interesting from the industrial standpoint. Complex **4.1a** and **4.1b** display a very comparable behaviour although it is unclear how **4.1b** has been activated. The fact that the trivalent **4.2a** does not show any activity towards either oligomerization or polymerization is intriguing.

In the last three chapters, we have explored the $NP^{III}N$ derivatives that allowed us to isolate interesting intermediates that shed more light on the reaction mechanism. Also, we have observed that alkylation of the P atom favored retention of alkyl aluminum residues, in the end, enabling the formation of single-component and switchable ethylene oligomerization and

polymerization catalysts. In the next chapter, we have eliminated the possibility of alkylating phosphorous by oxidizing it to the pentavalent state ($NP^{V}N$).

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Chapter Five

Publication:

Albahily. K.; Licciulli, S.; Gambarotta, S.; Korobkov, I.; Chevalier, R.; Schuhen, K. ; Duchateau, R. *Organometallics* **2011***, 30*, 3346.

Highly Active Ethylene Oligomerization Catalysts

5.1 Introduction

A considerable amount of research effort has been dedicated both recently and in the past to non-selective ethylene oligomerization with the aim of improving the comprehension of this industrially relevant catalytic process.[1-5] The mixtures of linear alpha olefins (LAO) produced by this process are in fact valuable commodity chemicals for a range of industrial and household applications depending on their molar mass distribution (detergents, surfactants, cosmetics, etc.).[6]

A non-selective oligomerization is closely reminiscent of a polymerization randomly truncated at the early stages of the chain growth (Cossee-Arlman mechanism).[7] The commonly accepted Cossee-Arlman chain-growth mechanism does not require a change of the metal oxidation state during the catalytic cycle. In some cases however, the redox metallacycle mechanism proposed for selective tri- and tetramerization[8] may also be employed by non-selective systems.[9] This is in the event that the two crucial steps, further ring-expansion and reductive elimination, possess comparable activation barriers.[10] Obviously, the possibility of discriminating between the two steps is central to obtain a general statistical oligomerization *versus* a selective process.

Trivalent chromium catalyst precursors comprise the majority of the catalytic systems used for both selective,[11,14,16a] as well as non-selective ethylene oligomerization,[12] and also account for an important class of ethylene polymerization catalysts.[13] The versatility of this element is likely to be ascribed to the large number of oxidation states available but, most of all, to the redox dynamism of the organochromium derivatives.[14] More specifically, the trivalent state, which is the most inert, is normally used to feed the metal into the catalytic cycle. Alkylating agents can then reduce the metal center to either the di- or monovalent state each with its own distinctive catalytic behavior.[14] What is remarkable is that the original trivalent state may also be regenerated during the catalytic cycles via simple disproportionation.[11o,15] Further reduction to the zero valent state may also occur during the catalytic cycle, eventually affording metallic chromium or inert complexes with consequent catalyst deactivation. The easy interconversion of the three catalytically active oxidation states (+I, +II and +III) and their occasional co-existence within the catalytic cycle explains the frequent occurrence of much unwanted polymer during the production of LAO and/or the occasional enrichment of the S-F distribution of α-olefins in 1-hexene and/or 1-octene.[11o,15]

The nature of the ligand plays a central role in stabilizing a particular oxidation state and consequently in determining the catalytic behavior. Work in chapter two on an anionic ligand system based on the NPN framework of trivalent phosphorous clearly indicated that this ligand frame is versatile for catalytic purposes, having allowed isolation of rare species and switchable catalytic systems.[16] In addition, we observed that it provides a reversal of the PNP motif of the unique Sasol catalytic tetramerization system.[15b,17] However, its chemistry appeared to be distinctively different. During the activation process of its chromium derivatives, the ligand-P atom was always attacked by the alkylating agent used for catalyst activation.[16] The alkylation at

the P atom in turn caused retention of alkyl aluminum residues, in the end enabling the formation of single-component and switchable ethylene oligomerization and polymerization catalysts. It was argued that eliminating the possibility of alkylation at the phosphorous atom might afford a different catalytic behavior. By oxidizing the P atom to the pentavalent state we have now obtained the first polymer-free highly active oligomerization system. Herein we describe our findings.

5.2 Experimental Part

All reactions were carried out under dry nitrogen atmosphere. Solvents were dried using an aluminum oxide solvent purification system. The liquid reaction mixtures were analyzed by using a CP 9000 gas chromatograph (GC) equipped with a 30 mL × 0.32 mm id, capillary CP-Volamine column and a FID detector. All single-point experiments were performed in duplicate. The yields were determined by ^{1}H NMR spectroscopy (Varian Mercury 400 MHz spectrometer). Samples for magnetic susceptibility were pre-weighed inside a VAC dry box equipped with an analytical balance and measured on a Johnson Matthey Magnetic Susceptibility balance. Elemental analyses were carried out with a Perkin-Elmer 2400 CHN analyzer. Data for X-ray crystal structure determination (Table 5.1) were obtained with a Bruker diffractometer equipped with a 1K Smart CCD area detector. Methylaluminoxane (MAO, 10% in toluene) was purchased from Aldrich. MMAO and PMAO were purchased from Akzo-Nobel. Ligands (*t*-Bu)N(H)PBr(Ph)$_2$N(H)(*t*-Bu), (*i*-Pr)N(H)PBr(Ph)$_2$N(H)(*i*-Pr), PhN(H)PBr(Ph)$_2$N(H)Ph were prepared according to literature procedures.[18]

Preparation of [(*t*-Bu)NP(Ph)$_2$N(*t*-Bu)]Cr(μ^2-Cl)$_2$Li(THF)$_2$ (5.1):

A solution of *t*-BuN(H)PBr(Ph)$_2$N(H)*t*-Bu (0.41 g, 1.0 mmol) in THF (10 mL) was treated with *n*-BuLi (0.84 mL, 2.1 mmol, 2.5 M in hexanes) at 25 °C and the mixture was stirred at room temperature for 24 h. The resulting clear yellow solution was added to a suspension of $CrCl_2(THF)_2$ (0.27 g, 1.0 mmol) in THF (5 mL) and stirring was continued at room temperature overnight affording a green solution. The solvent was removed *in vacuo* and the residue redissolved in toluene (10 mL). The mixture was centrifuged and the supernatant reduced to 4 mL and stored at -35 °C for 2 days. The resulting blue crystals of **5.1** were filtered, washed with cold hexanes (10 mL) and dried *in vacuo* (0.39 g, 0.56 mmol, 65%). μ_{eff} = 4.89 μ_B. El. Anal. Calcd. (found) for $C_{28}H_{44}Cl_2CrLiN_2O_2P$: C 55.91 (55.88), H 7.37 (7.21), N 4.66 (4.64).

Preparation of [(*i*-Pr)NP(Ph)$_2$N(*i*-Pr)]Cr(μ^2-Cl)$_2$Li(THF)$_2$ (5.2):

A solution of *i*-PrN(H)PBr(Ph)$_2$N(H)*i*-Pr (0.38 g, 1.0 mmol) in THF (10 mL) was treated with *n*-BuLi (0.84 mL, 2.1 mmol, 2.5 M in hexanes) at 25 °C. After stirring for 24 h at room temperature, the clear yellow solution was added to a suspension of $CrCl_2(THF)_2$ (0.27 g, 1.0 mmol) in THF (5 mL). Stirring was continued at room temperature overnight affording a green solution. The solvent was removed *in vacuo* and the residue redissolved in toluene (10 mL). After centrifugation, the supernatant was concentrated to 4 mL and stored at -35 °C for 3 days. The resulting blue crystals of **5.2** were filtered, washed with cold hexanes (10 mL) and dried *in vacuo* (0.30 g, 0.49 mmol, 51%). μ_{eff} = 4.91 μ_B. El. Anal. Calcd. (found) for $C_{26}H_{40}Cl_2CrLiN_2O_2P$: C 54.46 (54.39), H 7.03 (7.07), N 4.89 (4.93).

Preparation of [{[(Ph)NP(Ph)$_2$N(Ph)]Cr}$_2$(μ^2-Cl)$_3$][Li(DME)$_3$] (5.3):

A solution of PhN(H)PBr(Ph)$_2$N(H)Ph (0.45 g, 1.0 mmol) in dimethoxyethane (10 mL) was treated with *n*-BuLi (0.84 mL, 2.1 mmol, 2.5 M in hexanes) at 25 °C. The mixture was stirred at room temperature for 24 h affording a clear yellow solution. A suspension of $CrCl_2(THF)_2$ (0.27 g, 1.0 mmol) in dimethoxyethane (5 mL) was then added. The reaction mixture was stirred at room temperature overnight affording a green solution. The solvent was removed *in vacuo* and the residue redissolved in toluene (10 mL). After centrifugation, the supernatant was evaporated to 4 mL and stored at -35 °C for three days. The resulting blue crystals of **5.3** were filtered, washed with cold hexanes (10 mL) and dried *in vacuo* (0.35 g, 0.27 mmol, 55%). μ_{eff} = 4.97μ_B. El. Anal. Calcd. (found) for $C_{60}H_{70}Cl_3Cr_2LiN_4O_6P_2$: C 58.95 (58.90), H 5.77 (5.68), N 5.58 (5.51).

Preparation of {[(*t*-Bu)NP(Ph)$_2$N(*t*-Bu)]Cr}$_2$(μ^2-Cl)$_3$(μ^3-Cl)$_2${Li(THF)$_2$} (5.4):

A solution of *t*-BuN(H)PBr(Ph)$_2$N(H)*t*-Bu (0.41 g, 1.0 mmol) in THF (10 mL) was treated with *n*-BuLi (0.84 mL, 2.1 mmol, 2.5 M in hexanes) at 25 °C. The mixture was stirred at room temperature for 24 h affording a clear yellow solution. After addition of a suspension of $CrCl_3(THF)_3$ (0.37 g, 1.0 mmol) in THF (5 mL) the mixture was stirred at room temperature overnight giving a purple solution. The solvent was removed *in vacuo* and the residue redissolved in dimethoxyethane (10 mL). After centrifugation, the supernatant was concentrated to 4 mL and stored at -35 °C for 3 days. Purple crystals of **5.4** were filtered, washed with cold hexanes (10 mL) and dried *in vacuo* (0.40 g, 0.36 mmol, 36%). μ_{eff} = 3.82μ_B. El. Anal. Calcd. (found) for $C_{48}H_{72}Cl_5Cr_2LiN_4O_2P_2$: C 53.02 (53.00), H 6.67 (6.59), N 5.15 (5.09).

Preparation of {[(*t*-Bu)NP(Ph)$_2$N(*t*-Bu)]$_2$Cr}.{Me$_3$AlCl} (5.5):

Method A: A solution of *t*-BuN(H)PBr(Ph)$_2$N(H)*t*-Bu (0.41 g, 1.0 mmol) in THF (10 mL) was treated with *n*-BuLi (0.84 mL, 2.1 mmol, 2.5 M in hexanes) at 25 °C. The mixture was stirred at room temperature for 24 h affording a clear yellow solution. After the addition of a suspension of $CrCl_2(THF)_2$ (0.27 g, 1.0 mmol) in THF (5 mL), the reaction mixture was stirred at room temperature overnight affording a green solution. The solvent was removed *in vacuo* and the residue redissolved in toluene (10 mL). Neat $AlMe_3$ (0.36 g, 5.0 mmol) was added slowly at -35 °C, and the resulting mixture stirred for 1 hour at room temperature. The suspension was centrifuged and the supernatant concentrated to 4 mL and stored at -35 °C for 3 days. Brown-red crystals of **5.5** were filtered, washed with cold hexanes (10 mL) and dried *in vacuo* to give (0.15 g, 0.17 mmol, 18%). μ_{eff} = 3.89 μ_B. El. Anal. Calcd. (found) for $C_{43}H_{65}ALClCrN_4P_2$: C 63.42 (63.40), H 8.04 (8.01), N 6.88 (6.87).

Method B: Same procedure as method **A** was followed except using $CrCl_3(THF)_3$ (0.37 g, 1.0 mmol) producing 0.59 g of the product (73%).

5.3 X-ray Data

Table 5.1. Crystal Data and Structure Analysis Results of Complexes **5.1-5.5**.

Complex	**5.1**	**5.2**	**5.3**	**5.4**	**5.5**
Formula	$C_{35}H_{52}Cl_2CrLiN_2O_2P$	$C_{28}H_{44}Cl_2CrLiN_2O_{2.5}P$	$C_{64}H_{80}Cl_3Cr_2LiN_4O_8P_2$	$C_{48}H_{72}Cl_5Cr_2LiN_4O_2P_2$	$C_{53}H_{82}Al_2ClCrN_4P_2$
Mw	693.60	609.46	1312.55	1087.23	978.58
space group	Monoclinic, P2(1)/n	Triclinic, P-1	Monoclinic, C2/c	Triclinic, P-1	Monoclinic, C2/c
a (Å)	9.911(2)	11.552(3)	28.944(3)	12.2348(19)	13.8861(12)
b (Å)	16.784(3)	12.374(3)	14.4854(15)	12.872(2)	23.091(2)
c (Å)	22.967(5)	14.246(3)	22.613(2)	18.296(3)	18.7679(16)
α, (deg)	90	67.528(4)	90	71.893(3)	90
β, (deg)	91.307(3)	75.972(5)	128.525(2)	85.406(3)	105.589(2)
γ, (deg)	90	70.253(4)	90	87.256(3)	90
V (Å^3)	3819.7(13)	1756.1(7)	7418.4(13)	2729.1(7)	5796.4(9)
Z	4	2	4	2	4
Radiation	0.71073	0.71073	0.71073	0.71073	0.71073
T (K)	201(2)	200(2)	200(2)	200(2)	200(2)
D_{calcd} (g cm^{-3})	1.206	1.153	1.175	1.323	1.121
μ_{calcd} (mm^{-1})	0.512	0.549	0.493	0.741	0.364
F_{000}	1472	644	2752	1140	2100
R, wR^{2a}	0.0769, 0.2267	0.0774, .1621	0.0738, 0.1651	0.0839, 0.1859	0.0866, 0.2002
GoF	1.037	1.022	1.011	0.989	1.082

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

5.4 Results and Discussion

The three ligands RN(H)PBr(Ph)$_2$N(H)R (R = *t*-Bu, *i*-Pr, Ph), bearing pentavalent phosphorus, were prepared according to an existing literature procedure.[18] These species were subjected to double deprotonation with *n*-butyl lithium and reacted with an equimolar amount of $CrCl_2(THF)_2$ (Scheme 5.1). The structures of the corresponding divalent complexes [(*t*-Bu)NP(Ph)$_2$N(*t*-Bu)]Cr(μ^2-Cl)$_2$Li(THF)$_2$ (**5.1**) (Figure 5.1), [(*i*-Pr)NP(Ph)$_2$N(*i*-Pr)]Cr(μ^2-Cl)$_2$Li(THF)$_2$ (**5.2**) (Figure 5.1), and [{[(Ph)NP(Ph)$_2$N(Ph)]Cr}$_2$(μ^2-Cl)$_3$][Li(DME)$_3$] (**5.3**) (Figure 5.2) were authenticated by crystal structure analyses.

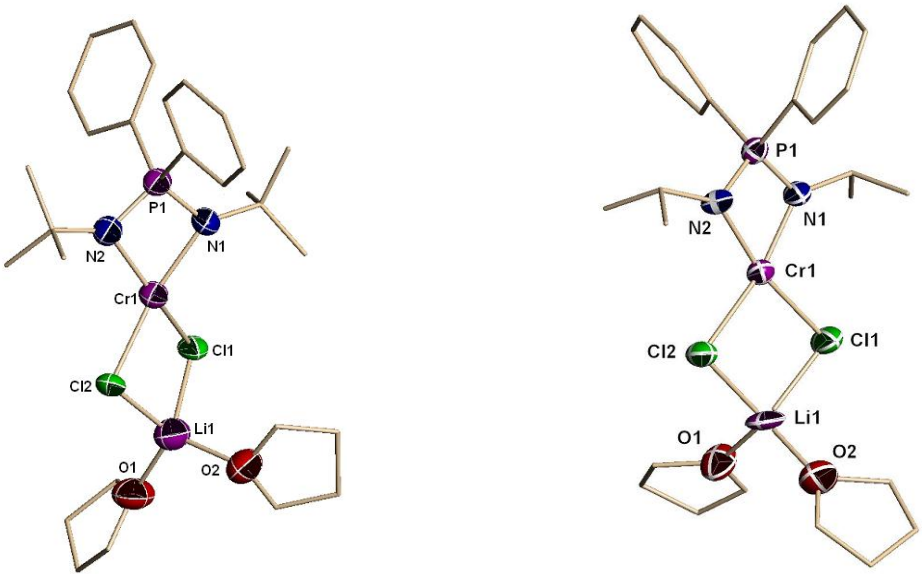
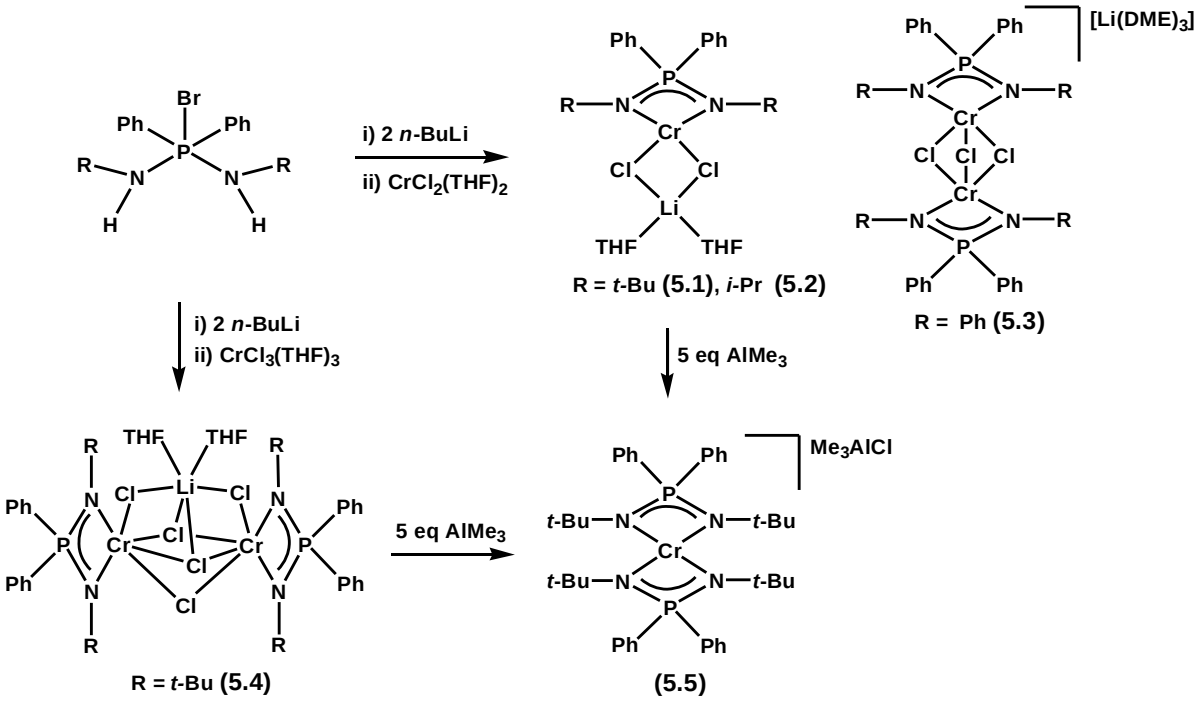


Figure 5.1. Partial thermal ellipsoid plot of **5.1** (left) and **5.2** (right) with ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (°) for **5.1**: Cr1-N1 = 2.053(4), Cr1-N2 = 2.052(4), Cr1-Cl2 = 2.4363(14), Cr1-Cl1 = 2.4556(15); N2-Cr1-N1 = 72.44(18), N2-Cr1-Cl1 = 156.66(14), N2-Cr1-Cl2 = 103.18(14), Cl2-Cr1-Cl1 = 90.41(5). For **5.2**: Cr1-N1 = 2.038(8), Cr1-N2 = 2.061(8), Cr1-Cl1 = 2.385(3), Cr1-Cl2 = 2.399(3), N1-Cr1-N2 = 71.5(3), N1-Cr1-Cl1 = 98.4(2), N1-Cr1-Cl2 = 169.7(3), Cl1-Cr1-Cl2 = 91.09(11).

Complexes **5.1** and **5.2** showed closely related geometries with the metal in the standard square-planar coordination geometry, the ligand chelating the chromium atom in a bidentate fashion and with two chlorine atoms bridging a THF-solvated lithium counter cation. Complex

5.3 is instead dimeric with three chlorine atoms bridging the two transition metals. The chromium atom displays a square pyramidal coordination geometry that, while not very common, is precedented.[19] A solvated lithium counter cation unconnected with the dimeric unit is also present in the lattice.

Scheme 5.1



The trivalent analogue of **5.1** was obtained in a similar manner via treatment of the doubly deprotonated ligand with $CrCl_3(THF)_3$. The corresponding trivalent {[(*t*-Bu)NP(Ph)$_2$N(*t*-Bu)]Cr(μ^2-Cl)$_3$(μ^3-Cl)$_2$}{Li(THF)$_2$} (**5.4)** was obtained as purple crystalline mass (Scheme 5.1). The structure was elucidated by X-ray diffraction (Figure 5.2) showing the dinuclear complex containing two trivalent chromium atoms with an overall face-sharing bi-octahedral structure. The bridging interaction between the two metal centers is realized through the facially oriented chlorine of the distorted octahedral geometry of each chromium center. One partially solvated

lithium cation is retained as a part of a trimetallic cluster structure being bridged to the two transition metals by four chlorine atoms.

As described below, all the complexes display an interesting catalytic activity upon activation by methylaluminoxane. We have thus attempted the isolation of the catalytically active species by reacting the complexes with MAO. The reactions proved to be difficult, invariably affording intractable materials. Therefore, treatment with simple $AlMe_3$ was considered to be the next step to obtain at least some information about the outcome of the interaction of the transition metal with the activator.[20] The reaction of the *divalent* **5.1** with five equivalents of $AlMe_3$ afforded the *trivalent* and cationic complex $\{[(t\text{-Bu})NP(Ph)_2N(t\text{-Bu})]_2Cr\}^{\cdot}\{Me_3AlCl\}$ (**5.5**) as a crystalline product (Scheme 5.1). The same species could also be obtained upon treatment of the trivalent **5.4** with $AlMe_3$ thus providing two alternate syntheses for the same species (figure 5.3).

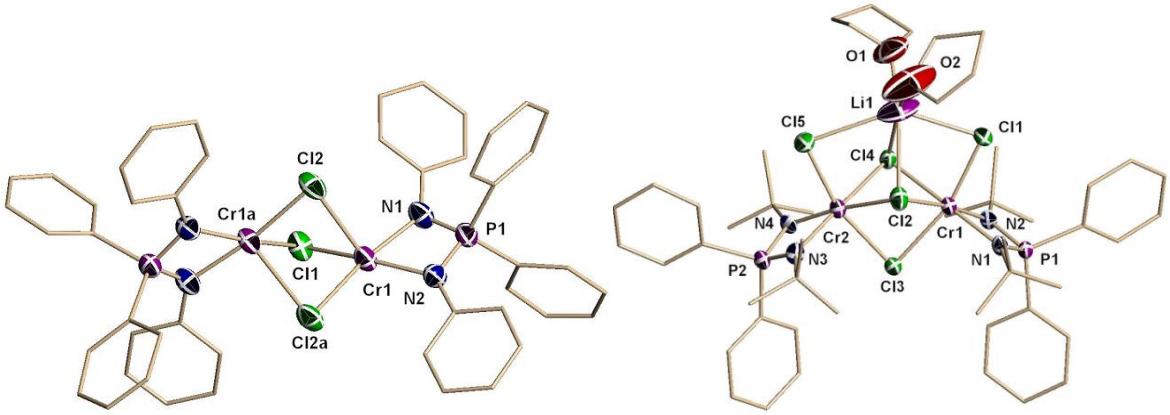


Figure 5.2. Partial thermal ellipsoid plot of **5.3** (left) and **5.4** (right) with ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (°) for **5.3**: Cr1-N1 = 2.065(5), Cr1-N2 2.088(6), Cr1-Cl1 = 2.434(2), Cr1-Cl2 = 2.688(2), Cr1-P1 = 2.749(2); N1-Cr1-N2 = 70.9(2), N1-Cr1-Cl1= 97.53(17), N2-Cr1-Cl1 = 160.84(17), Cl1-Cr1-Cl2 = 82.23(6). For **5.5**: Cr1-N2 = 1.995(8), Cr1-Cl1 = 2.343(3), Cr1-Cl3 = 2.440(3); N2-Cr1-N1 = 73.4(3), N2-Cr1-Cl = 198.2(2), N2-Cr1-Cl3 = 94.5(2), Cl1-Cr1-Cl2 = 87.86(11), Cl1-Cr1-Cl3 = 163.64(10), Cr2-Cl2-Cr1 = 83.72(10), Cr1-Cl3-Cr2 = 82.99(9).

The connectivity of **5.5** was revealed by an X-ray crystal structure and comprises a trivalent chromium center in a distorted tetrahedral environment defined by two ligand systems (Figure 5.5). One $[Me_3AlCl]^{(-)}$ counter anion, unconnected to the chromium-containing unit, is also present in the lattice thus conclusively assigning the trivalent state to the metal. The magnetic moment of **5.5** was in the expected range for the high-spin d^3 electronic configuration of trivalent chromium.

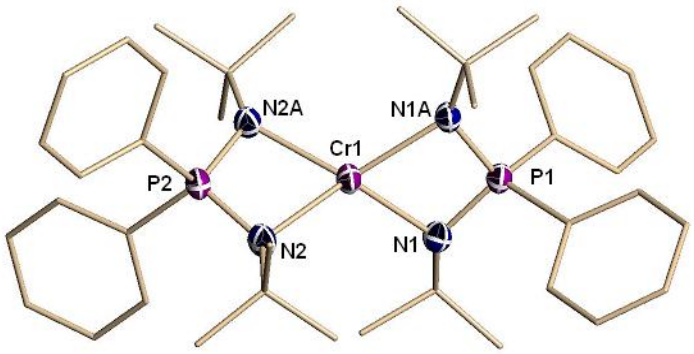


Figure 5.3. Partial thermal ellipsoid plot of **5.5** with ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (°): Cr(1)-N(1a) = 1.966(4), Cr(1)-N(2a) = 1.969(5), N(1a)-Cr(1)-N(1) = 73.9(3), N(1a)-Cr(1)-N(2a) = 132.34(18), N(1)-Cr(1)-N(2a) = 126.8(2).

The formation of **5.5** from **5.1** implies two separate processes: ligand scrambling and oxidation of the metal center. The acquisition by the chromium center of a second ligand during the reaction (ligand scrambling) in turns indicates that a second chromium-containing species must have been generated. Instead, the oxidation of the metal center during the reaction with an alkyl aluminum reagent is, at least in principle, surprising since these activators are known to act as reducing agents[14] and certainly not as oxidants. On the other hand, recent work[21] has indicated that the reoxidation of the chromium center in the presence of alkyl aluminum reagent is indeed possible via disproportionation as one of the distinctive aspects of the redox dynamism of chromium. This process is the direct result of the interaction of the metal center with the alkyl

aluminum activator. In the present case, the additional ligand necessary for the formation of **5.5** can simply be provided by the low-valent partner of the disproportionation of **5.1** on the way to form metallic chromium. Instead, the formation of **5.5** from **5.4** has a more straightforward explanation since the oxidation state remained unchanged. However, given the acquisition of the additional ligand and that the reduction of the trivalent center to the divalent state during the reaction with activators is widely documented,[14] it is tempting to suggest that the reaction proceeds with initial reduction of **5.4** to a divalent congener followed by similar disproportionation as observed in the case of **5.1**.

Table 5.2. Ethylene oligomerization results.

Catalyst	Co-Catalyst (equiv)	Co-Cat :Cr	Alkenes (mL)	Activity (g/mmolCr/ h)	C_6 (mol%)	C_8 (mol%)	C_{10} (mol%)	C_{12} (mol%)	C_{14} (mol%)	C_{16} (mol%)	C_{18} (mol%)
5.1	MAO	100	80	5,600	33	25	18	11	9	3	1
5.1	MAO	500	208	14,560	40	31	15	9	4	1	0
5.1	MAO	1000	120	8,400	37	26	18	11	5	2	1
5.1[a]	MAO	500	14	980	51	40	6	2	1	0	0
5.1[b]	MAO	500	20	1400	23	21	18	15	11	8	4
5.1[c]	MMAO	500	0	0	0	0	0	0	0	0	0
5.1	PMAO	500	144	10,080	37	23	17	11	7	4	1
5.1	DMAO[d]	500	240	16,800	36	26	17	11	6	3	1
5.1	DMAO[d]	1000	348	24,360	33	30	16	11	6	3	1
5.1	DMAO[d]	2000	420	29,400	42	30	14	9	4	1	0
5.2	MAO	500	112	7,840	31	30	16	10	7	4	2
5.3	MAO	500	100	7,000	35	25	18	11	7	3	1
5.4	MAO	500	16	1,120	25	27	20	14	8	4	2
5.5	MAO	500	0	0	0	0	0	0	0	0	0

Conditions: 100 mL of toluene, loading 10 μmol of complex, 35 bar of ethylene, reaction temperature 60 °C, reaction time 60 min; [a] T = 20 °C [b] T = 100 °C. [c] 100 mL of methylcyclohexane [d] DMAO = $AlMe_3$-depleted MAO.

When activated with methylaluminoxane, **5.1** yielded a very large amount of oligomers with a minor excess of 1-hexene and 1-octene over the statistical S-F distribution of α-olefins as calculated on the basis of the heavier oligomers (Table 5.2). Increasing the Al:Cr ratio results in a tremendous increase of catalytic activity as well as a significant increment of the selectivity

towards 1-hexene and 1-octene. The optimization was reached with an Al:Cr ratio of about 500 since larger excess downturned the activity as well as the selectivity. A similar rise in catalytic activity with increasing Al:Cr ratios was also observed for the original NPN system containing a trivalent phosphorous.[16a] In that case the selectivity was, however, unchanged. Temperatures higher or lower than 60 °C visibly decreased the activity. At low temperature, the lower activity was accompanied by a considerable increase of selectivity (91% 1-hexene / 1-octene and 9% heavier oligomers).

The outstanding feature of this catalytic system is the complete absence of polymer, which is highly desirable from an industrial standpoint. The use of different aluminoxane activators afforded variable activities. The most productive run was obtained with $AlMe_3$-depleted MAO (DMAO) which afforded an activity comparable to the highest ever observed for a LAO catalyst obtained with late transition metals[22] (420 mL polymer-free mixture of oligomers from 10 μmole of catalyst per hour). Interestingly, the high activity was also accompanied by a significant enrichment in 1-hexene and 1-octene, the two most important α-olefinic oligomers (Table 5.2).

The replacement of the *t*-Bu substituents by *i*-Pr or Ph groups gave a noticeable decrease of both activity and selectivity although the overall catalytic activity still remained quite acceptable. The fact that the large steric bulk of the *t*-Bu groups may play a central role in significantly enriching the oligomeric mixture in 1-hexene and 1-octene is intriguing. If the excess of these two oligomers is generated by a Cr(I) intermediate via a ring expansion mechanism, this would be of course in addition to the Cossee-Arlman mechanism, presumably operated by Cr(II) which produces the large amount of S-F distribution of oligomers. We therefore speculate, that the bulky substituents of **5.1** prevent dimeric aggregation of the monovalent chromium thus hindering its disproportionation but also decreasing the catalytic activity. In other words, the

ligand's steric bulk might lend some stability to highly reactive Cr(I) intermediates. However, we cannot exclude that the S-F distribution might also be generated by a ring expansion mechanism.[9] In such an event, one must assume that the presence of *t*-Bu groups somehow renders faster the reductive elimination of the seven and nine-member rings with respect to larger rings.

We have also attempted to utilize methylcyclohexane as solvent for the catalytic run since toluene is known to occasionally have poisoning effect on trimerization catalysts.[14b] In turn this has required the usage of MMAO for solubility reasons. The observed lack of catalytic behavior is likely to be ascribed to the strongly reducing *i*-Bu groups present in this particular activator most probably decomposing the catalyst to metallic chromium. The trivalent **5.4** displays only marginal catalytic activity compared to the divalent **5.1**.

5.5 Conclusions

In conclusion, in this work we have discovered an unprecedented and potentially useful catalytic system for non-selective ethylene oligomerization devoid of polymer. This feature, in combination with the near to record activity of **5.1**, makes the catalyst competitive with the best performing industrial systems. The general lack of selectivity and the chemical behavior of the complexes reported above, altogether suggest that the most active catalytically active species may contain divalent chromium. In this event, the non-selective oligomerization would not proceed through a ring expansion mechanism. It is worth reminding that divalent chromium, according to the current status of its chemistry, does not possess the reducing potential sufficient for coupling two ethylene molecules into a metallacycle. At this stage it is tempting to propose that the excess of 1-hexene and 1-octene observed in a few instances is likely to be generated by a monovalent chromium species produced in parallel to Cr(II) as a result of the redox dynamism.

The subtle effect of ligand substituents in determining the appearance of the excess of these two oligomers, together with the exceedingly high activity, encourage further attempts to transform these systems into highly active and truly selective oligomerization catalysts. In the next chapter following the same strategies of chapters 2 and 3, we have isolated a chromium(I) derivative of the NP^VN ligand system by using CH_2=CH-MgCl as a non-classical reducing agent.

5.6 References

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Chapter Six

Publication:

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Preparation and Characterization of a Reduced Chromium Complex via Vinyl Oxidative Coupling: Formation of a Self-Activating Catalyst for Selective Ethylene Trimerization

6.1 Introduction

Catalytic and selective ethylene trimerization is increasingly attracting the attention of academic researchers for the ongoing mechanistic debate[1] about the several aspects of this industrially relevant[2] and relatively rare process.[3] The current state of knowledge relies on the so-called ring expansion mechanism triggered by a transition metal (most often chromium) in a low oxidation state sufficiently reducing to perform the initial ethylene reductive coupling. [1,3,4]

From recent studies in chromium-catalyzed selective tri- and tetramerization it becomes apparent that the occurrence of selectivity in the catalytic process is directly related to the possibility of reaching the monovalent state.[5] There are substantial challenges however. This particular oxidation state can be stabilized on chromium by π-systems (arene, cyclopentadienyls) and/or CO and for which a large family of compounds has today been established.[6] These species, however, are catalytically inert unless procedures are followed for the extraction of the strongly stabilizing carbonyl ligands.[6i-k] Asides from them, only less than a handful of monovalent compounds have been isolated and crystallographically authenticated. A common feature among all these species is the clear evidence for a tremendous reducing power as

indicated by the fact that these species form dinitrogen[7] and arene inverted sandwich compounds,[8] or quintuple bonded dichromium systems.[9] Therefore, it comes as no surprise that the most convenient path to monovalent chromium selective catalysts commonly consists of reducing tri- or divalent complexes *in situ* with the aid of an alkylating agent as an activator.

In the most selective chromium catalytic trimerization systems reported so far, the activation process is performed mainly by a large amount of MAO[2,3] or near to stoichiometric amounts of TEAL/DEAC.[2a] It is well established that trivalent organochromium complexes may readily be reduced to the divalent state in the presence of alkyl aluminum reagents.[10] In this scenario, selective oligomerization does not occur while instead polymerization or non-selective oligomerization (S-F distribution) is observed.

In search for selective trimerization systems based on chromium, one possible strategy consists of bypassing the divalent state and to reduce the trivalent precursor *directly* to the monovalent via a concerted two-electron reduction.[5d] This might be achieved via double alkylation of the transition metal center followed by two-electron reductive elimination of organic units (e.g. heavier alkanes or alkanes/alkenes mixtures). Organo-aluminum species, although effective so far, are not ideal for the purpose since they may embark in alkyl/halogen exchange equilibria with the transition metal, in turn often requiring the employment of large amount of these dangerous and expensive chemicals. Even further, if during the dynamic alkyl exchange process, a substantial concentration of monoalkylated chromium species is generated, one-electron reduction to the stable divalent state may rapidly and irreversibly occur under the thermal conditions normally required by the catalytic cycle. In turn, this would negatively affect the selectivity by providing only S-F mixtures possibly enriched in 1-hexene depending on the extent of two- versus one-electron reduction.

Given this background, we are exploring the possibility of using stoichiometric amounts of organo-magnesium and -lithium derivatives for the purpose of cleanly generating catalytically active monovalent species. For this study, we have selected the vinyl-Grignard reagent with the purpose of performing alkylation and two-electron reduction of the metal center as discussed above.

As a substrate, in chapter five we focused on the recently prepared divalent [(*t*-Bu)NP(Ph)$_2$N(*t*-Bu)]Cr(μ^2-Cl)$_2$Li(THF)$_2$ (**5.1**) and this study has clearly identified its ready formation from a trivalent precursor in the presence of alkylating agents. This catalyst only produces a S-F distribution of oligomers. This behavior clearly speaks for the initial reduction of the trivalent species to the divalent state that is obviously preserved throughout the catalytic cycle. The resiliency to reach the monovalent state made this substrate ideal for probing the effect of stronger alkylating and more reducing activators.

In this chapter we describe its reaction with CH_2=CH-MgCl affording an oxidative coupling of two vinyl groups with formation of a reduced chromium complex storing additional spin density in a deprotonated butadiene residue. Its catalytic behavior as a single component selective trimerization catalyst is discussed.

6.2 Experimental Part

All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried using an aluminum oxide solvent purification system. Ligands (*t*-Bu)NH-PBr(Ph)$_2$-NH(*t*-Bu) were prepared according to literature procedure.[11] Vinylmagnesium chloride (1.6M in THF) was purchased from Aldrich and used as received. Liquid mixtures from catalytic runs were analyzed by using a CP 9000 gas chromatograph (GC) equipped with a 30 mL × 0.32 mm id, capillary CP volamine column and a FID detector. All single-point experiments were performed in duplicate.

The yield was determined by ^{1}H-NMR spectroscopy (Varian Mercury 400 MHz spectrometer). Elemental analysis was carried out with a Perkin-Elmer 2400 CHN analyzer.

Preparation of {π-[(*t*-Bu)N-P(Ph)$_2$-N(*t*-Bu)]Cr}$_2$(μ,μ',η^4,η^4'-C$_4$H$_4$){σ-[(*t*-Bu)N-P (Ph)$_2$-N(*t*-Bu)]Cr} (6.2):

A solution of [(*t*-Bu)NP(Ph)$_2$N(*t*-Bu)]Cr(μ^2-Cl)$_2$Li(THF)$_2$ (**5.1**) (0.601 g, 1.0 mmol) in THF (10 mL) was treated with vinylmagnesium chloride (1.1 mmol, 0.7 mL) and followed by the addition of 1,4-dioxane (1.1 mmol, 0.97 mL). The reaction was stirred for 18 h and then solvent was removed *in vacuo* and hexane (10 mL) was added. The suspension was centrifuged and the resulting solution was reduced to 4 mL and stored at -40 ^{o}C in the freezer for 4 days. The resulting brown crystals were filtered and washed with cold hexanes (10 mL) and dried *in vacuo* to give (0.154 g, 0.129 mmol, 39%). El. Anal. Calcd. (found) for $C_{64}H_{88}Cr_3N_6P_3$ (desolvated): C 64.58 (64.54), H 7.45 (7.46), N 7.06 (7.07). ESI-MS (rel. int.) *m/z* = 1190.722 ([M+H]$^+$, 0.10), 1145.777 ([M-3Me]$^+$, 0.16), 1101.825 ([M+H-6Me]$^+$, 0.12), 739.509 ([M+H-C25H40CrN2P]$^+$, 76.85) 693.541 ([M+H-C28H48CrN2P]$^+$, 100).

6.3 X-ray crystallography

Suitable crystals were selected, mounted on a thin, glass fiber with paraffin oil, and cooled to the data collection temperature. Data were collected on a Bruker AXS SMART 1 k CCD diffractometer. Data collection was performed with three batch runs at phi = 0.00 deg (600 frames), at phi = 120.00 deg (600 frames), and at phi = 240.00 deg (600 frames). Initial unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied. The systematic absences and unit-cell parameters were consistent for the reported space groups. The structures were solved by direct methods, completed with difference Fourier syntheses, and

refined with full-matrix least-squares procedures based on F2. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 6.12. Details of crystal data and structure analysis are given in Table 6.1.

Table 6.1. Crystal Data and Structure Analysis Results of Complex **6.2**.

	6.2
formula	$C_{66.63}H_{94.13}Cr_3N_6P_3$
Mw	1228.01
space group	Monoclinic, C2/c
***a* (Å)**	14.868(3)
***b* (Å)**	27.799(6)
***c* (Å)**	17.357(4)
***α*, (deg)**	90
***β*, (deg)**	99.206(4)
***γ*, (deg)**	90
***V* (Å^3)**	7082(3)
Z	4
radiation	0.71073
***T* (K)**	296(2)
D_{calcd} (g cm^{-3})	1.152
μ_{calcd} (mm^{-1})	0.560
***F*$_{000}$**	2612
***R*, *Rw*^{2a}**	0.0576, 0.1206
GoF	1.042

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

The initial solution suggested the presence of two co-crystallized, disordered and partially occupied toluene solvent molecules in the lattice. In order to maintain acceptable data to parameter ratio and because of the difficulties of modeling the disorder with moderate quality data set, the data were treated with the Squeeze routine of PLATON.[12] Such treatment resulted in removal of solvent generated reflections and appearance of void space per cell equal to 1383.1 Å^3 with an electron count per cell equal to 84 electrons. The electron count was consistent with

one and two/third toluene molecules per cell. Based on this calculation appropriate changes were made to the formula of the asymmetric unit.

6.4 Computational Details

DFT calculations were performed using the Gaussian 03 package[13] using the PBE[14] and B3LYP[15] exchange-correlation functionals and the TZVP[16] basis set. Tight SCF convergence criteria were used for all calculations. The converged wave functions were tested to confirm that they correspond to the ground-state surface. All calculations for the analysis of the electronic structure, including the generation of initial wave functions, Mulliken population analysis[17] and the calculation of Mayer bond order indices[18], atomic valences[19] and populations of fragment orbitals[19] were performed using the AOMix software package.[20]

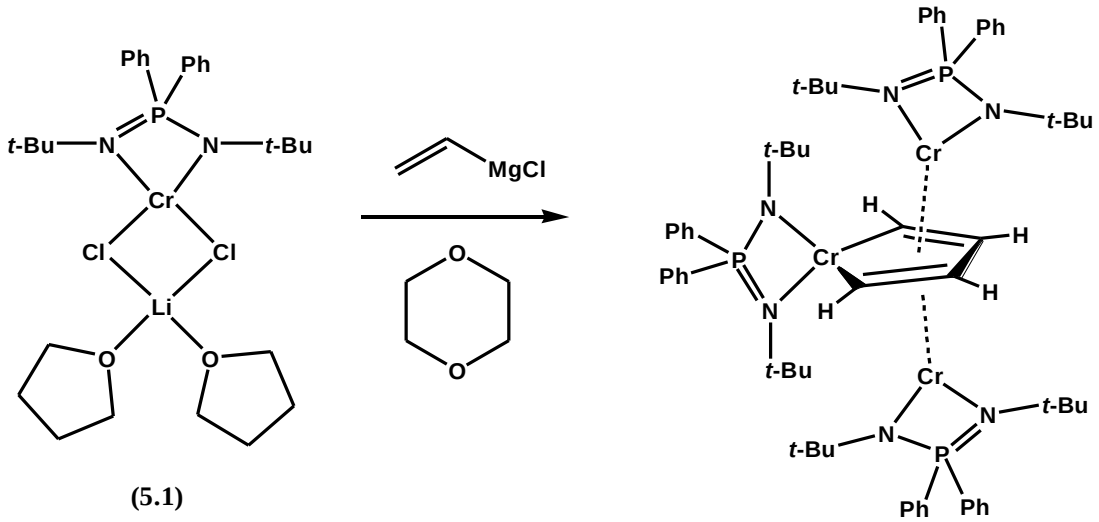
6.5 Magnetic Measurements

The magnetic susceptibility measurements were obtained using a Quantum Design SQUID magnetometer MPMS-XL7 operating between 1.8 and 300 K for dc-applied fields ranging from –7 to 7 T. Dc analyses were performed on polycrystalline samples, wrapped in a polyethylene membrane and under a field ranging from 0 to 7 T between 1.8 and 300 K. The magnetization data were collected at 100 K to probe the possible presence of ferromagnetic impurities. A diamagnetic correction was applied for the sample holder.

6.6 Results and Discussion

The reaction of divalent [(*t*-Bu)NP(Ph)$_2$N(*t*-Bu)]Cr(μ^2-Cl)$_2$Li(THF)$_2$ (**5.1**) with CH$_2$=CH-MgCl reproducibly afforded the new trinuclear {π-[(*t*-Bu)N-P(Ph)$_2$-N(*t*-Bu)]Cr}$_2$ (μ,μ',η^4,η^4'-C$_4$H$_4$){σ-[(*t*-Bu)N-P(Ph)$_2$-N(*t*-Bu)]Cr} (**6.2**) (Scheme 6.1).

Scheme 6.1



(5.1) **(6.2)**

The trinuclear structure of **6.2** was revealed by an X-ray diffraction analysis and consists of three metal centers bridged by one butadiene-di-yl unit (Figure 6.1). One metal center is coplanar with the C$_4$ unit and appears to be σ-bonded to the two terminal carbon atoms [Cr(1)-C(32) = 2.128(3)Å] thus forming a five-membered metallacycle. The coordination environment around this metal center is square-planar [N(1)-Cr(1)-N(1a) = 71.5(2)º, N(1)-Cr(1)-C(32) = 107.5(1)º, N(1a)-Cr(1)-C(32a) = 107.5(1)º] with little deviation from planarity and a narrower angle subtended by the two σ-bonded C atoms [C(32)-Cr(1)-C(32a) = 73.7(2)º]. The other two metal centers are symmetrically placed on the axis orthogonal to the plane of the C$_4$ unit with which

they form a π-bonding interaction as indicated by the comparable values of the Cr-C distances [Cr(2)-C(31) = 2.271(3)Å, Cr(2)-C(32) = 2.174(3)Å]. The coordination geometry around each of the two metal centers may also be regarded as square-planar if considering only the two terminal C atoms as bonded to the metal center [N(2)-Cr(2)-N(3) = 72.1(1)º, N(2)-Cr(2)-C(31) = 108.2(1)º, N(3)-Cr(2)-C(32a) = 106.4(1)º].

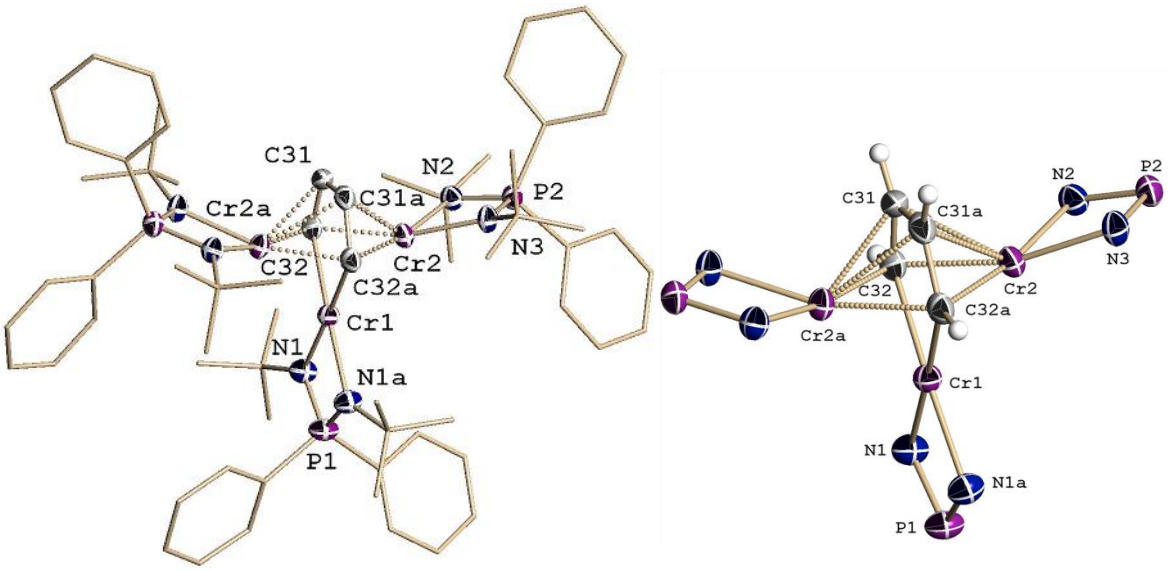


Figure 6.1. Partial thermal ellipsoid plot for **6.2** (left) and simplified plot showing the position of the hydrogen atoms (right). Cr(1)-N(1) = 2.086(3), Cr(1)-C(32) = 2.128(3), Cr(1)-Cr(2) = 2.4892(8), Cr(1)-P(1) = 2.7250(16), Cr(2)-N(2) = 2.062(2), Cr(2)-N(3) = 2.077(2), Cr(2)-C(32A) = 2.174(3), Cr(2)-C(31A) = 2.260(3), Cr(2)-C(31) = 2.271(3), Cr(2)-P(2) = 2.7132(10), C(31)-C(31A) = 1.416(6), C(31)-C(32A) = 1.435(5), C(31)-Cr(2A) = 2.260(3). N(1)-Cr(1)-N(1A) = 71.51(15), N(1)-Cr(1)-C(32A) = 177.07(10), N(1)-Cr(1)-C(32) = 107.45(11), C(32A)-Cr(1)-C(32) = 73.73(17), C(32)-Cr(1)-Cr(2) = 55.19(8), Cr(2)-Cr(1)-Cr(2A) = 89.42(4), N(2)-Cr(2)-N(3) = 72.06(10), N(2)-Cr(2)-C(32A) = 170.48(12), N(3)-Cr(2)-C(32A) = 106.35(10), N(2)-Cr(2)-C(31A) = 132.95(11), N(3)-Cr(2)-C(31A) = 103.23(11), C(32A)-Cr(2)-C(31A) = 37.70(12), N(2)-Cr(2)-C(31) = 108.23(11), N(3)-Cr(2)-C(31) = 126.30(12), C(32A)-Cr(2)-C(31) = 64.77(12), C(31A)-Cr(2)-C(31) = 36.43(16), C(32A)-Cr(2)-Cr(1) = 53.79(9), C(31)-Cr(2)-Cr(1) = 81.18(8), C(31A)-C(31)-C(32) = 113.33(17), C(31A)-C(31)-Cr(2A) = 72.20(18), C(32)-C(31)-Cr(2A) = 67.88(16), C(31A)-C(31)-Cr(2) = 71.37(18), C(32)-C(31)-Cr(2) = 67.07(17), Cr(2A)-C(31)-Cr(2) = 101.25(13), C(31)-C(32)-Cr(1) = 119.8(2).

The central and bridging C_4 unit has C-C distances [C(32)-C(31) = 1.435(5)Å, C(31)-C(31a) = 1.416(6)Å] as to be expected for a π-bonded butadiene type of system.[21] The Cr..Cr distance between the σ- and π-bonded metals [Cr(1)-Cr(2) = 2.4892(8)Å] is considerably short and falls in what might be regarded as a metal-metal bonding range. The σ-/π-orientation of the metals to the same C_4 unit is somewhat reminiscent of the trinuclear Ru complex reported by Adams containing a fluorinated residue.[21e] Structures containing two transition metals π-bonded to similar or same C_4 units have been also previously observed for both Cr[21f] and Ni.[21g]

The crystal structure was of sufficient quality to yield the position of the hydrogen atoms including those attached to the C_4 unit. Their position clearly suggested that the butadiene fragment is doubly deprotonated and is therefore in the form of a dianion. Attempts to degrade the complex with D_2O and to analyze the resulting mixture by NMR did not provide a definite answer in the sense that only partly deuterated butadiene oligomers have been identified. Fortunately, it was possible to obtain an informative ^{1}H-NMR spectrum which, in spite of the paramagnetism, showed relatively minor line broadening in the normal chemical shift range. The *t*-Bu groups showed a broad intense line at 1.02 ppm while the phenyl groups gave two broad lines at 8.19 and 7.57. The butadiene-di-yl moiety displays two poorly solved and broadened doublets of equal intensity at 7.95 and 7.43 ppm. All the peaks integrate with the expected ratio. Finally the MS-EI gave the parent peak and the fragmentation pattern as expected for the above formulation.

With three anionic NPN ligands, and one butadiene-di-yl dianion, charge count considerations indicate that the complex should be regarded as a Cr(II)/Cr(I)/Cr(II) mixed valence species. To clarify the electronic structure of the complex, DFT calculations were undertaken using the atomic coordinates as obtained from the crystal structure as a starting

geometry. Geometry optimization calculations at the spin-unrestricted PBE level on the full structure of **2** yielded geometrical parameters in excellent agreement with the experimental values (Figure 6.2). The calculated C-C distances of the butadiene-di-yl residue were only slightly longer for the central C-C bond and identical for the other two. The predicted Cr-Cr distances [2.46 and 3.46 for Cr1-Cr2 and Cr2-Cr2a, respectively] also were in very good agreement with the observed values [2.49 and 3.50].

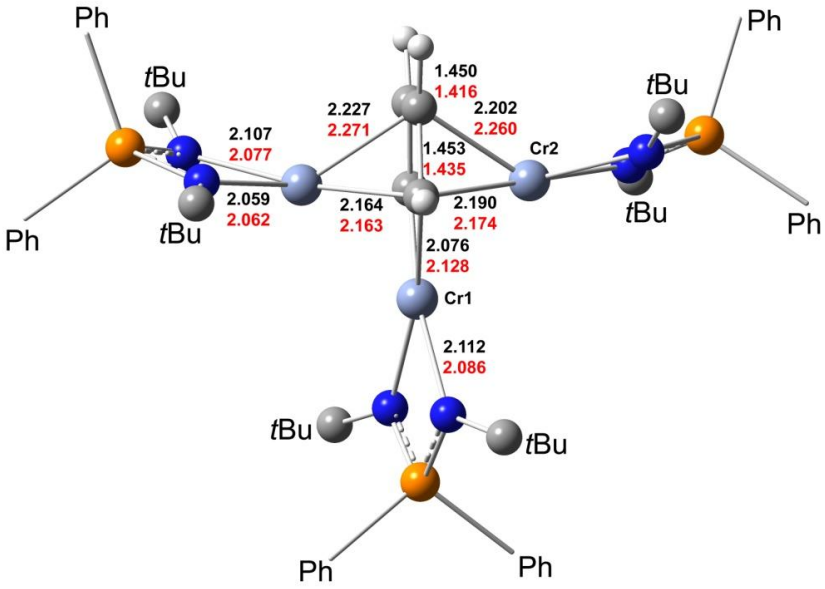


Figure 6.2. Optimized structure of **6.2** (at PBE/TZVP level). Calculated and experimental bond distances (Å) for selected bonds are shown in black and red, respectively.

Among the several possible spin states that have been used for calculation (Figure 6.3a), only that with three high-spin (S = 2) Cr(II) ions coupled through a butadiene-tri-yl monoradical (S = 1/2) trianion yielded the lowest energy and the best agreement between calculated and observed structural parameters thus lending credibility to the formulation. In particular, the two chromium atoms π-bonded to the C_4 unit appear to be ferromagnetically coupled to each other and antiferromagnetically coupled to the third chromium ion σ-bonded to the C_4 unit. In turn the

C_4 moiety carries an additional electron in its π-system antiferromagnetically coupled to the two π-bonded Cr(II) ions and ferromagnetically coupled to the σ-bonded Cr(II) ion. With a total of respectively eight and five electrons antiferromagnetically coupled, the observed magnetic moment of three unpaired electrons per cluster unit was correctly predicted (Figure 6.3). The same ground electronic state was obtained by running the analogous calculations using the hybrid B3LYP instead of the PBE functional.

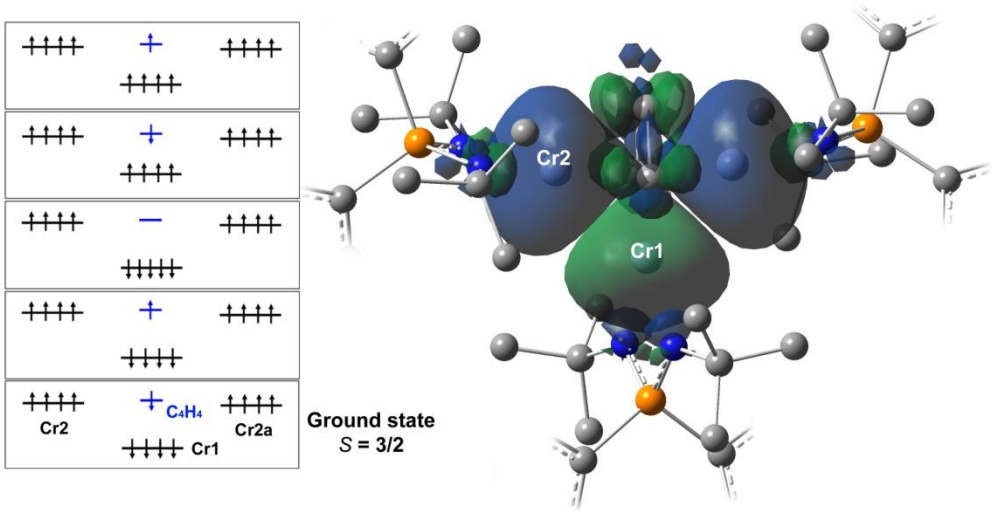


Figure 6.3. Left: possible spin coupling situation for the electronic states of **6.2**. Right: spin density of the ground electronic state of **6.2** (at the PBE/TZVP level). Isosurface contour value is 0.002 a.u.

The electronic interactions between the $[Cr2(L)]^+$ and $[(C_4H_4)Cr1(L)]^{2-}$ fragments results in the net bond order of 2.62 between $[Cr2(L)]^+$ and $[(C_4H_4)Cr1(L)]^{2-}$. Both Cr2-C and Cr1-Cr2 covalent interactions contribute to the stabilization of the structure. The bond orders for individual Cr1-C bonds are in the 0.27-0.36 range while the Mayer bond order for the Cr1-Cr2 interaction is 0.82. The calculated spin densities of the Cr atoms (3.18 on Cr1 and 3.26 on Cr2

from PBE calculations and 3.93 on Cr1 and 3.72 on Cr2 from B3LYP calculations) are consistent with the Cr(II) description for each metal in the structure. Lying 11.9 kcal mol^{-1} above the ground state is the next electronic state for **2**. It features two high-spin (S = 2) Cr(II) ions (Cr2 and Cr2a) coupled through a butadiene-tri-yl dianion with the intermediate-spin (S = 1) Cr(I) ion (Cr1).

The magnetic susceptibility measurements were carried out on two differently prepared samples of **6.2** by using a Quantum Design SQUID magnetometer MPMS-XL7 operating between 1.8 and 300 K for dc-applied fields ranging from –7 to 7 T. In the first sample the crystallinity was removed via desolvation of the hexane lattice molecule *in vacuo* and under moderate heating. The second sample was instead highly crystalline and special care was applied to make sure that no spontaneous desolvation occurred during the sample handling and preparation. The magnetization data for both samples collected at 100 K confirmed (Figure 6.4) the absence of ferromagnetic impurities as attested by the straight line at low fields.

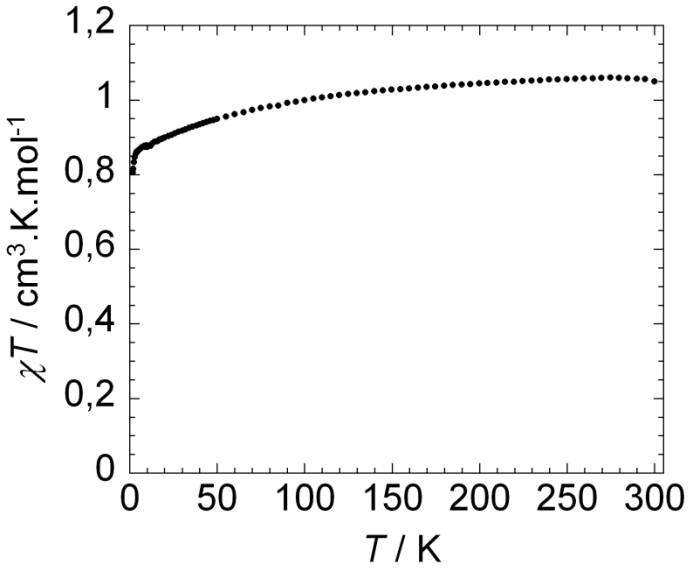


Figure 6.4. Temperature dependence of the χT product at 1000 Oe (with χT being the molar susceptibility per complex defined as M/H).

The dc magnetic properties of the amorphous sample **6.2** were investigated under a 1000 Oe fields in the temperature range 1.8-300 K. The plot of χT *vs.* T revealed a gradual decrease upon lowering of the temperature (Figure 6.4). The slight negative deviation of χT product can be attributed to antiferromagnetic interaction between the spin carriers and/or presence of magnetic anisotropy. At room temperature, the experimental value of χT of 1.05 $cm^3.K.mol^{-1}$ is close to the value of 1.125 $cm^3.K.mol^{-1}$ expected for three uncoupled electrons [S = 3/2, g = 2.0]. The value of χT reached at 1.8 K is 0.80 $cm^3.K.mol^{-1}$.

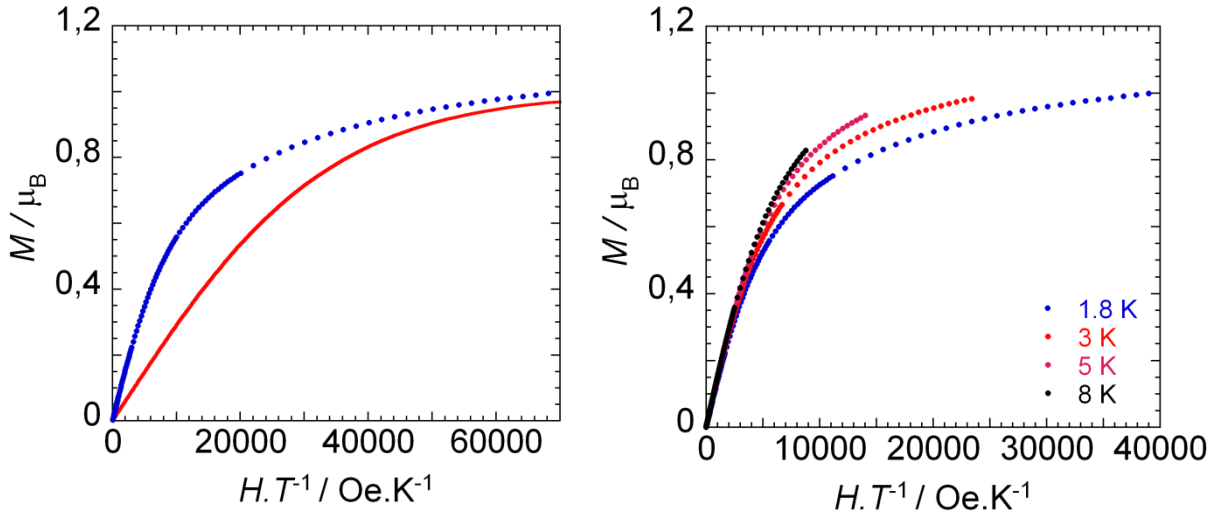


Figure 6.5. Left: Field dependence of the magnetization, M between 1.8 K and 8 K. Right: Field dependence of the magnetization at 1.8 K. The solid line corresponds to the Brillouin function for one S = 1/2 and g = 2.0.

The magnetization was studied up to 7 T (figure 6.5, left) at 1.8 K. As the field increased, the magnetization increases without real saturation up to 1.00 μB. An attempt to obtain a perfect fit for the data with a Brillouin function (S = 1/2 and g = 2.0.) was not successful (Figure 6.5 left, solid red line). Although the low temperature susceptibility and magnetization data suggests a possible S = 1/2 ground state, the intensity of the magnetic interactions between the spin carriers is not known as well as the non-saturation of the magnetization even at 1.8 K it is difficult to

precisely assign the spin ground state of the complex. Furthermore, the non-superposition of the different magnetization data on a single master curve as well as the non-saturation of the magnetization suggests the possible presence of magnetic anisotropy and/or low-lying excited states (Figure 6.5, right).

The behavior of the crystalline sample was surprisingly different. The dc magnetic properties were investigated under a 1000 Oe field in the temperature range 1.8-300 K (Figure 6.6). At room temperature, the experimental value of χT of 0.30 $cm^3.K.mol^{-1}$ is slightly lower than the value of 0.34 $cm^3.K.mol^{-1}$ expected for S = 1/2 (g = 1.9). The χT product remains roughly constant with decreasing temperature down to ~ 25 K, and then drops to a minimum value of 0.24 $cm^3.K.mol^{-1}$ at 1.8 K. The negative deviation of χT can be assigned to either intermolecular interaction between the molecules or magnetic anisotropy. The latter data can be fitted using a Curie-Weiss law leading to a small Weiss constant of θ = –0.65 K (Figure 6.6, solid red line) which indicates the presence of a weak exchange interaction.

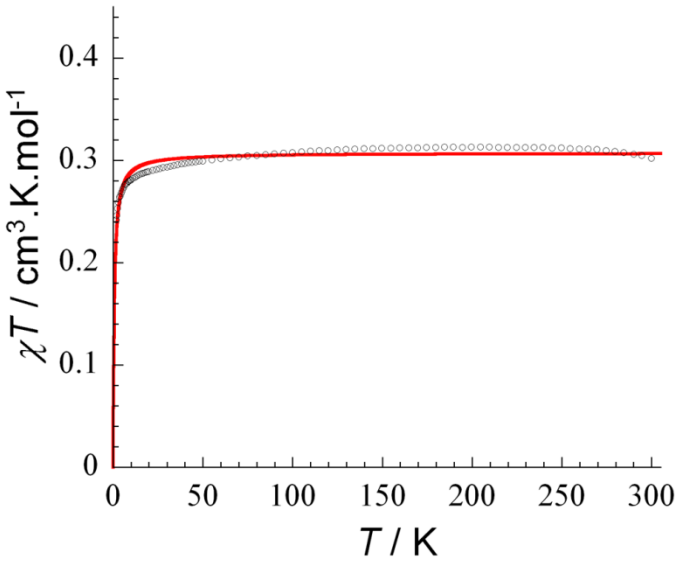


Figure 6.6. Temperature dependence of the χT product at 1000 Oe (with χT being the molar susceptibility per complex defined as M/H).

As shown in Figure 6.7 for the crystalline sample **6.2**, the low temperature magnetization measurements as a function of fields reveal a behavior similar to the desolvated batch. As before, the non-saturation and the non-superposition of the different magnetization data on a single master curve suggest the possible presence of magnetic anisotropy and/or low-lying excited states. Even though the presence of magnetic anisotropy might lead to the slow relaxation of the magnetization associated with a single-molecule magnet behavior due to the small spin ground state of the molecule, no such behavior was observed in the ac data.

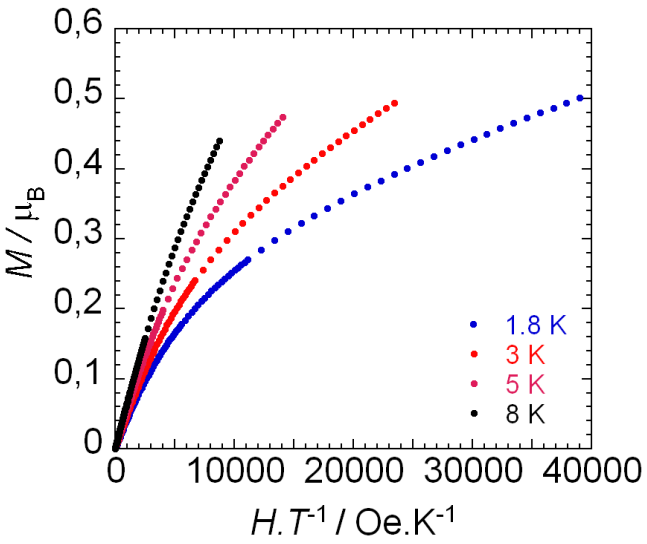
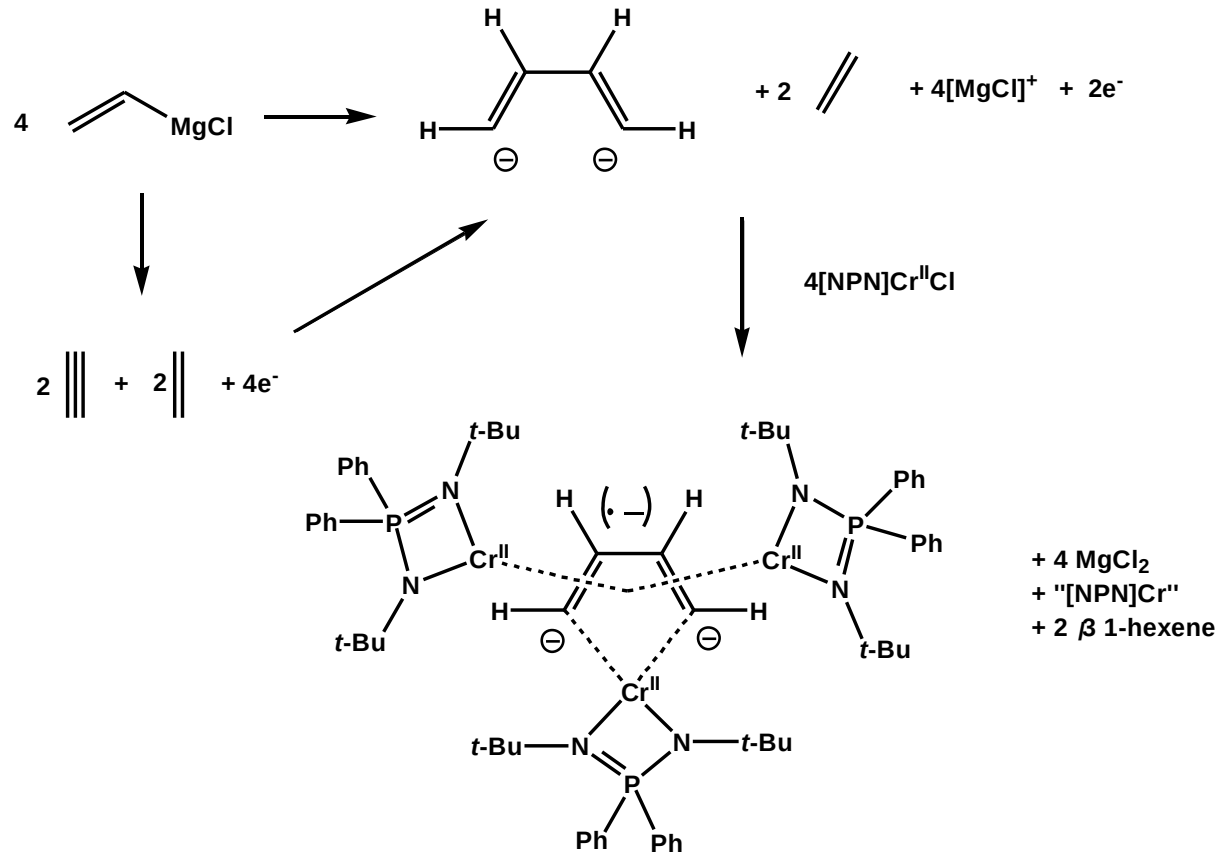


Figure 6.7. Field dependence of the magnetization, *M* between 1.8 K and 8 K.

In summary, the data can be fitted for both samples with a spin S = 1/2 Curie law at low temperature. However, while the spin state is preserved until room temperature in the crystalline sample, the amorphous one showed a spin increment to S = 3/2 as the temperature reached room values. This marked difference of behavior indicates that the intermolecular interactions between the triangular clusters are probably significant. The lack of crystallinity in the desolvated sample and the consequent lack of order obviously affects the spin coupling within molecules allowing to reach the spin state S = 3/2 as predicted by the DFT calculation for **6.2** as a magnetically

isolated system in gas phase. In crystalline samples the intermolecular magnetic coupling is instead maintained throughout the temperature variation.

Scheme 6.2



The formation of **6.2** requires a sequence of events. The oxidative coupling of two vinyl anions implies loss of two electrons (Scheme 6.2). This process is widely known for 2nd and 3rd row late transition metals (Pt, Pd, Os, Rh) and for which, due to their enhanced inclination towards reductive elimination reactions, a broad range of applications has been developed.[22] The fact that in **6.2** a doubly deprotonated butadiene unit is present can be rationalized with at least two different arguments. In the first scenario, the coupling of two coordinated vinyls may give rise to a neutral butadiene unit that is in turn deprotonated by two additional equivalents of

Grignard. From the *formal* point of view, the overall intervention of four vinyl units generates the C_4 dianion, two electrons and two molecules of ethylene (Scheme 6.2). Alternatively, four coordinated vinyl anions may afford two molecules of acetylene, two of ethylene and four electrons.[23] In turn, coupling of two acetylenes with the intervention of two of the four electrons may afford the same C_4 dianion and products. In any of the two scenarios, the involvement of four Cr(II) starting complexes to afford **6.2** has to be assumed not only to trigger the vinyl coupling but also to balance the redox and stoichiometry of the reaction. Of the two electrons generated by the vinyl oxidative coupling, one is hosted in the C_4 unit while the last could be used to reduce the fourth equivalent of chromium to some not yet identified low-valent species. Although its presence has to be admitted just for balancing the redox and stoichiometry of the reaction, interestingly, the GC-MS of the reaction mixture indicated the presence of a small amount of 1-hexene instead of the expected ethylene. It is tempting to speculate that an *in situ* generated Cr(I) byproduct is responsible for the transformation of the ethylene byproduct into 1-hexene.

Complex **6.2** is a reduced species *formally* containing one Cr(I) ion per trimeric structure. Although DFT clearly indicated that three metals are all divalent, yet the complex acts as a self-activating catalyst for ethylene selective trimerization (Table 6.2). In turn this indicates that it is capable of supplying a genuine monovalent chromium unit as a result of the self-activation. This behavior is closely reminiscent of the family of low-valent synthons of the bis-pyridine iminato ligand.[24] When solutions of **6.2** in methylcyclohexane were exposed to 35 bar of ethylene gas at 80 °C, a moderate amount of highly pure 1-hexene were formed. The moderate activity may be easily understood in terms of low concentration of the catalytically active species. Thermal conditions are also required for the initial dissociation of the trimer producing only one

catalytically active monovalent moiety. In situ generation of **6.2** by activating **5.1** with two equivalents of vinyl Grignard basically produced the same outcome at high temperature with a slight increase of activity. Remarkably, an identical run at room temperature doubled the activity, albeit with formation also of some polymer.

Table 6.2. Ethylene oligomerization results.

Catalyst	Co-Catalyst (equiv)	vinylMgCl :Cr	Alkenes (mL)	PE (g)	Activity (g/mmolCr/h)[c]	C_6 (mol%)	C_8-C_{20} (mol%)
6.2[a]	-	-	4	0	91	99.9	0
5.1[a]	$CH_2CHMgCl$	2	5	0	113	99.9	0
5.1[b]	$CH_2CHMgCl$	2	9	0.8	230	99.9	0

Conditions: loading 30 μmol of complex, 35 bar of ethylene, reaction temperature 80 °C, reaction time 60 min; [a)]100 mL of methylcyclohexane [b)] room T. [c)] Considering only one chromium per trimeric structure as active.

6.7 Conclusions

In conclusion, we have herein reported the second case of activation of a selective ethylene trimerization catalyst precursor by stoichiometric amount of a Grignard reagent. The surprising vinyl reductive coupling affording the butadiene-di-yl residue allowed the stabilization of a reduced species capable of feeding Cr(I) into the catalytic cycle. Also the fact that a moderate amount of 1-hexene accompanied the formation of **6.2** indicates that a catalytically active species of high potency might in fact be generated and well supported by this versatile ligand system. In the next chapter we have studied the possibility of forming active species via direct alkylation of both $NP^{III}N$-Cr(II) and $NP^{V}N$-Cr(II) by using simple organolithium reagents such as MeLi and EtLi.

6.8 References

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Chapter Seven

Publication:

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New Catalyst Precursors for Selective Ethylene Trimerization

7.1 Introduction

Linear α-olefins (LAO) are important commodity chemicals central to the industrial preparation of many diversified products essential to our modern life style.[1] These species are typically produced with rather simple catalytic systems, based mainly on combinations of chromium complexes with alkyl aluminum activators. The obtained statistical distribution of LAO is then followed by fractionation[2] since specific applications typically depend on molecular weight. Therefore, it becomes highly advantageous to be able to introduce selectivity in the catalytic cycle. The problem is particularly acute for the light LAO. With 1-hexene and 1-octene being in increasingly high demand, selective tri- and tetramerization catalysts are particularly being pursued.[3]

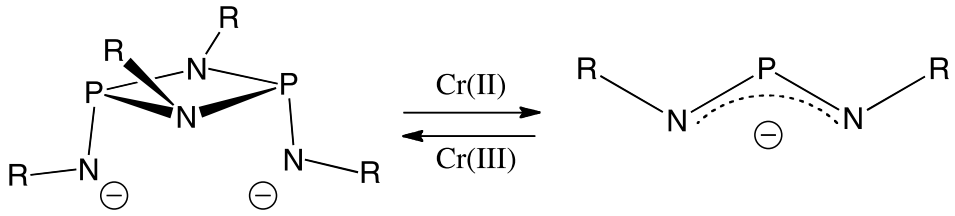
Besides the keen industrial relevance for discovering selective tri- and tetramerization catalysts, developing such systems poses genuine intellectual challenges. In fact, specific mechanistic pathways must be engineered in order for the desired selectivity to be introduced in the catalytic cycle. For example, it is commonly accepted that selective trimerization is achieved with the so-called ring expansion mechanism.[4] The same mechanism has been also proposed for rationalizing the behaviour of quasi-selective tetramerization catalysts (70%).[5] However, it

becomes increasingly apparent that a tetramerization with selectivity comparable to that of the existing trimerization systems cannot be achieved via the same ring expansion pathway but only through alternative mechanisms.[6]

In any event, the possibility of controlling the metal oxidation state is central to discover a selective catalytic system. Recent synthetic[7] and spectroscopic[8] work has established that the monovalent state of chromium is responsible for the selective oligomerization. Thus, clearly defined reductions and availability of ligands that can adequately stabilize the monovalent state may open the way to new and better performing catalytic systems. There are formidable challenges however. The monovalent state of chromium is characterized by an exceedingly high reactivity as clearly indicated by the occurrence of dinitrogen fixation,[9] arene coordination,[10] metal-metal quintuple bond formation,[11] etc. However, these intriguing species are, with only two exceptions,[12] catalytically inert. An ingenious alternative recently developed consists of the abstraction of CO from some representatives of the large family of highly stable monovalent chromium carbonyl derivatives.[13] However, a sensible solution to the difficulties posed by the high reactivity of the monovalent state may be found by designing catalyst precursors with the metal in its higher and more stable trivalent state to be reduced under the conditions required by the oligomerization reaction. However, even the *in situ* reduction of trivalent precursors poses a challenge, since during the reduction the divalent state must be necessarily bypassed. Due to its intrinsic stability, the divalent state often prevents further reduction and gives only unselective catalysts[14,2], albeit occasionally highly active. One strategy for bypassing Cr(II) consists of an initial double alkylation of trivalent precursors followed by a thermal two-electron reductive elimination.[15,4c,d,e]

In chapter two, we have found that the $NP^{III}N$ ligand may afford chromium complexes of switchable catalytic activity (from polymerization, to statistical oligomerization or trimerization) depending on the activation conditions. In turn, this indicates that this family of ligands has the ability to stabilize each of the three critical chromium oxidation states and to slow or prevent their interconversion. To this end, we have observed that: firstly, the original $NP^{III}N$ dimeric structure can be both cleaved and reformed depending on the coordination requirements of the metal oxidation state (Scheme 7.1). Secondly, the activators consistently alkylate the ligand P atom with its aluminum residues remaining connected to the molecular frame. Thirdly, given the occasional appearance of selective behaviour depending on solvent, activators and reaction conditions, it is clear that the ligand has sufficient capability to stabilize catalytically selective monovalent intermediates.

Scheme 7.1



In this chapter, we have analyzed the effect of the alkylation and oxidation of the P atom on the relative stability of the di- versus the trivalent state and its effect on the preparation of organo-chromium species that may in turn act as catalyst precursors.

7.2 Experimental Part

All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried using an aluminum oxide solvent purification system. The liquid product mixtures were analyzed by using a CP 9000 gas chromatograph (GC) equipped with a 30 mL × 0.32 mm id, capillary CP volamine

column and a FID detector. All single-point experiments were performed in duplicate. The yield was determined by ^{1}H-NMR spectroscopy (Varian Mercury 400 MHz spectrometer). Samples for magnetic susceptibility were pre-weighed inside a dry box equipped with an analytical balance and measured on a Johnson Matthey Magnetic Susceptibility balance. Elemental analysis was carried out with a Perkin-Elmer 2400 CHN analyzer. Data for X-ray crystal structure determination (Table 7.1) were obtained with a Bruker diffractometer equipped with a 1K Smart CCD area detector. Et_3Al (93 %, Strem), Et_2AlCl (97 %, Strem), $EtAlCl_2$ (1M in hexane, Aldrich) and MAO (10% wt, Aldrich) were used as received.

Preparation of [(*t*-Bu)NP(Me)N(*t*-Bu)]$_2$CrLi(OEt$_2$) (7.1):

A solution of [(*t*-Bu)NPN(*t*-Bu)]$_2$Cr **2.1** (0.398 g, 1.0 mmol) in THF (10 mL) was treated with MeLi (1.31 mL, 2.1 mmol, 1.6 M in diethyl ether) at -20 ^{o}C. The mixture was allowed to stir at room temperature for 20 h. Then the solvent was removed *in vacuo* and replaced with diethyl ether (5.0 mL). The resulting green suspension was centrifuged and the supernatant was then stored at -30 ^{o}C for 3 days forming deep green crystals of **7.1**. The crystals were washed with cold hexanes (10 mL) and dried *in vacuo* to give analytically pure **7.1** (0.209 g, 0.41 mmol, 41%). [μ_{eff} = 3.93 μ_B] El. Anal. Calcd. (found) for $C_{22}H_{52}CrLiN_4OP_2$: C 51.86 (51.87), H 10.29 (10.25), N 11.00 (10.96).

Preparation of {[(*t*-Bu)NP(Me)N(*t*-Bu)]$_2$CrMe}$_2${Li(THF)}$_2$ (7.2):

A solution of [(*t*-Bu)NPN(*t*-Bu)]$_2$Cr **2.1** (0.398 g, 1.0 mmol) in THF (20 mL) was treated with MeLi (2.06 mL, 3.3 mmol , 1.6 M in diethyl ether) at -20 ^{o}C. The solution was stirred at 40 ^{o}C for 1 day then cooled down to room temperature. Then the solvent was removed *in vacuo* and replaced with hexane (5 mL). The resulting brown solution was centrifuged and storing the resulting solution at -30 ^{o}C for 6 days afforded brown crystals of **7.2** which were filtered, washed

with cold hexanes and dried *in vacuo* (0.140 g, 0.21 mmol, 42 %). ^{1}H-NMR (C_6D_6, 300 MHz, 300 K) δ: -0.01(br, 6H, Cr-CH_3) 1.45 (br, 36H, C(CH_3)$_3$) 1.58 (br, 8H, THF) 2.1 (br, 6H, P-*CH3*) 3.59 (br, 8H, THF). ^{31}P{^{1}H}-NMR (C_6D_6, 300 MHz, 300K) δ: 87.05 (s). MS (ESI) *m/z* $(M+H)^+$ = 669.41. El. Anal. Calcd. (found) for $C_{28}H_{64}Cr_2Li_2N_4O_2P_2$: C 50.29 (50.25), H 9.65 (9.62), N 8.38 (8.39).

Preparation of {[(*t*-Bu)NP(Ph)$_2$N(*t*-Bu)]CrEt}$_2$ (7.3).

A green-blue solution of [(*t*-Bu)NP(Ph)$_2$N(*t*-Bu)]CrCl$_2$Li(THF)$_2$ (**5.1**) (0.601 g, 1.0 mmol) in THF (5 mL) was treated with slow addition of EtLi (2.2 mL, 1.1 mmol, 0.5 M in hexanes) at -35 ºC, and the resulting brown solution was stirred for 2 h at room temperature. The solvent was removed *in vacuo* and the residue re-dissolved in diethyl ether (10 mL). The suspension was centrifuged and the supernatant concentrated to 4 mL and stored at -35 ºC for 3 days. Brown crystals of **7.3** were filtered, washed with cold hexanes (10 mL) and dried *in vacuo* to give (0.26 g, 0.32 mmol, 64%). μ_{eff} = 2.79 μ_B. El. Anal. Calcd. (found) for $C_{44}H_{66}Cr_2N_4P_2$: C 64.69 (64.64), H 8.14 (8.13), N 6.86 (6.83).

Preparation of [(*t*-Bu)NP(Ph)$_2$N(*t*-Bu)]$_2$Cr (7.4).

In 50 mL round bottom Schlenk flask, (0.816 g, 1.0 mmol) of complex **7.3** were dissolved in toluene (20 mL). The solution was refluxed at 110 ºC for 3 h producing some insoluble black material while maintaining the original brown solution color. The suspension was centrifuged and the supernatant was dried *in vacuo*. The resulting brown powder was then dissolved in diethyl ether (5 mL) and stored at -35 ºC for 3 days. Brown crystals of **7.4** were filtered, washed with cold hexanes (10 mL) and dried *in vacuo* to give (0.33 g, 0.47 mmol, 47%). μ_{eff} = 4.92 μ_B. El. Anal. Calcd. (found) for $C_{40}H_{56}CrN_4P_2$: C 67.97 (67.89), H 7.99 (8.03), N 7.93 (7.96).

7.3 X-ray Data

Table 7.1. Crystal Data and Structure Analysis Results of Complexes **7.1-7.4**.

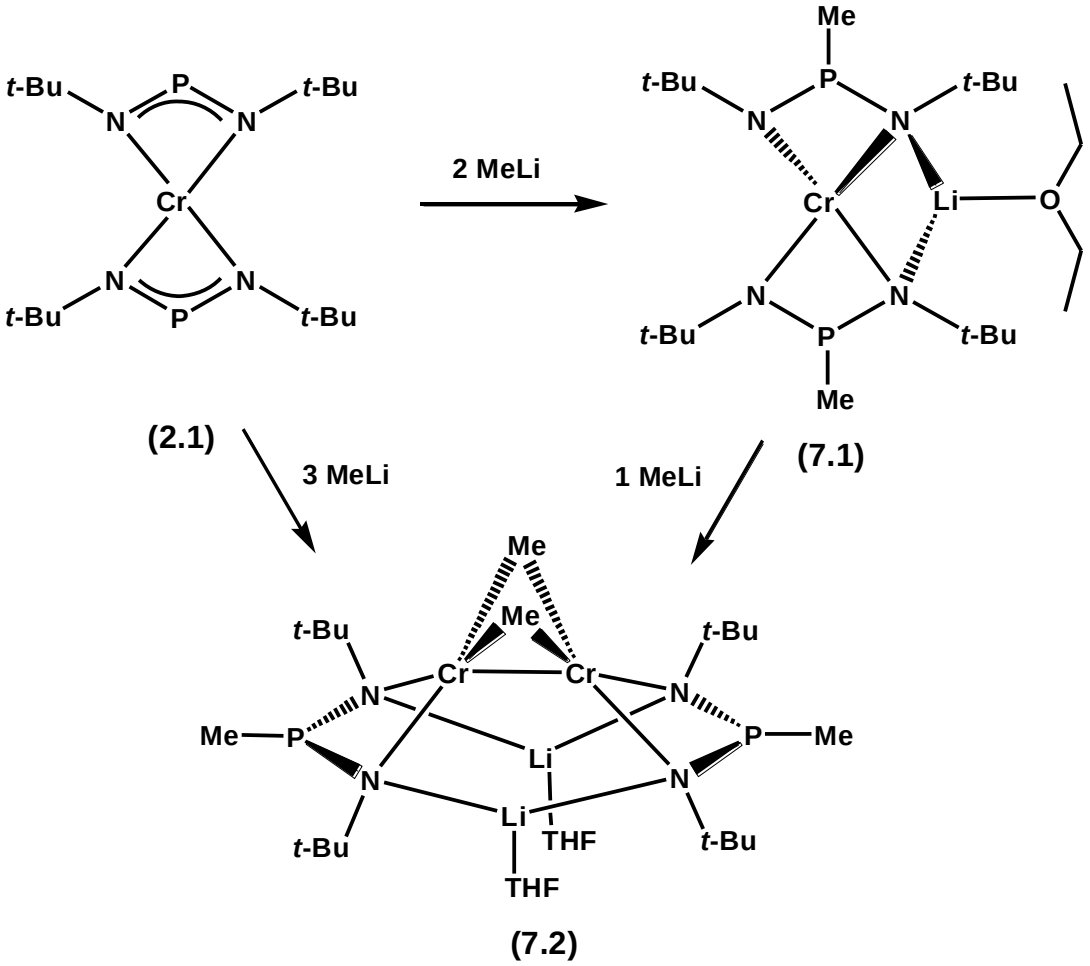
	7.1	**7.2**	**7.3**	**7.4**
formula	$C_{22}H_{52}CrLiN_4OP_2$	$C_{32}H_{72}Cr_2Li_2N_4O_3P_2$	$C_{46}H_{71}Cr_2N_4O_{0.50}P_2$	$C_{87}H_{126}Cr_2N_8O_{1.75}P_4$
Mw	509.56	740.76	854.01	1539.84
space group	C2/c	P2(1)/n	Monoclinic, P2(1)/n	Triclinic, P-1
***a* (Å)**	11.1079(11)	11.003(6)	14.1471(14)	13.8420(10)
***b* (Å)**	17.0588(17)	16.789(9)	9.7637(10)	17.7755(13)
***c* (Å)**	16.0537(16)	22.718(12)	34.114(3)	19.1806(14)
***α*, (deg)**	90°	90°	90	98.1650(10)
***β*, (deg)**	92.6750(10)°	90.297(7)°	92.404(5)	105.3420(10)
***γ*, (deg)**	90°	90°	90	101.9230(10)
***V* (Å^3)**	3038.7(5)	4196(4)	4707.9(8)	4355.2(5)
Z	4	4	4	2
radiation	0.71073	0.71073	0.71073	0.71073
***T* (K)**	201(2)	201(2)	200(2)	200(2)
D_{calcd} (g cm^{-3})	1.114	1.172	1.205	1.174
μ_{calcd} (mm^{-1})	0.500	0.627	0.565	0.372
***F*$_{000}$**	1108	1600	1828	1652
***R*, *Rw*^{2a}**	0.0442, 0.1178	0.0672, 0.1741	0.0425, 0.1021	0.0618, 0.1615
GoF	1.080	1.076	1.017	1.039

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

7.4 Results and Discussion

To deliberately alkylate the NPN framework, a simple MeLi reagent was the most obvious choice. The preparation and characterization of the divalent catalyst precursor [(*t*-Bu)NPN(*t*-Bu)]$_2$Cr (**2.1**) was previously described in chapter two. Its reaction with MeLi proceeds in a remarkably different manner depending on the stoichiometric ratio. The reaction with *two* equivalent of MeLi (Scheme 7.2) afforded the *trivalent* [(*t*-Bu)NP(Me)N(*t*-Bu)]$_2$CrLi(OEt$_2$) (7.**1**). In this complex both P atoms have been methylated and one lithium atom, partly solvated, was retained to provide electro-neutrality to the trivalent metal center. The oxidation of the metal

Scheme 7.2



center from the divalent to the trivalent state upon treatment with MeLi (certainly not an oxidizing agent) may only be explained by assuming a disproportionation between two divalent intermediates. In turn, this suggests that a monovalent complex is likely to have been formed as a partner of the formation of **7.1**. Unfortunately, all the attempts to isolate or even trap such a species via reoxidation reactions did not afford a characterized compound.

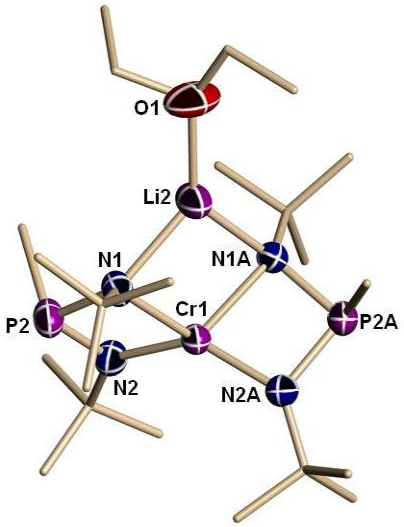


Figure 7.1. Plot of **7.1** with ellipsoids set at 50% probability and hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [º]: Cr(1)-N(2) = 1.902(2), Cr(1)-N(2A) = 1.902(2), Cr(1)-N(1) = 2.022(2), Cr(1)-N(1A) = 2.022(2), N(1)-Li(2) = 2.097(5), Li(2)-O(1) = 1.926(7), N(2)-Cr(1)-N(1) = 77.67(8), N(1)-Cr(1)-N(1A)= 102.89(12), N(2)-Cr(1)-N(1A) = 130.72(9), N(2A)-Cr(1)-N(1) = 130.71(9), N(2)-P(2)-N(1) = 91.16(10), N(1A)-Li(2)-N(1) = 97.9(3).

The crystal structure of **7.1** shows the trivalent chromium atom in a distorted tetrahedral coordination environment [N(2)-Cr(1)-N(1) = 77.67(8)º, N(1)-Cr(1)-N(1A)= 102.89º, N(2)-Cr(1)-N(1A)= 130.72(9)º, and N(2A)-Cr(1)-N(1) = 130.71(9)º] defined by the four nitrogen donor atoms of two separate NPN anions (Figure 7.1). This distortion has clearly to be attributed to the retention of a lithium atom bridging two nitrogens of the two ligands [N(1)-Li(2) = 2.097(5) Å].

The reaction with *three* equivalent of MeLi afforded instead an interesting dinuclear and almost diamagnetic complex formulated as $\{[(t\text{-Bu})NP(Me)N(t\text{-Bu})]_2CrMe\}_2\{Li(THF)\}_2$ (**7.**2) (Scheme 7.2). The third equivalent of MeLi is required for the reduction of the metal center to the divalent state in the initially formed **7.1**. Accordingly, **7.2** may also be formed by treating **7.1** with MeLi. The ^{1}H-NMR spectrum of **7.2** shows a minor line broadening but all the expected lines with expected intensity were clearly identified.

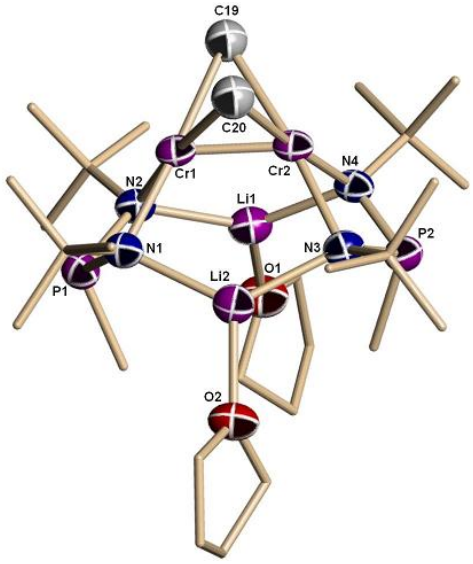


Figure 7.2. Plot of **7.2** with ellipsoids set at 50% probability and hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [^{o}]: Cr(1)-Cr(2) = 2.0148(15), Cr(1)-C(19) = 2.199(5), Cr(1)-C(20) = 2.296(5), Cr(2)-C(20) = 2.187(5), Cr(2)-C(19) = 2.295(5), Cr(1)-N(1) = 2.061(4), Cr(1)-N(2) = 2.073(4), N(1)-Li(2) = 2.122(9), Cr(1)-C(19)-Cr(2) = 53.22(11), Cr(2)-C(20)-Cr(1) = 53.35(11), N(1)-Cr(1)-N(2) = 76.92(15), N(1)-Cr(1)-C(19) = 176.71(17), N(1)-Cr(1)-C(20) = 102.85(18), Cr(2)-Cr(1)-C(19) = 65.85(15), Cr(2)-Cr(1)-C(20) = 60.55(13), N(1)-Li(2)-N(3) = 125.2(4).

The crystal structure of **7.2** consists of two chromium atoms, each chelated by one methylated ligand, and bridged by two methyl groups (Figure 7.2). The Cr_2Me_2 core is severely folded with a very short Cr-Cr contact [Cr(1)-Cr(2) = 2.0148(15)Å]. The coordination environment around each chromium atom is slightly distorted square planar [N(1)-Cr(1)-C(19) = 176.71(17)º; N(1)-Cr(1)-N(2) = 76.92(15)º; N(1)-Cr(1)-C(20) = 102.85(18)º] and is defined by

the two N donor atom of the chelating ligand [C(1)-N(1) = 2.061(4)Å; Cr(1)-N(2) = 2.073(4)Å] as well as by the two bridging methyl groups [Cr(1)-C(19) = 2.199(5)Å and Cr(1)-C(20) = 2.296(5)Å]. Two lithium atoms, each solvated by one THF, bridge one nitrogen atom of each ligand [N(1)-Li(2) = 2.122(9) Å].

Both **7.1** and **7.2** display a rather disappointing catalytic behaviour. Activation was only possible with MAO and strictly unselective behaviour was observed albeit with very good activity (Table 7.2). Complex **7.2** was also tested for single component catalytic behaviour and thermolyzed under ethylene atmosphere. No activity was observed, nor degradation of the complex. In turn, this emphasizes the high stability of divalent organochromium complexes and reiterates the need for bypassing this oxidation state. Interestingly, activation of **7.2** with $EtAlCl_2$ in MeCy selectively produced 1-hexene, along with a small amount of polymer as a by-product. This behaviour was also observed in toluene, the only difference being a substantially lower activity. This is in agreement with the often-observed poisoning effect of aromatic solvents which are possibly responsible for an excessive stabilization of intermediate monovalent species.

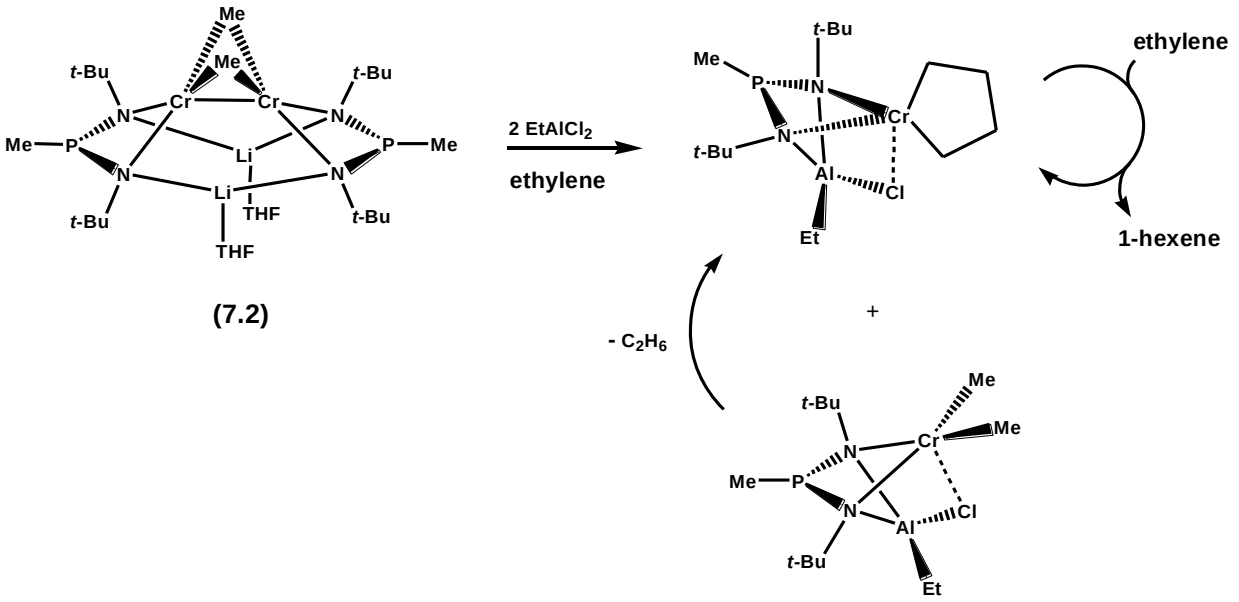
Table 7.2. Oligomerization of ethylene:

Catalyst	Al:Cr	Co-Catalyst	Alkenes (mL)	PE (g)	Activity (g/mmolCr/h)	C6 (mol%)	C8 (mol%)	C10-20 (mol%)
7.1 [a]	1000	MAO	90	0.8	2,130	24	23	53
7.1 [a]	500	MAO	63	2.6	1,560	33	27	40
7.1 [b]	5	Et_3Al	0	traces	0	0	0	0
7.1 [b]	5	Et_2AlCl	0	0	0	0	0	0
7.1 [b]	5	$EtAlCl_2$	0	traces	0	0	0	0
7.2 [b, c]	-	-	0	0	0	0	0	0
7.2 [a]	1000	MAO	59	1.1	1420	28	25	47
7.2 [a]	500	MAO	42	2.9	1,080	29	25	46
7.2 [b]	5	Et_3Al	0	traces	0	0	0	0
7.2 [b]	5	Et_2AlC	0	0	0	0	0	0
7.2 [b]	5	$EtAlCl_2$	2	0.2	54	99.9	0	0
7.2 [b]	2	$EtAlCl_2$	5	0.9	147	99.9	0	0
7.2 [a]	2	$EtAlCl_2$	1	0.4	37	99.9	0	0

Conditions: loading 30 μmol of chromium complex, 35 bar of ethylene, reaction temperature 60 °C, reaction time 60 min; [a] 100 mL of toluene, [b] 100 mL of methylcyclohexane, [c] Reaction temperature 100 °C.

The selective behaviour observed upon activation with $EtAlCl_2$ also indicates the necessity for the presence of chlorine in the catalytically active species. The "chlorine effect" is a primary characteristic of the commercially used pyrrolato-based catalytic system and the characterization of its catalytically active intermediates has fully elucidated the role of chlorine in their stabilization. For example, in the case of the divalent and dimeric tetramethylpyrrolato catalyst precursor $[(Me_4C_4N)CrMe]_2$, also a Me-bridged dimer,[7b] the very strong chlorine effect is mainly due to its ability to trigger the disproportionation to the tri- and monovalent states. We reasoned that in this present case the effect might be very similar (Scheme 7.3). The intervention of aluminum may be initially limited to the replacement of Li and, because of the presence of coordinating chlorine, it is not inconceivable that it will promote disproportionative cleavage of the dimeric structure via establishing a bridging interaction between Al and Cr. Two-electron reductive elimination even in this case may directly yield the catalytically active Cr(I) species ready to couple ethylene molecules.

Scheme 7.3



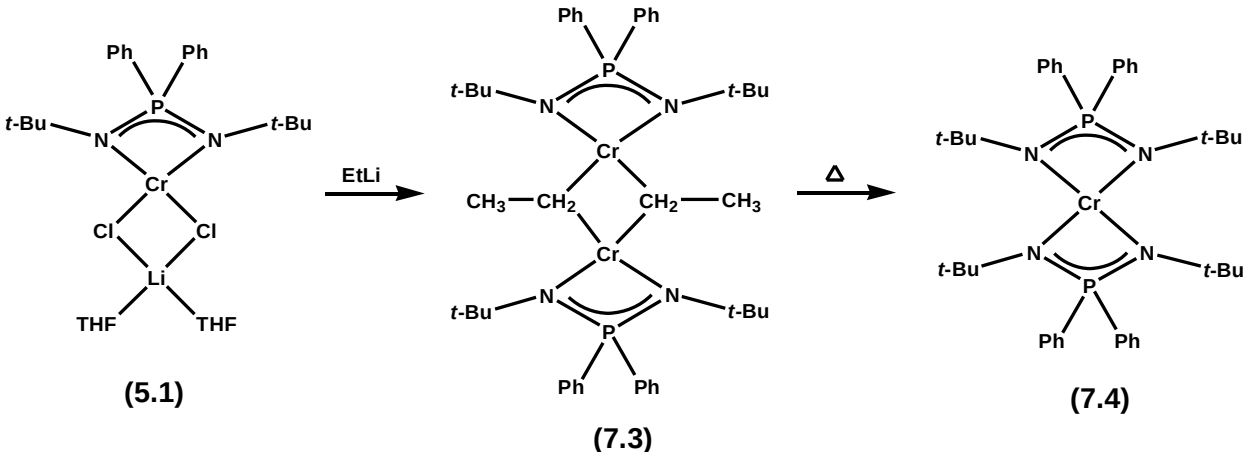
The data above indicates that the divalent **7.2** may in fact be used as a precursor to selective trimerization catalysts, but only in the presence of activators capable of triggering disproportionation and consequent reduction to the monovalent state. Activators such as MAO (or $AlMe_3$) do not possess such ability and gave only S-F distributions of oligomers, in turn indicating that neither reduction of the divalent state nor disproportionation to the tri- and monovalent states occurred.

Given the critical role of the aluminate species in determining the catalytic behaviour of NPN complexes, we have now oxidized the trivalent P atom to its pentavalent state. This modification was aimed at verifying the possible role of the ligand P atom in the retention of the aluminate residue. With such a modified ligand the role of the aluminate would be confined to only that of an alkylating agent. We were also hoping that an increased electron-withdrawing effect, as resulting from the higher oxidation state of phosphorus, could possibly better stabilize monovalent chromium intermediates via charge-transfer. In chapter five, we have described the the synthesis of the divalent [(*t*-Bu)NP(Ph)$_2$N(*t*-Bu)]Cr(μ^2-Cl)$_2$Li(THF)$_2$ (**5.1**) and reported the near to record catalytic activity of this species in producing polymer-free S-F distributions of oligomers upon activation with MAO. Assuming that the oxidation of the P atom would make the retention of aluminate residues more difficult, we have alkylated the divalent [(*t*-Bu)NP(Ph)$_2$N(*t*-Bu)]Cr(μ^2-Cl)$_2$Li(THF)$_2$ (**5.1**) complex with EtLi. In our hope ethyl groups bonded to chromium could make the metal more inclined towards elimination to the monovalent state.

The reaction proceeded smoothly at room temperature affording the corresponding dinuclear and paramagnetic {[(*t*-Bu)NP(Ph)$_2$N(*t*-Bu)]CrEt}$_2$ (**7.3**) (Scheme 7.4). The structure of **7.3**, is the result of a straightforward chlorine replacement by an ethyl group with additional dissociation of

LiCl. Besides the absence of Li, the dimeric arrangement with the two bridging ethyl groups is closely reminiscent of **7.2**.

Scheme 7.4



(5.1) **(7.3)** **(7.4)**

The dimeric structure of **7.3** (Figure 7.3) consists of two [(*t*-Bu)NP(Ph)$_2$N(*t*-Bu)]Cr units bridged by two ethyl groups [Cr(1)-C(41) = 2.143(2), Cr(2)-C(43) = 2.145(2)] forming a folded Cr_2Et_2 core. The coordination geometry around each metal center is distorted square planar [N(2)-Cr(1)-N(1) = 72.07(6), N(2)-Cr(1)-C(41) = 107.29(8), N(1)-Cr(1)-C(41) = 144.04(7), N(2)-Cr(1)-Cr(2) = 120.45(5), N(1)-Cr(1)-Cr(2) = 150.78(5), C(41)-Cr(1)-Cr(2) = 61.72(6)] and is defined by the two bridging carbon atoms and both of the ligand's nitrogen donor atoms [Cr(1)-N(2) = 2.0542(16), Cr(1)-N(1) = 2.0970(16)]. The deviation from the square-planarity is probably due to the long range steric interaction between the *t*-Bu groups of two units. This is in striking contrast to the perfect planarity of the metal centers in **7.2** as a possible result of the rigidity introduced by the two alkali cations. The absence of the bridging alkali cations in **7.3** is also likely to be responsible for the much longer intermetallic distance [Cr(1)-Cr(2) = 2.3282(5)] indicating a release of the compression of the dinuclear frame.

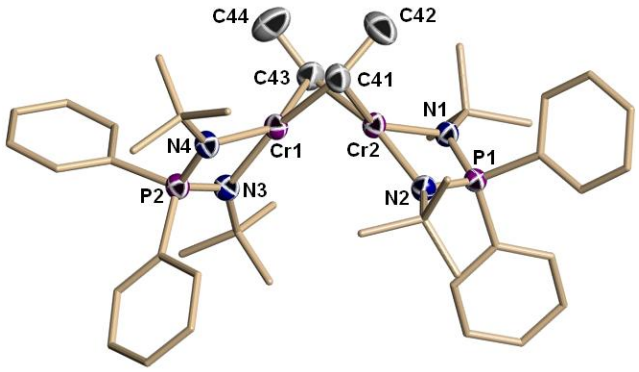


Figure 7.3. Drawing of **7.3**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Cr(1) - N(2) = 2.0542(16), Cr(1) - N(1) = 2.0970(16), Cr(1) - C(41) = 2.143(2), Cr(1) - Cr(2) = 2.3282(5), Cr(2) - C(43) = 2.145(2); N(2) - Cr(1) - N(1) = 72.07(6), N(2)-Cr(1)-C(41) = 107.29(8), N(1)-Cr(1)-C(41) = 144.04(7), N(2)-Cr(1)-Cr(2) = 120.45(5), N(1)-Cr(1)-Cr(2) = 150.78(5), C(41)-Cr(1)-Cr(2) = 61.72(6).

There is an interesting comparison that can be made between the structures of **7.2** and **7.3**. In complex **7.2**, the ligand frame is dianionic due to the alkylation of the P atoms. In turn, this requires the Cr_2R_2 core to retain two lithium counterions between the two ligands, thus providing additional bridging interactions. In complex **7.3,** the ligand bears instead the formal charge of (-1) for which there is no necessity for retention of the alkali cation. This has a profound effect on the Cr-Cr distance, being remarkably elongated comparatively to **7.2**, as well as on the magnetism of the complex (paramagnetic versus almost diamagnetic). In our opinion, this provides once again a good illustration of the intriguing and yet elusive nature of the Cr-Cr interaction.[9,10,11] In the present case, the Cr-Cr distance is affected by the ligand's formal charge and the presence of the alkali cations. Only these two factors appear to be the responsible for the occurrence of the short Cr-Cr contact of **7.2** and consequent diamagnetism.

The presence of the two Et groups in the dinuclear structure of **7.3**, the absence of alkali cations as well as the mono-anionic nature of the ligand, altogether make this species better

suited to form a monovalent, catalytically-active intermediate, comparatively to **7.2**. Upon having observed that solutions of **7.3** have a tendency to slowly decompose at room temperature, a deliberate attempt to flash-thermolyze the complex was carried out by heating its solution to 110 ºC (Scheme 7.4). As anticipated, the thermolysis afforded a new divalent chromium complex, where one of the metal centers has basically extracted the other's ligand forming the square-planar and paramagnetic [(*t*-Bu)NP(Ph)$_2$N(*t*-Bu)]$_2$Cr (**7.4**) along with some colloidal chromium metal.

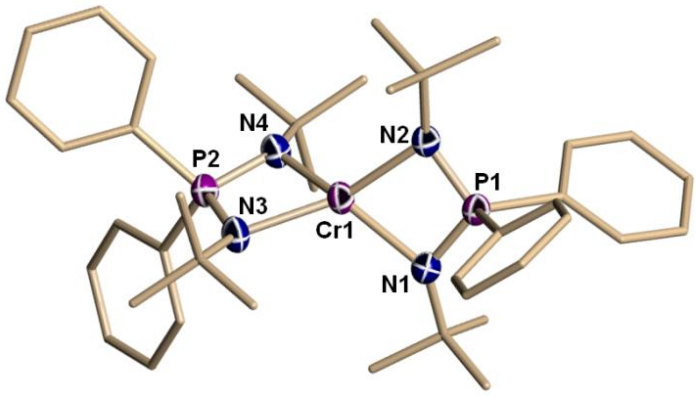


Figure 7.4. Drawing of **7.4**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [^{o}]: Cr(1)-N(1) = 2.100(3), Cr(1)-N(4) = 2.104(3), Cr(1)-N(3) = 2.112(3), Cr(1)-N(2) = 2.111(3). N(1)-Cr(1)-N(4) = 144.06(13), N(1)-Cr(1)-N(3) = 119.53(14), N(4)-Cr(1)-N(3) = 71.47(13), N(1)-Cr(1)-N(2) = 71.30(12), N(4)-Cr(1)-N(2) = 120.69(13), N(3)-Cr(1)-N(2) = 145.59(13).

The crystal structure of **7.4** (Figure 7.4) shows the symmetry-generated, square-planar chromium atom [N(1)-Cr(1)-N(4) = 144.06(13), N(1)-Cr(1)-N(3) = 119.53(14), N(4)-Cr(1)-N(3) = 71.47(13), N(1)-Cr(1)-N(2) = 71.30(12), N(4)-Cr(1)-N(2) = 120.69(13), N(3)-Cr(1)-N(2) = 145.59(13)] surrounded by the four nitrogen donor atoms of the two ligands [Cr(1)-N(1) = 2.100(3), Cr(1)-N(4) = 2.104(3), Cr(1)-N(3) = 2.112(3), Cr(1)-N(2) = 2.111(3)].

Table 7.3. Ethylene oligomerization results:

Catalyst	Al:Cr	Co Catalyst	Alkenes (mL)	Temp °C	PE (g)	Activity (g/mmolCr/h)	C_6 (mol%)	C_8 (mol%)	C_{10}-C_{16} (mol%)
7.3 [a]	-	-	4	100	0	93	99	traces	traces
7.3[a,c]	1000	MAO	106	100	0	4,947	37	26	37
7.3 [b]	-	-	8	60	0.3	197	39	32	29
7.4 [a]	1000	MAO	9	60	0	210	24	22	54

Conditions: loading 30 μmol of complex, 35 bar of ethylene, reaction time 60 min; [a)] 100 mL of toluene, [b)] 100 mL of methylcyclohexane [c)] catalyst loading 15 μmol.

The formation of **7.4**, as a result of the thermolysis, is rather indicative of the inclination towards disproportionative decomposition pathways. The reaction may simply be envisioned with the initial elimination of ethylene/ethane/butane mixture (observed when the thermolysis was carried out in sealed and centrifuged NMR tubes) and intermediate formation of a monovalent intermediate "[(*t*-Bu)NP(Ph)$_2$N(*t*-Bu)]Cr", most likely dinuclear. This species may rapidly regain stability via ligand scrambling, and consequent oxidation of one of the two centers to the divalent state. The second metal instead disproportionated to the zero-valent state and, being deprived of the ligand, has no option but forming colloidal metallic chromium. In agreement with this proposal, complex **7.3** indeed acts as a self-activating single-component trimerization catalyst (Table 7.2). This is in further striking contrast to the behaviour of **7.2**, which required activation by at least stoichiometric amount of $EtAlCl_2$. In what seems to be now a distinctive feature of the (NPN)Cr catalytic systems, the solvent has a marked effect on the catalytic behaviour. An identical single component experiment carried out in methylcyclohexane as solvent, doubled the activity but replaced the highly selective formation of 1-hexene with a S-F distribution. Activation with MAO in both solvents gave the usual non-selective oligomerization but with surprisingly high activity. Complex **7.4** is instead a mediocre non-

selective catalyst as expected from the fact that one of the two ligands cannot easily be extracted by the activator.

7.5 Conclusions

In conclusion, we have herein reported the synthesis and characterization of two closely related divalent organochromium complexes. The only differences are: 1) the oxidation state of the P atom not directly involved in bonding interactions, and 2) the ligand's anionic charge (mono- versus divalent). These differences affect not only the Cr-Cr interaction but also the catalytic behaviour. In turn, this speaks for the different accessibility provided by the two ligands to the selective monovalent chromium. The comparison between the two species is not as rigorous as may be desired given the different nature of the alkyl functions bonded to chromium in both complexes (Me *versus* Et). Unfortunately, any attempt to prepare and characterize the ethyl analogue of **7.2** failed. Nonetheless, the fact that **7.2** may be activated into a selective trimerization catalyst with only two equivalents of $EtAlCl_2$ suggests that both ligands can indeed sufficiently stabilize a monovalent chromium intermediate during the catalytic cycle. The main difference between the behaviour of the two species relies mainly on the apparently easier pathway provided by the monoanionic ligand.

In the next chapter, and as a follow up of previous work from our lab, we have modified the Phillips pyrrolato-system to prevent the coordination of alkyl aluminum residues. This was in an attempt to probe the necessity for the alkylaluminum residue to be present in the molecular frame.

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Chapter Eight

Publication:

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Design and Synthesis of New Pyrrole-Chromium Selective Trimerization Catalysts. Isolation of the first Chromium Ethylidene as a Potent Catalyst for Selective Ethylene Trimerization*

8.1 Introduction

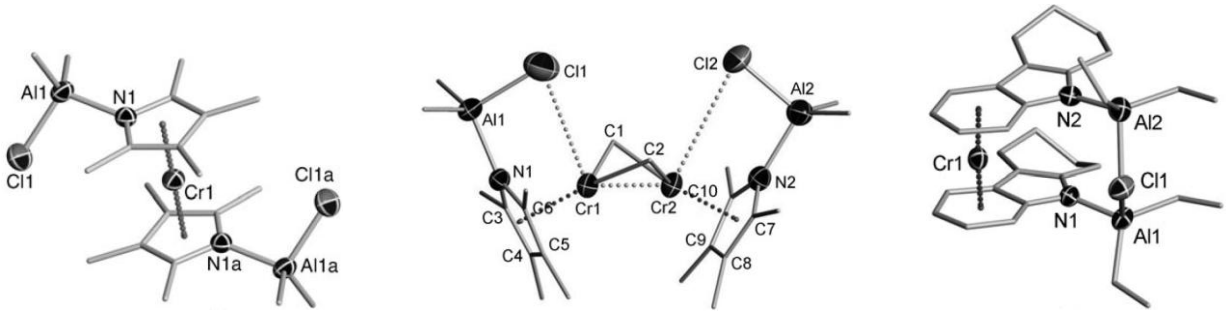
The factors transforming a statistical ethylene oligomerization process into selective tri- or tetramerization are intensively scrutinized in both industrial and academic research.[1] Their identification also poses a genuine intellectual challenge since the design of a selective catalytic system requires a complete understanding of the mechanistic features. The so-called ring-expansion mechanism for selective trimerization[2,3] is today unchallenged to the point that it is a paradigm among workers in the field.

Central to the understanding of the mechanism and to tailoring new catalysts is the question of the metal oxidation state.[1a] In the case of the chromium systems which cover the majority of these catalysts, the +I state has been conclusively linked to selective trimerization by both synthetic and spectroscopic work.[4-6] One of the characteristics of chromium, however, is the possibility of readily interconverting between +I, +II and +III states as a part of a redox dynamism.[7] Since each one of these oxidation states has its own distinctive catalytic behavior,[6a,b]

stabilizing the desired one and slowing at the same time the dynamism is central to obtain selective behavior.

Mechanistic and synthetic work from our lab on the commercially used pyrrole-based Phillips trimerization system[6a,b] has elucidated the structures of single-component self-activating precatalysts (Scheme 8.1). All these species consist of the pyrrolide ring being either σ- or π-bonded to the metal center and of an aluminate residue invariably σ-coordinated to the pyrrolide nitrogen donor atom. There are two main features in this particular structural motif. Firstly the coordination of the aluminate introduces a zwitterionic type of electronic structure that in turn provides partial cationic character to the chromium center. Secondly, the alkyl group migrates from the aluminate to chromium during the dissociation of one of the pyrrolide rings, in the form of an aluminum pyrrolide complex. The specific nature of the aluminum residue seems to play a very important role in the activation of the catalytic center for this system.[6a,b]

Scheme 8.1



However, the importance of its coordination to the pyrrolide N atom remains unclear. Is it the zwitterionic structure introduced by the coordination of Al? Or is it the alkyl transfer that makes the metal prone to further reduction to the +I state? In an attempt to address these and other questions important for tailoring the design of new catalysts, we have now probed the

nature of the pyrrolide anion. The anion chosen bears two bulky *t*-butyl groups in the two α-positions, which could possibly prevent coordination of aluminum while maintaining an enhanced tendency for η^5-coordination.[8] Elimination of the aluminate coordination to pyrrole will simplify the catalyst and make easier to understand the mechanistic pathway for the selectivity. In this chapter, synthesis and testing of these new pyrrole-based chromium catalysts will be discussed in detail including a new suggested mechanism for the selective ethylene trimerization.

8.2 Experimental Part

All reactions were carried out under a dry nitrogen atmosphere on a Schlenk line or in a purified nitrogen-filled drybox. Solvents were dried using an aluminum oxide solvent purification system except for anhydrous DMF which was purchased from Sigma-Aldrich and used as received. Pinacolone, butyl lithium (2.5M in hexane) and ethyl lithium (0.5M in benzene/cyclohexane) were purchased from Sigma-Aldrich and used as received. KH was purchased from Strem Chemicals, washed with hexane and dried prior to use. Ammonium acetate was purchased from Alfa Aesar and used as received. $CrCl_3(THF)_3$ was prepared by continuous extraction of $CrCl_3$ with boiling THF. Triethylaluminum was purchased from Strem Chemicals and used as received. Ethylene was purchased from BOC Gases (polymer grade 3.0) and used as received. GC-MS analysis of the ligands and the oligomers was obtained with a Hewlett–Packard HP 5973 gas chromatograph using an Agilent DB1 column. Elemental analyses were carried out with a Perkin-Elmer 2400 CHN analyzer. Infrared spectra were recorded on ABB Bomem FT-IR instrument from Nujol mulls prepared in a drybox. Samples for magnetic susceptibility were weighed inside a drybox equipped with an analytical balance and sealed into calibrated tubes and measurements were carried out with a Johnson Matthey Magnetic

Susceptibility balance at room temperature. Data for the X-ray crystal structure determinations (Table 8.1) were obtained with a Bruker diffractometer equipped with a Smart CCD area detector and a Bruker Kappa APEXII CCD diffractometer. NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer; all chemical shifts have been quoted relative to deuterated solvent signals, δ in ppm. All the oligomerization reactions were performed in a Pall high pressure 300 ml reactor. The preparation of 2,5-di-(*t*-Bu)-1H-pyrrole was modified from the literature.[9]

Preparation of 2,5-di-(*t*-Bu)-1H-pyrrole

3-methylbutan-2-one (20.0 g, 200.0 mmol) was added dropwise under N_2 with stirring to a suspension of KH (10.0 g, 250.0 mmol) in dry THF (290 ml) cooled at 0 °C. The resulting pale yellow suspension was stirred at 0 °C for 1h and then cooled to -78 °C. A solution of anhydrous $CuC1_2$ (29.6 g, 220 mmol) in DMF **(**240 ml) cooled at -35 °C was then added by cannula and the resulting brown solution stirred for 2 h while the temperature was allowed to rise to room temperature. Stirring was then continued for 3 h at 60 °C and the resulting brown solution allowed to cool at room temperature overnight while stirring. A mixture of HCl (1M, 300 mL) and diethyl ether (300 ml) was added at 0 °C to quench the reaction and the mixture was stirred for 1 h. The two phases were separated and the aqueous layer was extracted with diethyl ether (2 x 180 mL). The combined organic layers were dried over Na_2SO_4 and evaporated at reduced pressure to give a pale yellow oil (2,2,7,7-tetramethyloctane-3,6-dione, 18.8 g) which was sufficiently pure (^{1}H-NMR and GC-MS analysis) to be used for the next step.

The pale yellow oil (18.8 g, 94.9 mmol) was dissolved in acetic acid (35 ml) and CH_3COONH_4 (25.6 g, 332 mmol) was added to the solution. The reaction mixture was refluxed at 100 °C for 4 h then cooled at 0 °C and quenched by addition of a saturated aqueous solution of

K_2CO_3 (160 ml, slowly!) and diethyl ether (180 mL). The organic phase was separated and the aqueous phase was extracted with diethyl ether (2 x 130 mL). The combined organic layers were washed with H_2O (120 ml), brine (100 ml), dried over Na_2SO_4 and evaporated at reduced pressure to give a dark red oil which in turn was distilled under vacuum to give pure 2,5-di-tert-butyl-1H-pyrrole as colorless oil (16.9 g, overall yield 94%).

Complex 8.1

BuLi (2.0 mmol, 800 µL) was added dropwise to a solution of 2,5-di-tert-butyl-1H-pyrrole (0.359 g, 2.0 mmol) in THF (8 ml) and the mixture stirred overnight. After the addition of $CrCl_3(THF)_3$ (0.750 g, 2.0 mmol) the reaction mixture was stirred for 3 h. The yellow suspension turned violet/blue. The suspension was evaporated to dryness and diethyl ether (4 ml) was added to the residue. A clear violet/blue solution was separated through centrifugation from the insoluble materials. Diethyl ether was evaporated to 1/3 of the original volume and the resulting solution was stored at -30 °C. Single crystals of **8.1** suitable for X-ray crystallography were obtained overnight. The mother liquor was decanted and the crystals were washed with cold hexane (4 x 1 ml) and dried in vacuum (0.373 g, 1.0 mmol, yield 50%). Calculated (Found) for $C_{16}H_{28}Cl_2CrNO$: C 51.48 (51.58), H 7.56 (7.71), N 3.75 (3.78). μ_{eff} = 3.89 μ_B.

Complex 8.2

BuLi (2.0 mmol, 800 µL) was added dropwise to a solution of 2,5-di-tert-butyl-1H-pyrrole (0. 359 g, 2.0 mmol) in hexane (10 ml) and the mixture stirred overnight. $CrCl_3(THF)_3$ (0.750 g, 2.0 mmol) was added and the reaction mixture was stirred for 2 h. The yellow suspension turned violet/blue. Neat triethylaluminum (0.274 g, 2.4 mmol) was added dropwise to the suspension previously cooled at -20 °C and the mixture stirred at room temperature for 2 h. The violet/blue suspension turned rapidly deep red. The clear red solution was separated through centrifugation

from a small amount of insoluble material and its volume reduced by evaporation to 1/4 of the original value. The resulting thick solution was stored at -30 °C; single crystals suitable for X-ray crystallography were obtained overnight. The mother liquor was decanted and the crystals of **8.2** were washed with cold hexane (4 x 1 ml) and dried under vacuum (0.260 g, 0.44 mmol, yield 44%). Calculated (Found) for $C_{28}H_{50}Cl_2Cr_2N_2$: C 57.04 (57.40), H 8.55 (8.64), N 4.75 (4.80). μ_{eff} = 3.37 μ_B.

Complex 8.3

BuLi (1.0 mmol, 400 µL) was added dropwise to a solution of 2,5-di-tert-butyl-1H-pyrrole (0.179 g, 1.0 mmol) in toluene (5 ml) and the mixture stirred overnight. $CrCl_3(THF)_3$ (0.375 g, 1.0 mmol) was added and the reaction mixture was stirred for 2 h. The yellow suspension turned violet/blue. Neat triethylaluminum (0.057 g, 0.5 mmol) was added dropwise to the suspension at room temperature. and the resulting mixture stirred at 60 °C for 18h. The violet/blue suspension turned immediately deep red and then slowly blue. The clear blue solution was separated through centrifugation from insoluble materials and then evaporated to dryness. The resulting blue oily residue was dissolved in diethyl ether (2 ml) and the solution was stored at -30 °C; single crystals suitable for X-ray crystallography were obtained upon overnight standing at low temperature. The mother liquor was decanted and crystals of **8.3** were washed with cold hexane (4 x 1 ml) (0.112 g, 0.2 mmol, yield 40%). Calculated (Found) for $C_{26}H_{44}Cl_2Cr_2N_2$: C 55.81 (56.14), H 7.93 (7.98), N 5.01 (5.04). μ_{eff} = 3.20 μ_B. ESI-MS (assignment, rel. intensity): m/z: 672.602 ($[M+H+CH_3CN+THF]^+$, 31), 541.101 ($[M-H-t\text{Bu-THF}]^+$, 4), 469.040 ($[M-H-2t\text{Bu-}CH_3\text{-THF}]^+$, 13), 341.252 ($[M\text{-Pyrrole-Cr-}CHCH_3\text{-THF}]^+$, 10), 329.251 ($[M\text{-H-Pyrrole-Cr-2Cl-}CH_3CN]^+$, 100).

Complex 8.4

Complex **8.2** (0.590 g, 1.0 mmol) was dissolved in toluene (5 mL). After heating the solution at 60 °C, triethylalumium (0.228 g, 2.0 mmol) was added and the mixture stirred at room temperature for 2 h. The resulting green solution was separated through centrifugation from insoluble materials and then evaporated to dryness. The green residue was dissolved in THF (3 mL) followed by addition of diethyl ether (3 mL). The solution was stored at -30 °C upon which, single blue crystals of **8.4** suitable for X-ray crystallography were obtained overnight. The mother liquor was decanted and the crystals were washed with cold hexane (4 x 1 ml) (0.331 g, 0.49 mmol, yield 49%). Calculated (Found) for $C_{32}H_{56}Cl_2Cr_2N_2O_2$: C 56.88 (56.71), H 8.35 (8.26), N 4.15 (4.11). μ_{eff} = 4.95 μ_B.

8.3 X-ray Data

Table 8.1. Crystal Data and Structure Analysis Results of Complexes **8.1**-**8.4**.

	8.1	**8.2**	**8.3**	**8.4**
formula	C16 H28 Cl2 Cr N O	C28 H50 Cl2 Cr2 N2	C13 H22 Cl Cr N	C32 H56 Cl2 Cr2 N2
Mw	373.29	589.60	279.77	675.69
space group	Orthorhombic, Pbca	Tetragonal, I4(1)cd	Monoclinic, C2/c	Rhombohedral, R-3
***a* (Å)**	11.9665(12)	13.7917(10)	23.2095(9)	23.6447(2)
***b* (Å)**	10.2463(10)	13.7917(10)	6.8348(3)	23.6447(2)
***c* (Å)**	30.029(3)	33.352(5)	18.2996(6)	17.6741(3)
***α*, (deg)**	90	90	90	90
***β*, (deg)**	90	90	100.082(2)	90
***γ*, (deg)**	90	90	90	120
***V* (Å^3)**	3681.9(7)	6343.9(11)	2858.08(19)	8557.27(18)
Z	8	8	8	9
radiation	0.71073	0.71073	0.71073	0.71073
***T* (K)**	200(2)	200(2)	200(2)	200(2)
D_{calcd} (g cm$^-$	1.347	1.235	1.300	1.180
μ_{calcd} (mm^{-1})	0.910	0.871	0.963	0.739
***F*$_{000}$**	1576	2512	1184	3240
***R*, *Rw*^{2a}**	0.0428, 0.1049	0.0512, 0.1220	0.0683, 0.1648	0.0484, 0.1354
GoF	1.065	1.060	1.054	1.035

[a] $R = \sum|Fo| - |Fc|/\sum|Fo|$. $Rw = [\sum(|Fo| - |Fc|)2/\sum wFo2]^{1/2}$

8.4 Result and Discussions

Deprotonation of 2,5-di-*t*-butylpyrrole followed by reaction with $CrCl_3(THF)_3$, afforded [η^5-(*t*-Bu)$_2$C$_4$H$_2$N]CrCl$_2$(THF) (**8.1**) isolated as dark violet-blue crystals. The pseudo-tetrahedral piano-stool arrangement of **8.1** was elucidated by an X-ray crystal structure (Figure 8.1). When activated with $AlEt_3$ (5-15 equivalents), complex **8.1** is a highly active and selective trimerization catalyst (Table 8.2). The reaction time as well as the temperature and quantity of alkyl aluminum activator affected both yield and purity of 1-hexene with respect to the side-product 2-hexene.

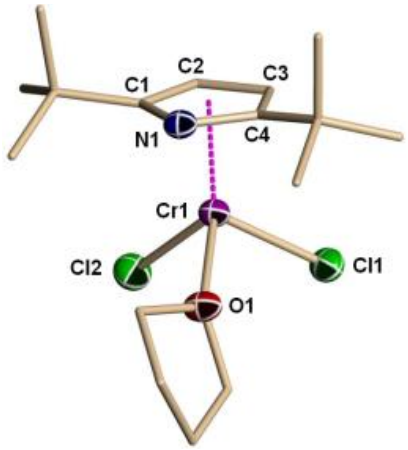


Figure 8.1. Partial thermal ellipsoid plot of **8.1** with ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (°): Cr(1)-O(1) = 2.045(2), Cr(1)-N(1) = 2.199(3), Cr(1)-C(4) = 2.213(3), Cr(1)-C(1) = 2.249(3), Cr(1)-C(3) = 2.257(3), Cr(1)-Cl(2) = 2.2847(10), Cr(1)-Cl(1) = 2.2873(10), Cr(1)-C(2) = 2.286(4), N(1)-C(1) = 1.377(4), N(1)-C(4) = 1.387(4), C(1)-C(2) = 1.434(5), C(2)-C(3) = 1.401(5), C(3)-C(4) = 1.414(5), O(1)-Cr(1)-N(1) = 92.58(11), O(1)-Cr(1)-C(4) = 103.32(11), N(1)-Cr(1)-C(4) = 36.65(11), O(1)-Cr(1)-C(1) = 117.44(11), N(1)-Cr(1)-C(1) = 36.05(11), C(4)-Cr(1)-C(1) = 59.90(13), O(1)-Cr(1)-Cl(2) = 91.92(8), N(1)-Cr(1)-Cl(2) = 125.34(8), Cl(2)-Cr(1)-Cl(1) = 96.51(4), O(1)-Cr(1)-Cl(1) = 92.00(7).

In an attempt to isolate the catalytically active species, we have reacted **8.1** with a stoichiometric amount of $AlEt_3$. The violet-blue solution turned immediately dark-red affording deep-red crystals of the dinuclear {[η^5-(*t*-Bu)$_2$C$_4$H$_2$N]CrEt}$_2$(μ-Cl)$_2$ (**8.2**) (Scheme 8.1). The

dinuclear nature and connectivity of this rare chromium(III)-ethyl derivative were clarified by an X-ray crystal structure (Figure 8.2).

Table 8.2. Oligomerization Results

Entry #	Catalyst	$AlEt_3$ (equiv)	Temp (°C)	Alkenes (mL)	PE (g)	C_6 (mol%)	1-C_6 (mol%)	Oligomerization Activity (g/mmoleCr/h)
1	8.1[a]	10	85	31	0	99	84	700
4	8.2[b]	0	120	2	0.3	99	98	55
5	8.2[c]	5	115	32	0.6	99	89	1,486
6	8.2 [b]	10	85	35	0	99	95	791
7	8.2 [b]	10	100	39	0	99	93	881
8	8.2 [b]	10	110	40	0.4	99	89	917
9	8.2 [b]	10	150	4	0	95	73	90
10	8.2 [b]	15	85	25	0	99	91	565
11	8.2 [b]	50	85	15	0	99	92	339
12	8.3 [b]	0	120	0	0	0	0	0
13	8.3[c]	5	115	71	1.3	99	91	3,296
14	8.4[b]	10	0	0	0	0	0	0

Conditions: Methylcyclohexane 100 mL, 30 min reaction time, 35 bar ,[a)] 60 µmol, [b)] 30 µmol. [c)] 15 µmol.

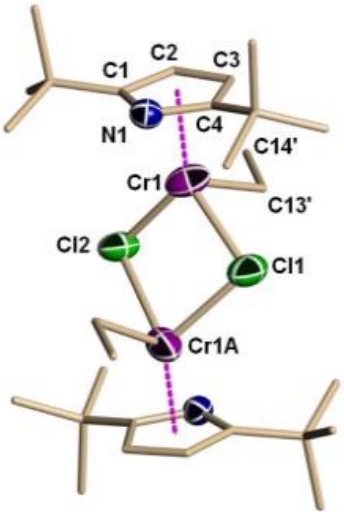
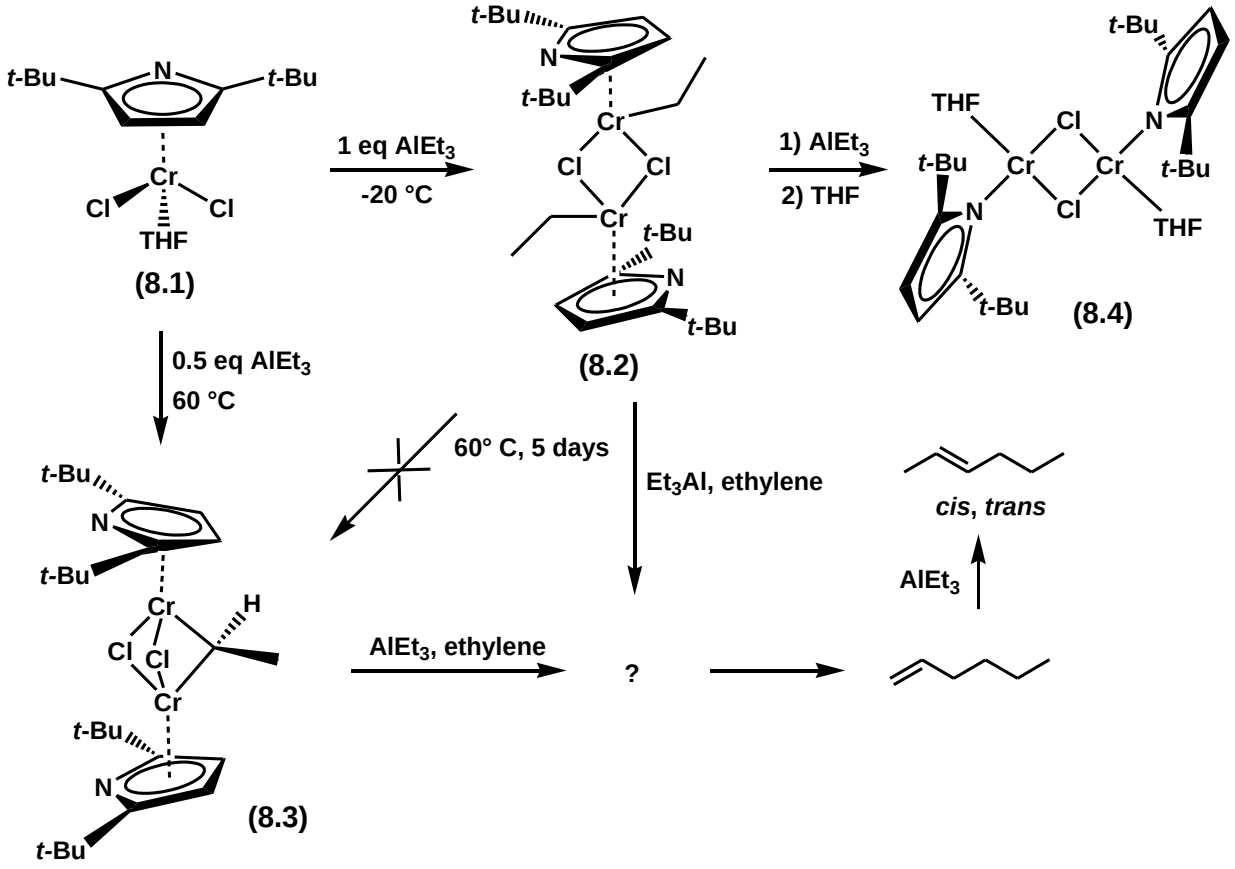


Figure 8.2. Partial thermal ellipsoid plot of **8.2** with ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (°): Cr(1)-Cl(2) = 2.188(3), Cr(1)-C(13') = 2.202(15), Cr(1)-C(3) = 2.226(6), Cr(1)-C(2) = 2.225(5), Cr(1)-C(1) = 2.281(5), Cr(1)-C(4) = 2.289(5), Cr(1)-N(1) = 2.312(3), Cr(1)-Cl(1) = 2.3439(19), N(1)-C(4) = 1.382(7), N(1)-C(1) = 1.364(7), C(1)-C(2) = 1.418(8), C(2)-C(3) = 1.374(8), C(3)-C(4) = 1.405(7), C(13')-C(14') = 1.496(14), Cr(1)-Cl(1)-Cr(1A) = 89.39(10), Cl(2)-Cr(1)-Cl(1) = 93.76(7), C(13')-Cr(1)-Cl(1) = 99.6(4).

The structure consists of two edge-sharing tetrahedral with two identical piano-stool units connected by two bridging chlorides. The low magnetic moment is to be expected for the planar Cr_2Cl_2 core with an intermetallic distance shorter than the sum of the Van der Waals radii. The complex is reasonably thermally robust, but turned slowly brown upon heating for about 30 minutes in toluene.

Scheme 8.1



During the preparation of **8.2**, if only 0.5 equivalent of $AlEt_3$ was added dropwise to solutions of **8.1** and the reaction was slowly carried out at room temperature, a distinctively different blue color developed thus indicating the formation of a different species. The color did not appreciably change upon heating overnight. A new paramagnetic complex, formulated as

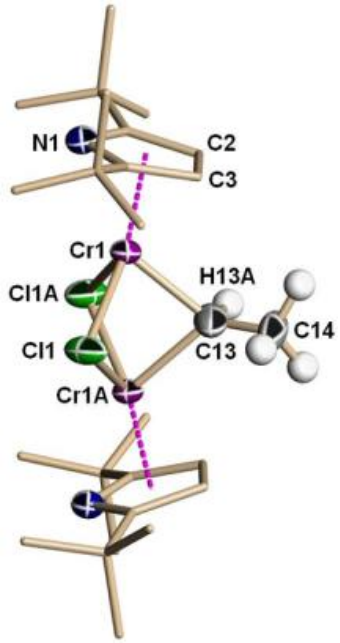


Figure 8.3. Partial thermal ellipsoid plot of **8.3** with ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (°): Cr(1)-C(13) = 2.048(13), Cr(1)-C(3) = 2.239(2), Cr(1)-C(2) = 2.238(2), Cr(1)-C(1) = 2.256(2), Cr(1)-C(4) = 2.260(2), Cr(1)-N(1) = 2.2791(18), Cr(1)-Cl(1) = 2.359(3), Cr(1)-Cl(1A) = 2.384(3), Cr(1)-Cr(1A) = 2.6739(6), N(1)-C(1) = 1.377(3), N(1)-C(4) = 1.377(3), C(1)-C(2) = 1.417(4), C(2)-C(3) = 1.423(4), C(3)-C(4) = 1.415(4), C(13)-C(14) = 1.505(9), Cl(1)-Cr(1)-Cl(1A) = 99.58(8), Cr(1)-Cl(1)-Cr(1A) = 68.63(8), Cr(1)-C(13)-Cr(1A) = 81.7(2).

{[η^5-(*t*-Bu)$_2$C$_4$H$_2$N]Cr}$_2$(μ-Cl)$_2$(μ-CHCH$_3$) (**8.3**), was isolated as deep blue crystals from the aforementioned blue solutions. The crystal structure revealed a dimeric chromium complex with a face sharing bi-tetrahedral arrangement (Figure 8.3). The two distorted tetrahedra are bridged by two chlorine atoms and one carbon atom of a C_2 residue. The C-C distance of this particular unit [C(13)-C(14) = 1.505(9)] is in the range of a C-C single bond. Chemical degradation experiments carried out with a D_2O/H_2O mixture in C_6D_6 followed by centrifugation and NMR characterization of the solution phase helped to partially simplify the spectrum. The ^{2}H-NMR spectrum acquired with ^{1}H decoupling showed two peaks at 0.75 and 0.73 ppm indicating the presence of the two isotopomers (Figure 8.4). The ^{13}C-NMR resonance unequivocally showed the presence of a mixture of the isotopomers CD_2HCH_3, CDH_2CH_3 and CH_3CH_3 (Figure 8.5).

The ^{1}H-NMR showed complete absence of olefinic residues (Figure 8.6). The resonances of a mixture of (partly deuterated) ethanes were present at 0.778 ppm as a complex signal resulting from both ^{1}H-^{1}H and ^{1}H-^{2}H coupling (Figure 8.7). Deuterium decoupling could not be properly located due to dilution and line broadening. However, the ^{1}H^{13}C-HMQC resonance at 0.778 ppm of the proton section clearly showed coupling with the position at 6.78 ppm of the ^{13}C-NMR (Figure 8.8). The ^{13}C resonance was not clearly visible due to low intensity and very possibly line broadening. These findings compare reasonably well with literature data.[10] Finally, ESI-MS analysis provided the expected value for the molecular ion of the proposed formulation of **8.3**.

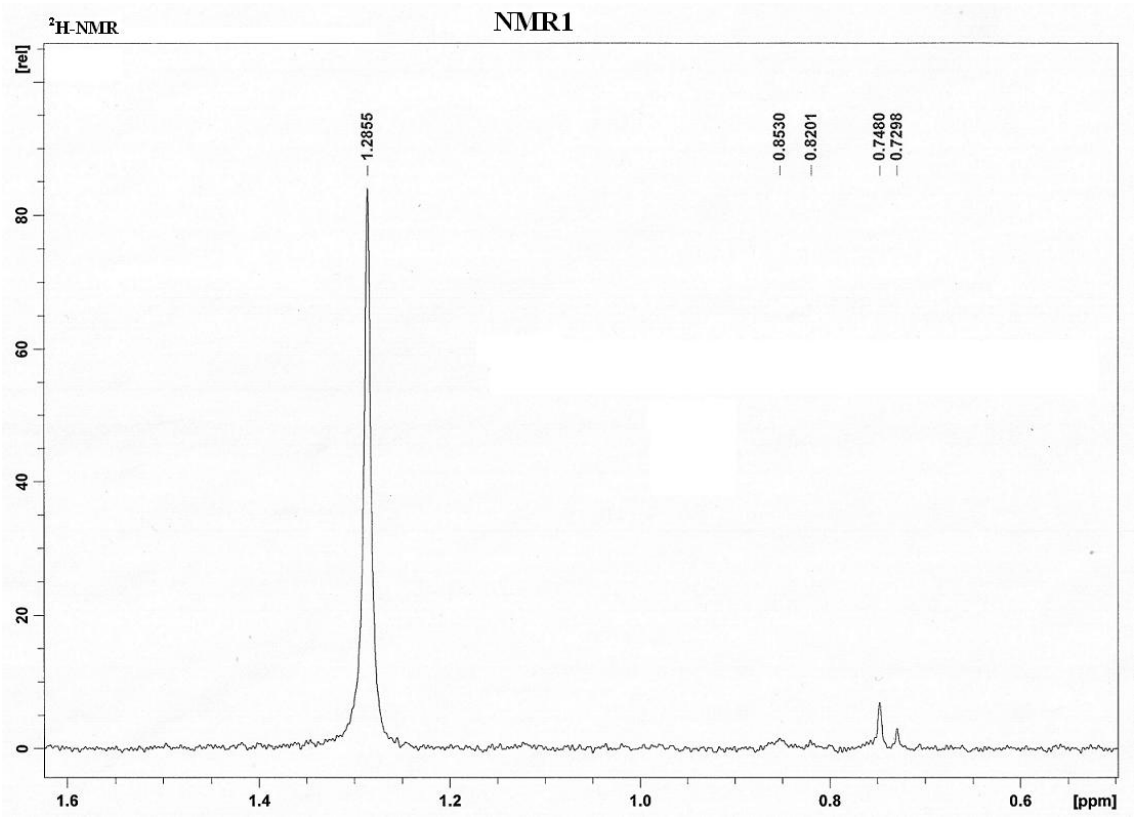


Figure 8.4. ^{2}H-NMR spectrum of complex **8.3**.

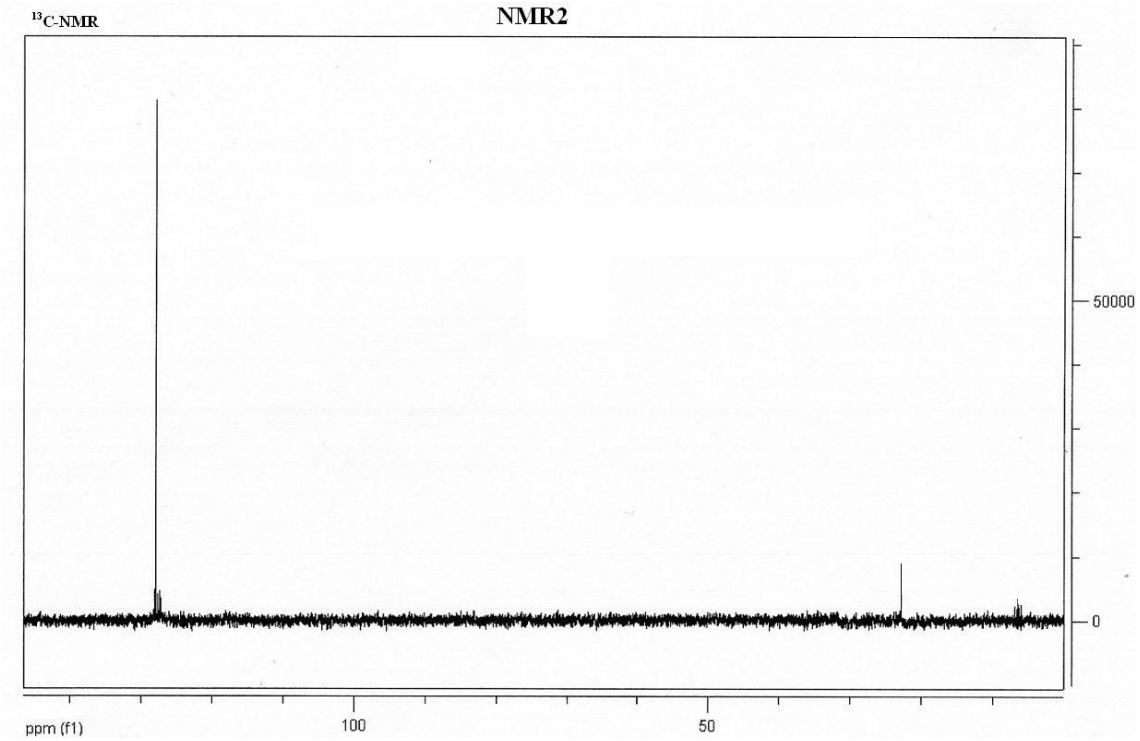


Figure 8.5. ^{13}C-NMR spectrum of complex **8.3**.

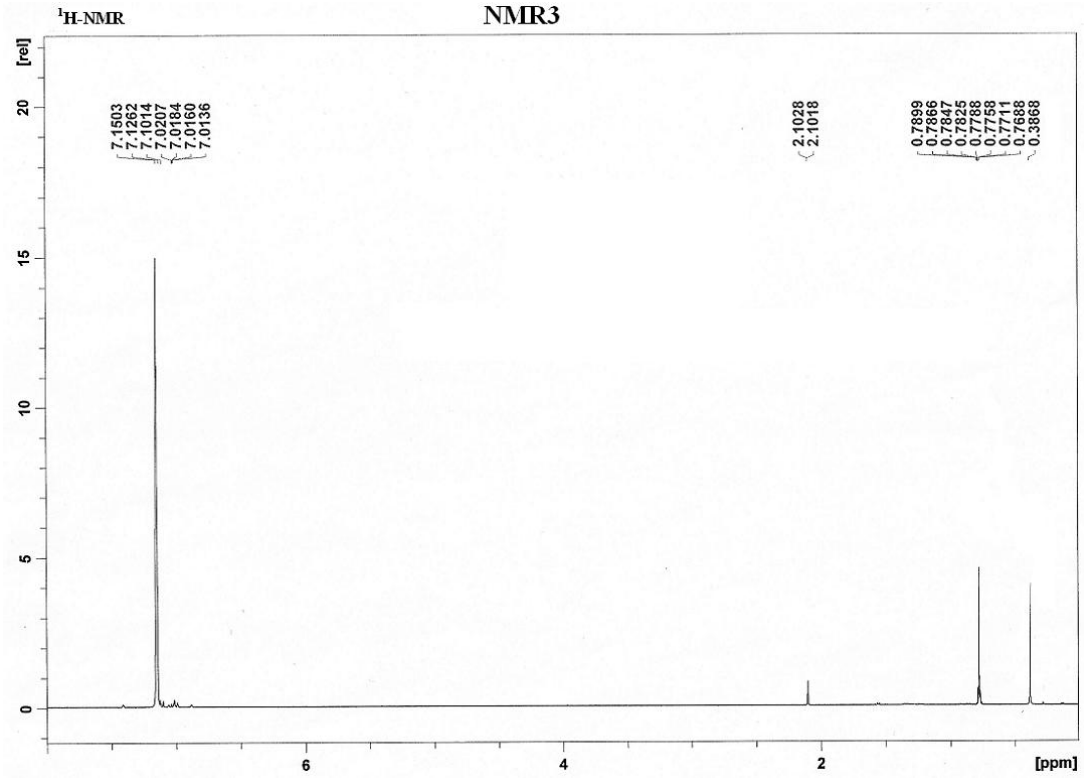


Figure 8.6. ^{1}H-NMR spectrum of complex **8.3**.

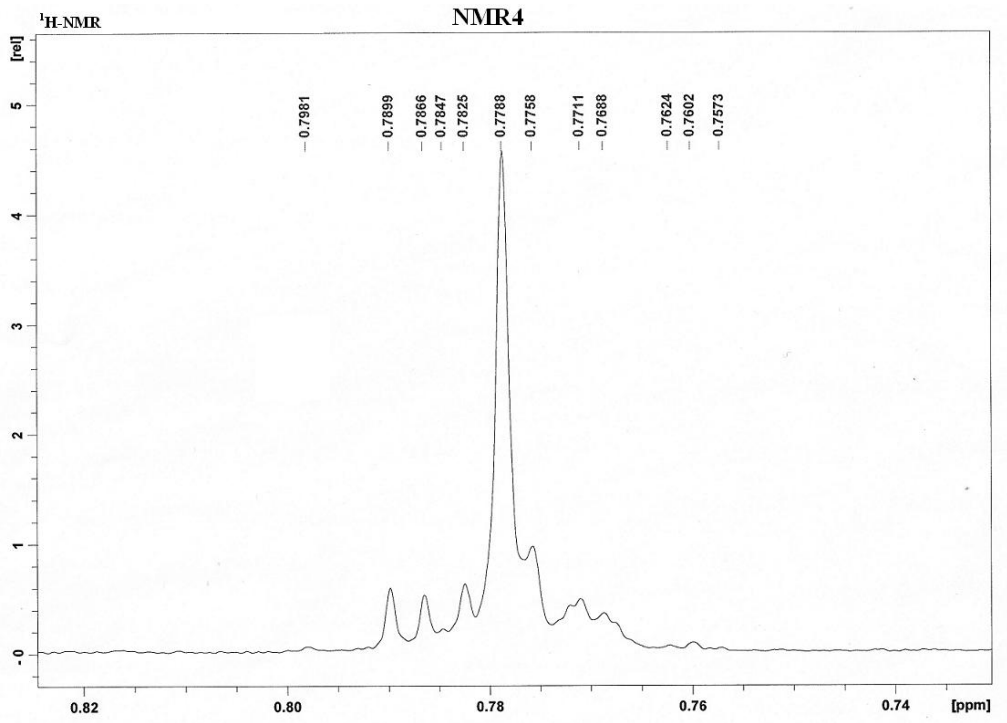


Figure 8.7. ^{1}H-NMR spectrum of complex **8.3**.

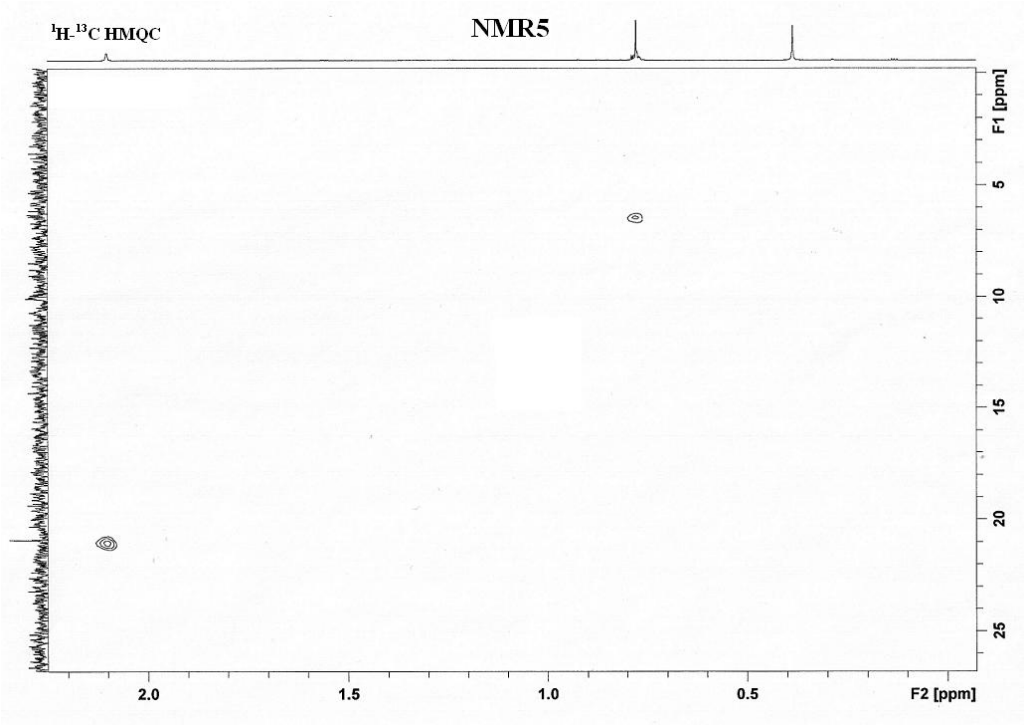
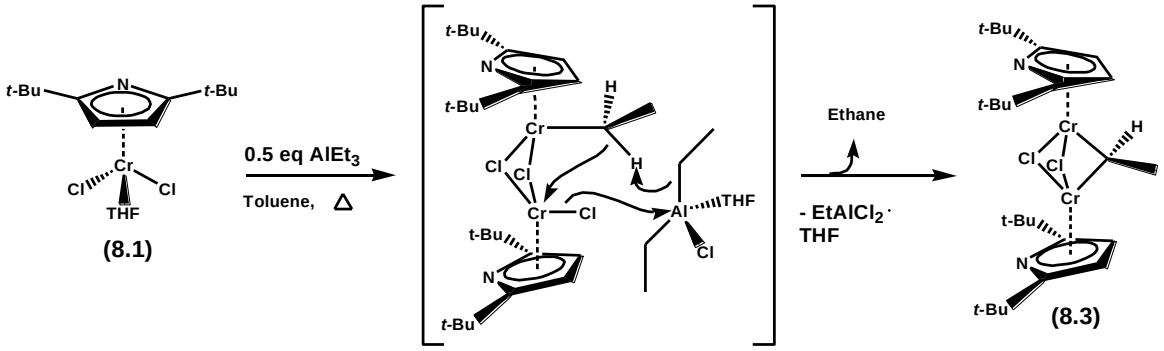


Figure 8.8. $^{1}H^{13}C$-HMQC spectrum of complex **8.3**.

The formation of **8.3** is puzzling. In principle, the most direct way to form the bridging ethylidene could be a simple C-H σ-bond metathesis from the two ethyl groups present in **8.2**. This does not seem to be the case though, since thermolysis of **8.2** led to brown decomposition products with no evidence for the formation of the blue **8.3**. Complex **8.3** could only be formed from **8.1** under the conditions previously discussed (Scheme 8.1). Therefore, its formation seems to be a reaction pathway alternative and not subsequent to the formation of **8.2**, being triggered at higher temperature by a lower Al:Cr ratio.

Scheme 8.2



The sequence depicted in Scheme 8.2 is a reasonable speculation, with one keeping in mind the lower alkylating power of Et_2AlCl (resulting from the first alkylation) and its stronger ionic character with respect to $AlEt_3$. Attempts to rationally form **8.3** by treating solutions of analytically pure **8.2** with either $AlEt_3$ or Et_2AlCl failed. Upon a second alkylation, the dimer cleaves and further reductive elimination affords chromium(I). This intermediate is not stable in the absence of ethylene and rearranges to the most preferred divalent oxidation state, forming another dimer and chromium metal as black residue. Therefore, the reactions afforded the dinuclear, square-planar $\{[\sigma\text{-}(t\text{-}Bu)_2C_4H_2N]Cr^{II}(THF)\}_2(\mu\text{-}Cl)_2$ (**8.4**) isolated as blue crystals (Figure 8.9) after crystallization of the dried reaction residue from THF (Scheme 8.3). The

retention of chlorine in the structure suggests that formation of **8.4** also proceeds through a non-straightforward mechanism. The σ-bonding of the pyrrolide anion in **8.4** is most likely due to the treatment with THF, which was required for triggering crystallization. Complex **8.4** is catalytically inactive.

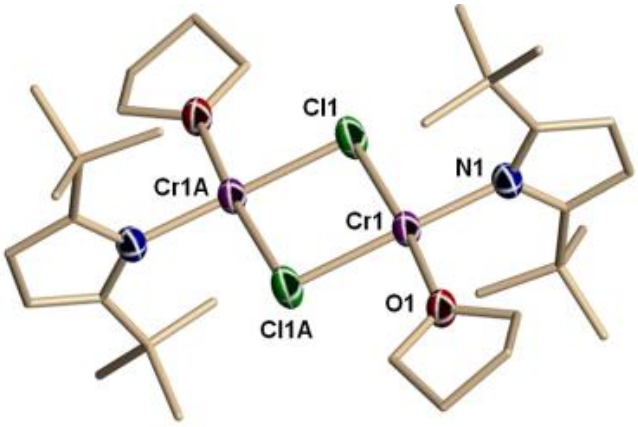
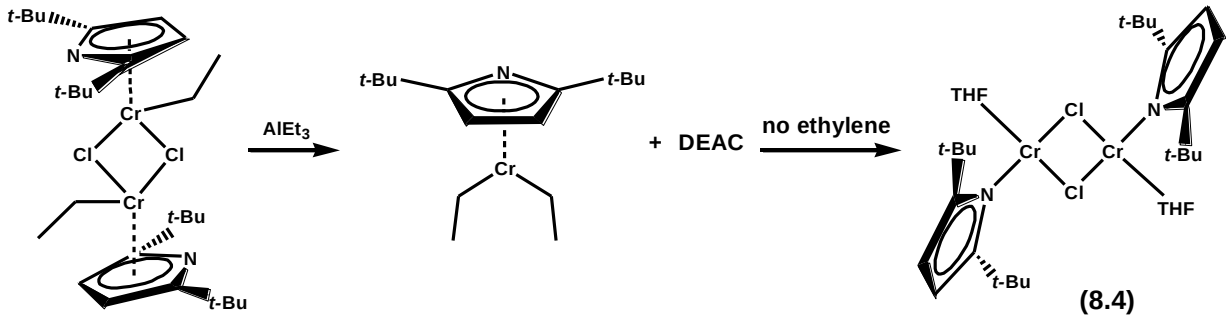


Figure 8.9. Partial thermal ellipsoid plot of **8.4** with ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (°): Cr(1)-N(1) = 2.0121(19), Cr(1)-O(1) = 2.0774(17), Cr(1)-Cl(1A) = 2.3909(7), Cr(1)-Cl(1) = 2.4048(7). N(1)-Cr(1)-O(1) = 92.41(7), N(1)-Cr(1)-Cl(1A) = 175.45(7), O(1)-Cr(1)-Cl(1A) = 90.30(5), N(1)-Cr(1)-Cl(1) = 93.60(6), O(1)-Cr(1)-Cl(1) = 172.93(5), Cl(1A)-Cr(1)-Cl(1) = 83.95(2), Cr(1A)-Cl(1)-Cr(1) = 96.05(2).

Scheme 8.3



(8.2) **(8.4)**

Complex **8.2** is indeed a single component, self-activating precatalyst producing highly pure 1-hexene. The low-activity is likely to be ascribed to both the robust dimeric structure, not easily dissociated in solution, and to partial catalyst poisoning due to impurities (Figure 8.10).

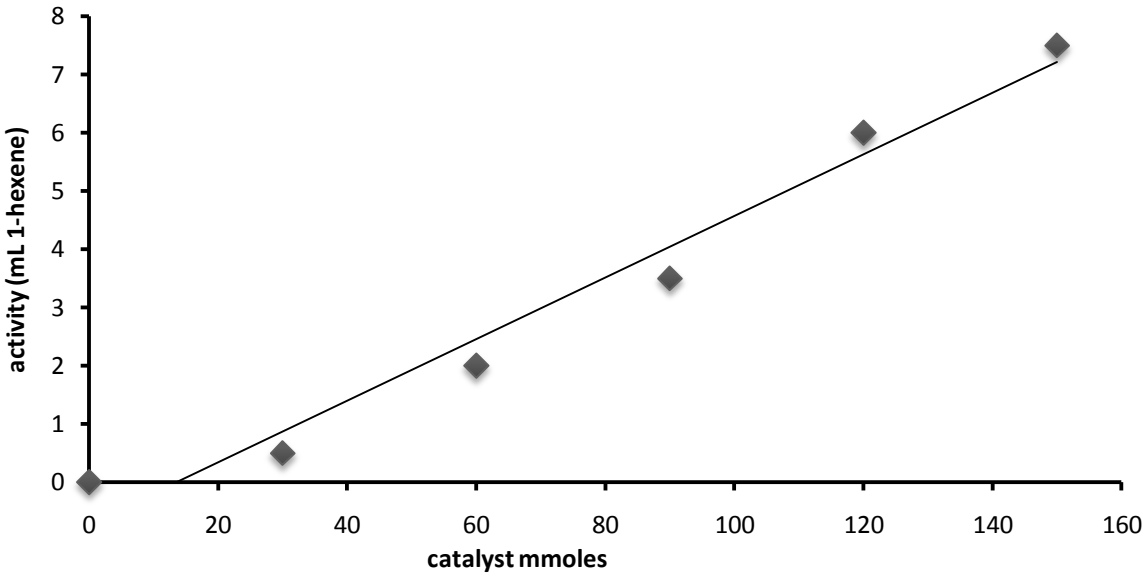
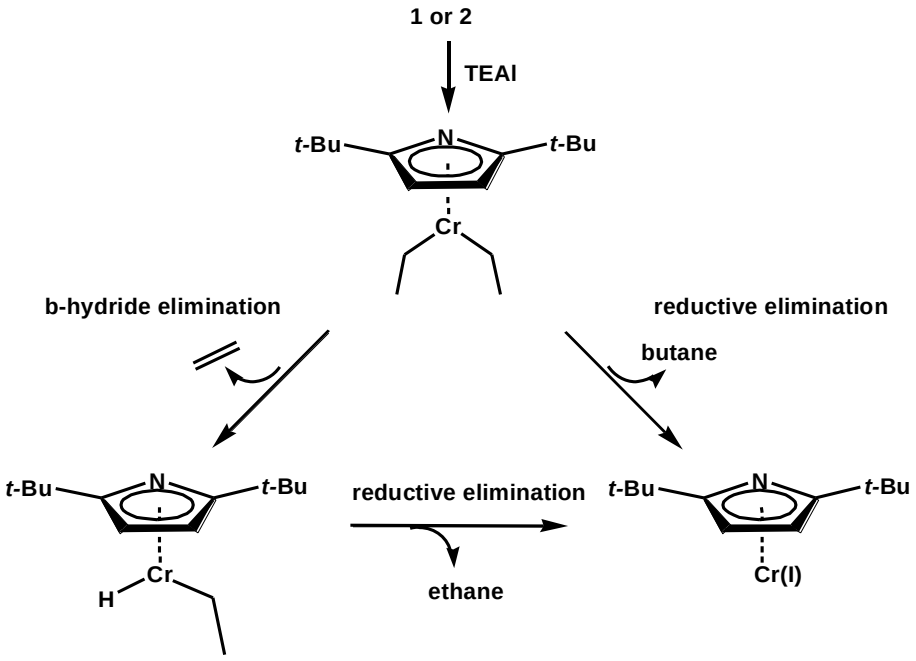


Figure 8.10: Plot of single component catalytic behavior of **8.2**.

In addition, the formation of the Cr(I) catalytically active species from **8.2** will require a preliminary ethyl/chlorine exchange in order to generate a "(Ligand)$CrEt_2$" function ready to undergo thermal reductive elimination. When treated with a few equivalents of $AlEt_3$, **8.2** became an excellent trimerization catalyst producing a large amount of 1-hexene with minor extent of isomerization. The reaction outcome was very sensitive to the temperature and catalyst and activator loadings. Higher loadings of $AlEt_3$ always resulted in an increase of 2-hexene while in combination with higher temperatures.

Scheme 8.4



The high activity and selectivity obtained with complex **8.2** is explained by the catalyst's ability to convert to chromium(I), thus initiating metallacycle formation. The addition of TEAL to the catalyst induces double alkylation at the chromium metal center. Based on the NMR analysis in C_6D_6 (Figure 8.11) for all the gaseous by-products formed during the activation with 2 equivalents of TEAL in toluene, there are two possible pathways to the selective monovalent state: 1) the direct reductive elimination with the release of butane, and 2) the two-step process of initial β-hydride elimination, followed by reductive elimination, with the release of ethylene and ethane molecules as by-products (Scheme 8.4). Chromium(I) further coordinates two ethylene molecules, forming the metallacyle, which is expanded by insertion of more ethylene. The cycle is completed and the catalyst is regenerated after the formation of 1-hexene through the β-hydride and reductive elimination steps (Scheme 8.5).

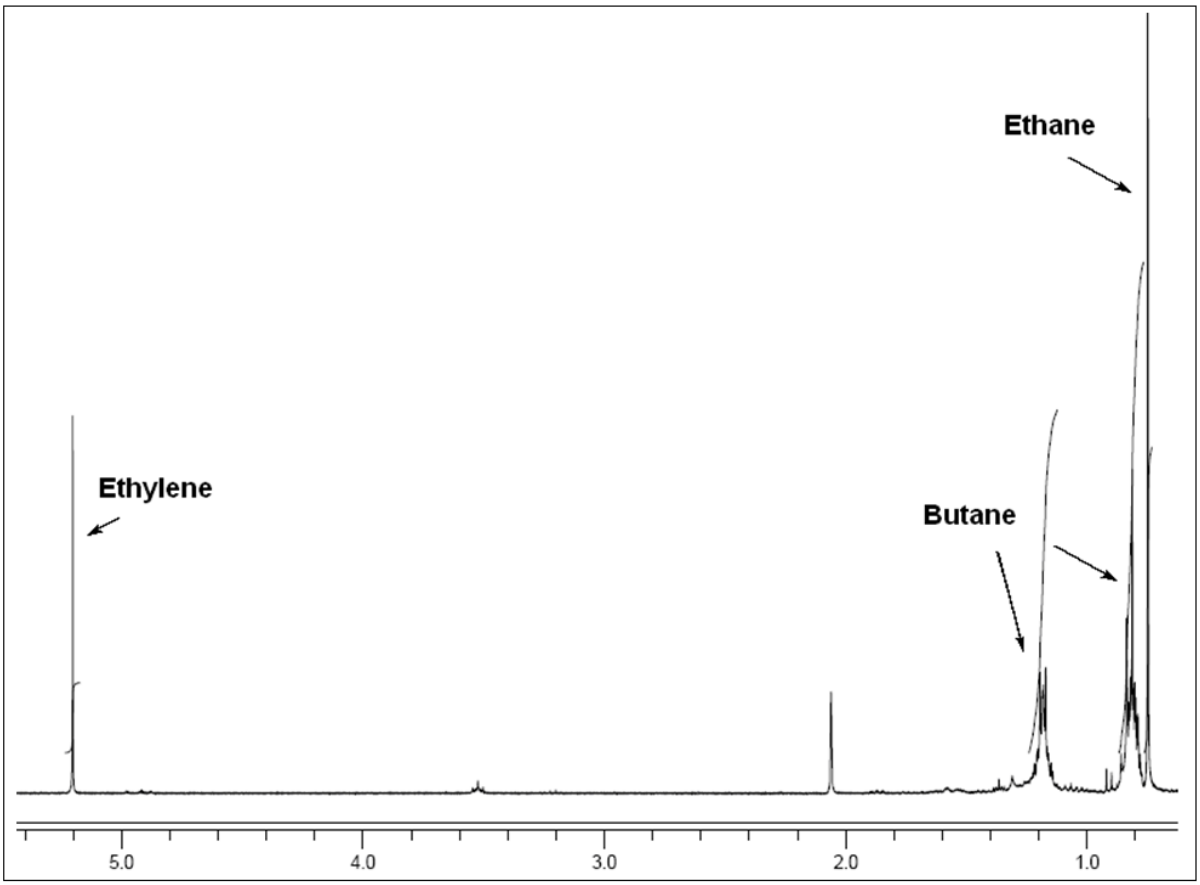
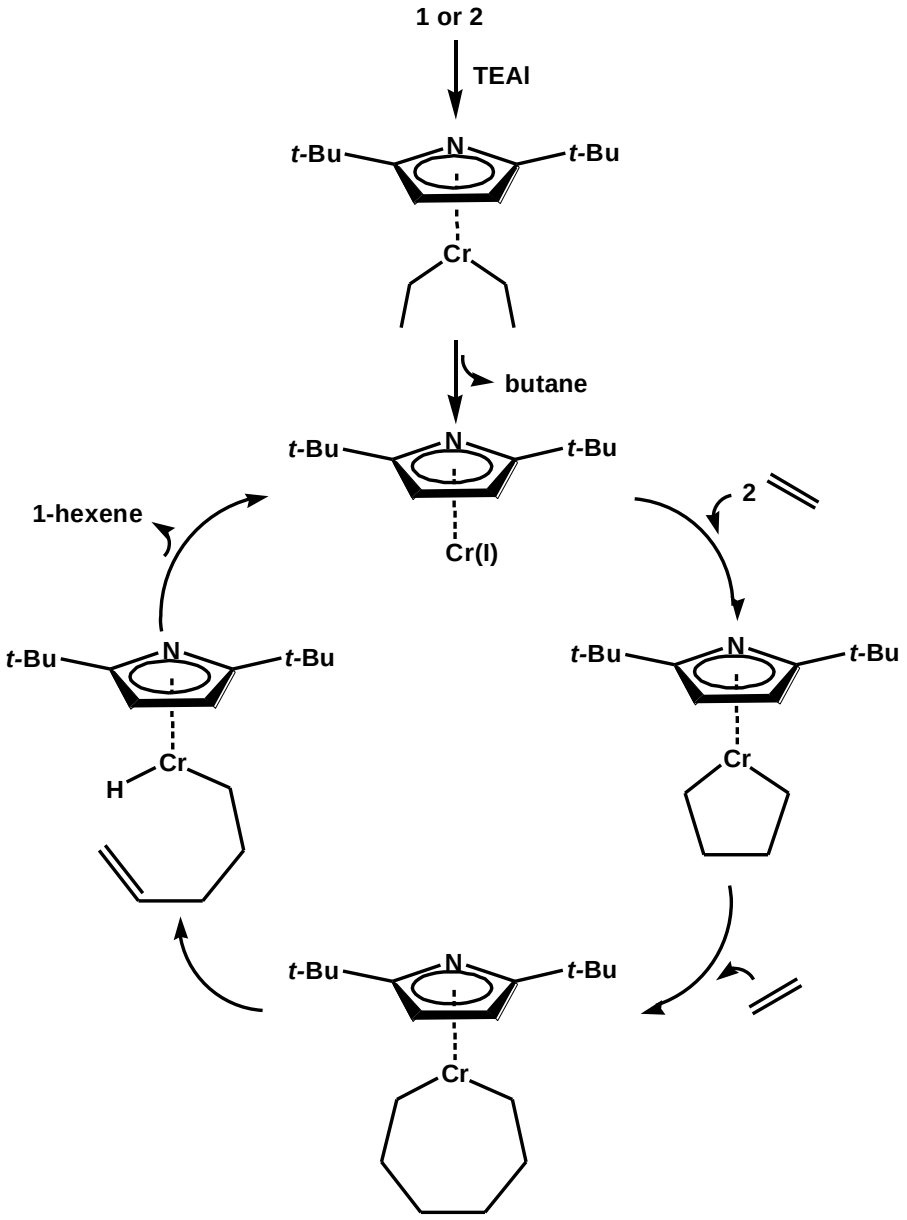


Figure 8.11. ^{1}H-NMR spectrum of all the gaseous by-products formed upon complex **8.2** treatments with 2 equivalents of TEAL.

The catalytic behavior of the ethylidene bridged **8.3** is similar to **8.2**. While no single-component catalytic behavior was observed even under harsh conditions, activation with a small amount of $AlEt_3$ and high temperatures gave record activity and good selectivity with the usual isomerization to *cis*- and *trans*-2-hexene (30:70). The similarities in catalytic behavior between **8.2** and **8.3** when activated does not relate to the preliminary conversion of **8.2** to **8.3,** but rather to the fact that both species may possibly generate the same catalytically active Cr(I) intermediate.

Scheme 8.5



Finally, the variable amount of isomerization of 1-hexene observed during this work (also observed with the commercial process using the Phillips catalytic system) is simply due to the alkyl aluminum activator. The degree of isomerization was found to increase with the temperature and the loading of $AlEt_3$ and did not depend on chromium. In a blank run with only $AlEt_3$, we found that at 110°C pure 1-hexene can be isomerized (93%) in 1 hour to a

thermodynamic mixture of *cis* and *trans* isomers (30:70%) of 2-hexene. No 3-hexene was ever observed. It is therefore important to strike the right balance between reaction conditions and activator loading to maximize 1-hexene production.

8.5 Conclusions

We have introduced in this chapter a novel ethylene trimerization system related to the previously reported intermediates of the Phillips system.[6a,b] Different from those complexes, however, the bulky π-bonded pyrrolide ligand does not allow retention of AlR_3 at the pyrrole N-atom without detracting from the trimerization performance. In this system, the role of the organo-aluminum seems to be exclusively confined to that of an alkylating agent. The serendipitous discovery of the first case of a Schrock-type chromium ethylidene is quite intriguing. We found it particularly stimulating vis-à-vis the recent mechanistic debate[11] regarding the possibility of a dinuclear Schrock type of alkylidene being a catalytically active intermediate in the oligomerization or even a polymerization process.[12] The isolation of such a species, closely reminiscent of the Takai olefination intermediate,[13] indicates that chromium Schrock carbenes may indeed exist. In the next chapter we have attempted to probe the generality of these ideas with a mechanistic study on another commercial selective catalyst such as the Sasol (SNS) system.

8.6 References

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* I contributed to the ligand synthesis and the isolation of complex **8.4**. Also, I reproduced all the intermediate complexes **8.1**, **8.2** and **8.3**. and done the characterizations, and proposed the mechanistic pathway based on the NMR studies as well.

Chapter Nine

Publication:

Albahily, K.; Ahmed, Z.; Korobkov, I.; Gambarotta, S.; Korobkov, I.; Duchateau, R. *Organometallics*. (Submitted)

Ethylene Oligomerization Promoted by a Silylated-SNS Chromium Systems

9.1 Introduction.

Ethylene oligomerization for the production of α-olefins is an active field of research in organometallic chemistry.[1] The several industrial applications of α-olefins – particularly as co-monomers for the synthesis of linear low density polyethylene, PVC plasticizers, household detergents, shampoos and lubricants[2] – have spurred a resurgence of interest for finding new catalytic systems for their production.[1,3] The focus has been on developing more efficient catalysts with the ultimate goal of improving the activity and, most of all, the selectivity.

The most remarkable results with respect to selective ethylene oligomerization have been obtained through the use of trivalent chromium catalyst precursors.[4] Although this process can also be promoted by other transition metal complexes,[5] chromium-based catalytic systems remain the most performing.[4] The current mechanistic hypothesis for the chromium promoted selective formation of 1-hexene and 1-octene is a redox ring-expansion pathway[3b,5j,4l,6] The two critical steps, oxidative addition and reductive coupling of two ethylene molecules, require the intermediate formation of a sufficiently reducing chromium species. Although its oxidation state was long debated,[3a,6,7] today there is a general agreement that the ability of a trivalent precursor

to generate a monovalent catalytically active intermediate is a prerequisite for the initial ethylene reductive coupling, ultimately responsible for the selectivity of the catalytic cycle. [3a,b,c,4l,6]

The McGuinness-Wasserscheid SNS-Cr catalyst[4b-c] is one of the most performing selective trimerization system. Our contribution to understand this highly active catalyst was to identify the role of the chromium redox dynamism.[8] In other words, the three critical states (+I, +II, +III) readily interconvert through series of reductions,[8a,b,9] and disproprotionations,[4o,9c] possibly favored by dimeric aggregation and triggered by the alkyl aluminum activators. The possibility for the ligand to either remain neutral or being anionized, and the presence of soft donor atoms in the ligand scaffold, together seem to play a particularly delicate role in determining the selectivity of the cycle. In an attempt to further understand the role of the unique features of this ligand in stabilizing the different chromium oxidation states, we have modified the ligand by replacing the methylene carbons flanking the nitrogen atom of the SNS system with dimethyl silyl groups. This simple modification had profound effects on the catalytic activity of the SNS system. Herein we describe our findings and their implications.

9.2 Experimental Part

All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried using an aluminum oxide solvent purification system. The liquid product mixtures were analyzed by using a CP 9000 gas chromatograph (GC) equipped with a 30 mL × 0.32 mm id, capillary CP volamine column and a FID detector. All single-point experiments were performed in duplicate. The yield was determined by ^{1}H-NMR spectroscopy (Varian Mercury 400 MHz spectrometer). Infrared spectra were recorded on an ABB Bomem FTIR instrument from Nujol mulls prepared in a VAC dry box. Samples for magnetic susceptibility were pre-weighed inside a dry box equipped with an analytical balance and measured on a Johnson Matthey Magnetic Susceptibility balance.

Elemental analysis was carried out with a Perkin-Elmer 2400 CHN analyzer. Data for X-ray crystal structure determination (Table 9.1) were obtained with a Bruker diffractometer equipped with a 1K Smart CCD area detector. Diethyl aluminum chloride, trimethylaluminum, aluminum trichloride and dimethyl aluminum chloride were purchased from Strem and were used as received. Methylaluminoxane (MAO, 10% in toluene) was purchased from Aldrich.

Preparation of $CySCH_2Si(CH_3)_2N(H)Si(CH_3)_2CH_2SCy$ (9.a).

A solution of cyclohexanethiol (15.0 g, 129.1 mmol) in THF (150 mL) was cooled to 0 ^oC and treated with a suspension of potassium hydride (5.7 g, 142.5 mmol) in THF (50 mL). The reaction mixture was stirred for 1.5 h at room temperature when 1,3-bis-chloromethyl-1,1,3,3-tetramethyl-disilazane (15.0 g, 65.1 mmol) was syringed in at 0 ^oC. The reaction was stirred overnight at room temperature and filtered. The solvent was removed *in vacuo* to give **9.a** as a colorless oil (20.3 g, 52.2 mmol, 80%). ^{1}H-NMR ($CDCl_3$, 300 MHz, 300 K) δ: 0.15 (s, 12H, Si*CH*$_3$) 1.19-1.39 (m, 10H, *Cy*) 1.58-1.65 (m, 2H, *Cy*) 1.78-1.85 (m, 4H, *Cy*) 1.77 (s, 4H, Si*CH*$_2$S) 1.9-2.05 (m, 4H, *Cy*) 2.07 (s, 1H, *NH*) 2.42-2.6 (m, 2H, *Cy*). ^{13}C-NMR ($CDCl_3$, 75 MHz, 300 K) δ 0.60 (Si*CH*$_3$) 17.60 (Si*CH*$_2$S) 25.95, 26.18, 32.97, 46.13 (*Cy*). MS (ESI) *m/z* $(M+H)^+$ = 390.3. El. Anal. Calcd. (found) for $C_{18}H_{39}NS_2Si_2$: C 55.46 (55.42), H 10.08 (10.07), N 3.59 (3.57). IR (Nujol): ν_{N-H} = 3358 cm^{-1}.

Preparation of *t*-$BuSCH_2Si(CH_3)_2N(H)Si(CH_3)_2CH_2S$*t*-Bu (9.b).

A solution of 2-methyl-2-propanethiol (8.57 g, 95.0 mmol) in THF (150 mL) was cooled to 0 ^oC and treated with a suspension of potassium hydride (4.0 g, 100 mmol) in THF (50 mL). The reaction was stirred for 1.5 h at room temperature and then treated with neat 1,3-bis-chloromethyl-1,1,3,3-tetramethyl-disilazane (10.93 g, 47.5 mmol) at 0 ^oC. The reaction was stirred overnight at room temperature. After filtration, the solvent was removed *in vacuo*

affording **9.b** (15.1 g, 44.7 mmol, 94%) as a colorless oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, 300 K) δ 0.15 (s, 12H, Si*CH*$_3$) 1.27 (s, 18H, C(*CH*$_3$)$_3$) 1.73 (s, 4H, Si*CH*$_2$S) 2.07 (s, 1H, *NH*). ^{13}C-NMR ($CDCl_3$, 75 MHz, 300 K) δ 0.67 (Si*CH*$_3$) 15.73 (Si*CH*$_2$S) 29.99 (C(*CH*$_3$)$_3$) 41.40 (*C*(CH$_3$)$_3$). (ESI) *m/z* $(M+H)^+$ = 338.090. El. Anal. Calcd. (found) for $C_{14}H_{35}NS_2Si_2$: C 49.79 (49.77), H 10.45 (10.44), N 4.15 (4.14). IR (Nujol): ν_{N-H} = 3369 cm^{-1}.

Preparation of PhSCH$_2$Si(CH$_3$)$_2$N(H)Si(CH$_3$)$_2$CH$_2$SPh (9.c).

A 250 mL round bottom flask was charged with benzenethiol (10 g, 90.7 mmol) and THF (150 mL). The solution was cooled to 0 ^{o}C and treated with a suspension of potassium hydride (3.99 g, 99.7 mmol) in THF (50 mL). The mixture was stirred for 1 h at room temperature and then 1,3-bis-chloromethyl-1,1,3,3-tetramethyl-disilazane (10.36 g, 45.0 mmol) was syringed in at 0 ^{o}C. Stirring was continued overnight at room temperature followed by filtration. The solvent was removed *in vacuo* affording **9.c** as a colorless oil (16.14 g, 42.7 mmol, 95%). ^{1}H-NMR ($CDCl_3$, 300 MHz, 300 K) δ 0.42 (s, 12H, Si*CH*$_3$) 2.37 (s, 4H, Si*CH*$_2$S) 2.63 (s, 1H, *NH*) 7.23-7.29 (m, 2H, S*Ph*), 7.38-7.46 (m, 8H, S*Ph*). ^{13}C-NMR ($CDCl_3$, 75 MHz, 300 K) δ 0.64 (Si*CH*$_3$) 20.15 (Si*CH*$_2$S) 124.61, 126.10, 128.62, 140.04 (S*Ph*). (ESI) *m/z* $(M+H)^+$ = 378.101. El. Anal. Calcd. (found) for $C_{18}H_{27}NS_2Si_2$: C 57.24 (57.21), H 7.21 (7.20), N 3.71 (3.69). IR (Nujol): ν_{N-H} = 3386 cm^{-1}.

Preparation of CySCH$_2$Si(CH$_3$)$_2$N(CH$_3$)Si(CH$_3$)$_2$CH$_2$SCy (9.d).

A suspension of potassium hydride (0.62 g, 15.4 mmol) in THF (30 mL) was added portion wise to a solution of **9.a** (5.0 g, 12.8 mmol) in THF (50 mL) at 0 ^{o}C. The mixture was refluxed overnight and then treated with neat iodomethane (2.19 g, 15.4 mmol) at room temperature. The mixture was stirred overnight and filtered. The solvent was removed *in vacuo* affording **9.d** (5.10 g, 12.6 mmol, 98%) as a colorless oil. ^{1}H-NMR ($CDCl_3$,300 MHz, 300 K) δ 0.17 (s, 12H, Si*CH*$_3$)

1.18-1.38 (m, 10H, *Cy*) 1.57-1.65 (m, 2H, *Cy*) 1.76-1.83 (m, 4H, *Cy*) 1.81 (s, 4H, Si*CH*$_2$S) 1.9-2.03 (m, 4H, *Cy*) 2.42-2.58 (m, 2H, *Cy*) 2.49 (s, 3H, N*CH*$_3$).^{13}C-NMR ($CDCl_3$, 75 MHz, 300 K) δ -0.430 (Si*CH*$_3$) 16.255 (Si*CH*$_2$S) 25.95, 26.18, 32.96, 46.13 (*Cy*) 31.18 (N*CH*$_3$). MS (ESI) *m/z* $(M+H)^+$ = 404.122. El. Anal. Calcd. (found) for $C_{19}H_{41}NS_2Si_2$: C 56.51 (56.49), H 10.23 (10.22), N 3.47 (3.46).

Preparation of [CySCH$_2$Si(CH$_3$)$_2$N(H)Si(CH$_3$)$_2$CH$_2$SCy]CrCl$_3$ (9.1a).

Solid $CrCl_3(THF)_3$ (0.375 g, 1.0 mmol) was added to a solution of **9.a** (0.389 g, 1.0 mmol) in toluene (10 mL). The mixture was refluxed for 30 minutes and then allowed to stir at room temperature for 18 h. Following centrifugation, the supernatant was concentrated and stored at -30 ^oC for 4 days. The resulting product was filtered and washed with cold hexanes (10 mL) and dried *in vacuo* affording **9.1a** (0.494 g, 90.1 mmol 90%) as dark blue-purple colored crystalline material. μ_{eff} = 3.84 μ_B. El. Anal. Calcd. (found) for $C_{18}H_{39}Cl_3CrNS_2Si_2$: C 39.44 (39.42), H 7.17 (7.16), N 2.56 (2.54). IR (Nujol): ν_{N-H} = 3138 cm^{-1}.

Preparation of {[CySCH$_2$Si(CH$_3$)$_2$NSi(CH$_3$)$_2$CH$_2$SCy]CrCl(μ-Cl)}$_2$ (9.2a).

A solution of **9.a** (0.778 g, 2.0 mmol) in THF (10 mL) was treated with *n*-BuLi (0.84 mL, 2.1 mmol, 2.5 M in hexanes) at 0 ^oC and stirred at room temperature for 18 h. The resulting solution was added to a suspension of $CrCl_3(THF)_3$ (0.750 g, 2.0 mmol) in THF (5 mL). The mixture was stirred at room temperature overnight. The solvent was removed *in vacuo* and the residue suspended in toluene (10 mL). Following centrifugation, the volume of the supernatant was reduced to 4 mL and stored at -30 ^oC for 6 days. The resulting product was filtered and washed with cold hexanes (10 mL) and dried in vacuo affording **9.2a** (0.317 g, 0.31 mmol, 31%) as green crystalline material. μ_{eff} = 3.89 μ_B. El. Anal. Calcd. (found) for $C_{36}H_{76}Cl_4Cr_2NS_4Si_4$: C 42.25 (42.23), H 7.49 (7.50), N 2.74 (2.73).

Preparation of {[CySCH$_2$Si(CH$_3$)$_2$N(H)Si(CH$_3$)$_2$CH$_2$SCy]Cr(μ-Cl)$_2$} {Al(CH$_2$CH$_3$)$_2$Cl}$_2$ (9.3a).

Method A. Solid $CrCl_3(THF)_3$ (0.375 g, 1.0 mmol) was added to a solution of **9.a** (0.389 g, 1.0 mmol) in toluene (10 mL). The mixture was refluxed for 30 minutes and allowed to stir at room temperature for 18 h. Neat diethylaluminum chloride (1.21 g, 10.0 mmol) was then added drop wise. The reaction mixture was stirred for 2 h at room temperature, centrifuged and the supernatant was concentrated and stored at -30 ^{o}C for 2 days. The resulting product was filtered, washed with cold hexanes (10 mL) and dried *in vacuo* affording **9.3a** (0.346 g, 0.46 mmol, 46%) as blue crystalline material. μ_{eff} = 4.89 μ_B. El. Anal. Calcd. (found) for $C_{26}H_{59}Al_2Cl_4CrNS_2Si_2$: C 41.43 (41.41), H 7.89 (7.88), N 1.86 (1.86). IR (Nujol): ν_{N-H} = 3098 cm^{-1}.

Method B**.** Solid $CrCl_2(THF)_2$ (0.268 g, 1.0 mmol) was added to a solution of **9.a** (0.389 g, 1.0 mmol) in toluene (10 mL). The mixture was cooled to -35 ^{o}C and neat diethylaluminum chloride (1.21 g, 10.0 mmol) was added drop wise. The reaction mixture was stirred for 2 h, centrifuged and the resulting solution was concentrated and stored at -30 ^{o}C for 3 days. The resulting product was filtered and washed with cold hexanes (10 mL) and dried *in vacuo* affording **9.3a** (0.595 g, 0.789 mmol, 79%) as blue crystalline material.

Preparation of {[CySCH$_2$Si(CH$_3$)$_2$NSi(CH$_3$)$_2$CH$_2$SCy]Cr(μ-Cl)}$_2$ (9.4a).

A solution of *n*-BuLi (0.84 mL, 2.1 mmol., 2.5 M in hexanes) was added to a solution of **9.a** (0.780 g, 2.0 mmol) in THF (10 mL) at 0 ^{o}C and allowed to stir at room temperature for 18 h. The resulting solution was added to a suspension of $CrCl_2(THF)_2$ (0.536 g, 2.0 mmol) in THF (10 mL). The mixture was stirred at room temperature overnight. The solvent was removed *in vacuo* and the residue suspended in toluene (10 mL). Following centrifugation, the supernatant was concentrated and stored at -30 ^{o}C for 4 days. The resulting product was filtered and washed

with cold hexanes (10 mL) and dried in vacuo affording **9.4a** (0.534 g, 0.56 mmol, 56%) as blue crystalline material. μ_{eff} = 4.93 μ_B. El. Anal. Calcd. (found) for $C_{36}H_{76}Cl_2Cr_2N_2S_4Si_4$: C 45.39 (45.38), H 8.04 (8.02), N 2.94 (2.95).

Preparation of {[*t*-BuSCH$_2$Si(CH$_3$)$_2$NSi(CH$_3$)$_2$CH$_2$S*t*-Bu]Cr(μ-Cl)}$_2$ (9.4b).

A solution of **9.b** (0.337 g, 1.0 mmol) in THF (10 mL) was treated with *n*-BuLi (0.44 mL, 12.1 mmol , 2.5 M in hexanes) at 0 ^oC and stirred at room temperature for 18 h. The resulting solution was added to a suspension of $CrCl_2(THF)_2$ (0.268 g, 1.0 mmol) in THF (10 mL). The mixture was stirred at room temperature overnight. The solvent was removed in vacuo and the residue suspended in toluene (10 mL). Following centrifugation, the supernatant was concentrated and stored at -30 ^oC for 4 days. The resulting product was filtered, washed with cold hexanes (10 mL) and dried *in vacuo* affording **9.4b** (0.301 g, 0.71 mmol, 71%) as blue crystalline material. μ_{eff} = 4.80 μ_B. El. Anal. Calcd. (found) for $C_{28}H_{68}Cl_2Cr_2N_2S_4Si_4$: C 39.64 (39.62), H 8.08 (8.07), N 3.30 (3.28).

Preparation of {[CySCH$_2$Si(CH$_3$)$_2$N(H)Si(CH$_3$)$_2$CH$_2$SCy]Cr(μ-Cl)$_2$} {AlCl$_3$}$_2$ (9.5a).

A solution of **9.a** (0.389 g, 1.0 mmol) in toluene (10 mL) was treated with $CrCl_2(THF)_2$ (0.268 g, 1.0 mmol). Solid aluminum trichloride (0.668 g, 5.0 mmol) was added to the corresponding solution cooled to -35 ^oC. The mixture was stirred for 2 h, and then centrifuged and the supernatant concentrated and stored at -30 ^oC for 2 days. The resulting product was filtered, washed with cold hexanes (10 mL) and dried *in vacuo* affording **9.5a** (0.420 g, 0.54 mmol, 54%) as blue crystalline material. μ_{eff} = 4.99 μ_B. El. Anal. Calcd. (found) for $C_{18}H_{39}Al_2Cl_8CrNS_2Si_2$: C 27.74 (27.72), H 5.04 (5.03), N 1.80 (1.79). IR (Nujol): ν_{N-H} = 3113 cm^{-1}.

Preparation of {[PhSCH$_2$Si(CH$_3$)$_2$N(H)Si(CH$_3$)$_2$CH$_2$SPh]Cr(μ-Cl)$_2$} {AlCl$_3$}$_2$ (9.5c).

Solid $CrCl_2(THF)_2$ (0.268 g, 1.0 mmol) was added to a solution of **9.c** (0.378 g, 1.0 mmol) in toluene (10 mL). Solid aluminum trichloride (0.668 g, 5.0 mmol) was added at -35 ^oC to the corresponding suspension. The reaction mixture was stirred for 4 h, centrifuged and the supernatant concentrated and stored in a freezer at -30 ^oC for 2 days. The resulting product was filtered and washed with cold hexanes (10 mL) and dried *in vacuo* affording **9.5c** (0.120 g, 0.16 mmol, 15%) as blue crystalline material. μ_{eff} = 4.89 μ_B. El. Anal. Calcd. (found) for $C_{18}H_{27}Al_2Cl_8CrNS_2Si_2$: C 28.18 (28.15), H 3.55 (3.56), N 1.83 (1.82). IR (Nujol): ν_{N-H} = 3126 cm^{-1}.

Preparation of {[CySCH$_2$Si(CH$_3$)$_2$N(Al(CH3)$_2$-μ-Cl)Si(CH$_3$)$_2$CH$_2$SCy]Cr(μ-Cl)}{Al(CH$_3$)$_3$} (9.6a).

Solid $CrCl_2(THF)_2$ (0.268 g, 1.0 mmol) was added to a solution of **9.a** (0.389 g, 1.0 mmol) in toluene (10 mL). After cooling to -35 ^oC, neat trimethyl aluminum (0.72 g, 10.0 mmol) was added dropwise to the mixture. Stirring was continued for 30 minutes followed by centrifugation. The resulting solution was concentrated and stored at -30 ^oC for 10 days. The resulting product was filtered and washed with cold hexanes (10 mL) and dried *in vacuo* affording **9.6a** (0.198 g, 0.31 mmol, 31%) as blue crystalline material. μ_{eff} = 4.91 μ_B. El. Anal. Calcd. (found) for $C_{23}H_{53}Al_2Cl_2CrNS_2Si_2$: C 43.11 (43.12), H 8.34 (8.35), N 2.19 (2.20).

Preparation of {[CySCH$_2$Si(CH$_3$)$_2$N(CH$_3$)Si(CH$_3$)$_2$CH$_2$SCy]Cr(μ-Cl)}$_2${(Al(CH$_3$)$_2$Cl)$_2$)(μ-Cl)}$_2$ (9.7d).

Solid $CrCl_2(THF)_2$ (0.268 g, 1.0 mmol) was added to a solution of **9.d** (0.403 g, 1.0 mmol) in toluene (10 mL). The mixture was cooled to -35 ^oC and neat dimethylaluminum chloride (0.462 g, 5.0 mmol) was added dropwise. The reaction mixture was stirred for 4 h, centrifuged

and the supernatant concentrated and stored at -30 ^{o}C for 3 days. The resulting product was filtered, washed with cold hexanes (10 mL) and dried *in vacuo* affording **9.7d** (0.336 g, 0.24 mmol, 47%) as blue crystalline material. μ_{eff} = 4.90 μ_B. El. Anal. Calcd. (found) for $C_{46}H_{106}Al_4Cl_8Cr_2N_2S_4Si_4$: C 38.81 (38.80), H 7.51 (7.50), N 1.97 (1.95).

9.3 X-ray Data

Table 9.1. Crystal Data and Structure Analysis Results of Complexes **9.1a-9.7d**.

	9.1a	**9.2a**	**9.3a**	**9.4a**	**9.4b**
formula	$C_{18}H_{39}Cl_3CrNS_2Si_2$	$C_{21.50}H_{42}Cl_2CrNS_2Si_2$	$C_{26}H_{59}Al_2Cl_4CrNS_2Si_2$	$C_{25}H_{46}ClCrNS_2Si_2$	$C_{14}H_{34}ClCrNS_2Si_2$
Mw	548.15	557.76	753.80	568.38	424.17
space group	Fdd2	P2(1)/c	P-1	P-1	P-1
***a* (Å)**	16.510(6)	12.426(3)	12.161(3)	11.638(5)	9.4189(8)
***b* (Å)**	24.278(9)	18.116(5)	12.476(3)	11.837(5)	10.2886(9)
***c* (Å)**	13.791(5)	13.335(3)	15.493(4)	12.589(6)	12.5226(11)
***α*, (deg)**	90	90	74.217(3)	66.699(5)	96.8850(10)
***β*, (deg)**	90	104.054(4)	77.582(3)	80.602(5)	103.7370(10)
***γ*, (deg)**	90	90	62.952(3)	85.647(5)	108.1910(10)
***V* (Å^3)**	5528(4)	2912.2(13)	2003.2(9)	1571.3(12)	1094.87(16)
Z	8	4	2	2	2
radiation	0.71073	0.71073	0.71073	0.71073	0.71073
***T* (K)**	213(2)	203(2)	204(2)	203(2)	200(2)
D_{calcd} (g cm^{-3})	1.317	1.272	1.250	1.201	1.287
μ_{calcd} (mm^{-1})	0.948	0.812	0.778	0.672	0.940
***F*$_{000}$**	2312	1184	800	608	452
***R*, *Rw*^{2a}**	0.0532, 0.1191	0.0378, 0.0970	0.0380, 0.0978	0.0387, 0.1058	0.0375, 0.0986
GoF	1.044	1.069	1.057	1.026	1.042

	9.5a	**9.6a**	**9.5c**	**9.7d**
formula	$C_{25}H_{46}Al_2Cl_8CrNS_2Si_2$	$C_{23}H5_3Al_2Cl_2CrNS_2Si_2$	$C_{21.50}H_{31}Al_2Cl_8CrNS_2Si_2$	$C_{46}H_{106}Al_4Cl_8Cr_2N_2S_4Si_4$
Mw	870.49	640.82	813.33	1423.45
space group	P2(1)/n	P-1	P-1	P2(1)/n
***a* (Å)**	11.0381(13)	9.383(2)	10.6989(5)	12.877(4)
***b* (Å)**	11.9963(14)	19.572(4)	12.7272(6)	15.896(4)
***c* (Å)**	31.581(4)	20.136(4)	17.6487(7)	19.071(5)
***α*, (deg)**	90	102.870(4)	70.641(2)	90
***β*, (deg)**	93.935(2)	100.293(4)	75.413(2)	92.071(5)
***γ*, (deg)**	90	102.156(4)	87.628(3)	90
***V* (Å^3)**	4172.0(9)	3424.0(12)	2191.88(17)	3901.4(19)
Z	4	4	2	2
radiation	0.71073	0.71073	0.71073	0.71073
***T* (K)**	200(2)	200(2)	200(2)	200(2)
D_{calcd} (g cm^{-3})	1.386	1.243	1.232	1.212
μ_{calcd} (mm^{-1})	1.005	0.747	0.952	0.795
***F*$_{000}$**	1796	1368	826	1504
***R*, *Rw*^{2a}**	0.0635, 0.1541	0.0600, 0.1223	0.0714, 0.2010	0.0863, 0.2052
GoF	1.062	1.022	1.053	1.061

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

9.4 Description of Crystal Structures

Complex 9.1a. The structure of **9.1a** (Figure 9.1) consists of a meridionally arranged $CrCl_3$ unit [Cr(1)-Cl(1) = 2.323(2) Å; Cr(1)-Cl(1a) = 2.323(2) Å; Cr(1)-Cl(2) = 2.269(4) Å], surrounded by the three donor atoms of the ligand system in an overall distorted octahedral geometry. The long Cr-N bond distance [Cr(1)-N(1)= 2.190(12) Å] along with the pyramidal geometry of the N atom clearly indicates the presence of a hydrogen atom on nitrogen. The two sulfur atoms are *trans* positioned [Cr(1)-S(1)1a = 2.433(2) Å; Cr(1)-S(1) = 2.433(2) Å], and exhibit a minor deviation from linearity [S(1a)-Cr(1)-S(1) = 173.56(13)°]. The distortion of the octahedral structure is apparent on the Cl-Cr bond angles [Cl(1a)-Cr(1)-Cl(2)= 72.12(19)°; Cl(2)-Cr(1)-Cl(1)= 93.94(10)°].

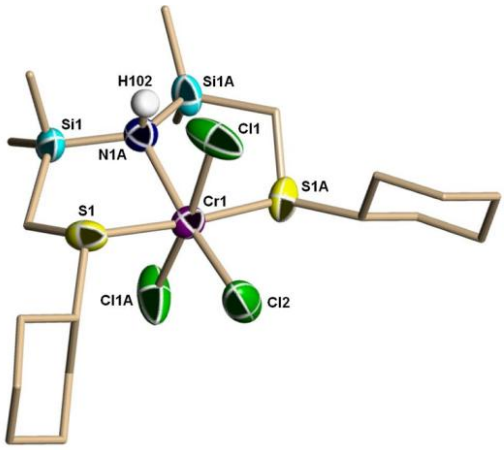


Figure 9.1. Partial thermal ellipsoid plot of **9.1a** with ellipsoids drawn at 50% probability.

Complex 9.2a. The complex is a symmetry generated dimer (Figure 9.2) with two chlorine atoms bridging the two metal centers [Cr(1)-Cl(1) = 2.4129(11) Å; Cr(1)-Cl(1a) = 2.4420(11) Å] and forming a square Cr_2Cl_2 core. The slightly distorted octahedral geometry of each metal center [Cl(2)-Cr(1)-Cl(1) = 93.10(4)°; Cl(1)-Cr(1)-Cl(1a)= 80.37(3)°; Cl(2)-Cr(1)-Cl(1a) =173.20(4)°] is completed by one terminally bonded chlorine [Cr(1)-Cl(2)= 2.2930(11) Å] and

the three donor atoms of the deprotonated ligand system. The N atom is trigonal planar as a result of the deprotonation of the N atom and forms with the metal a bonding distance shorter than in **9.1a** [Cr(1)-N(1) = 1.984(3) Å] and in the expected range for a chromium amido derivative. The two sulfur atoms are located *trans* to each other with a minor deviation of the S-Cr-S vector from the linearity [S(2)-Cr(1)-S(1) = 173.84(4)°].

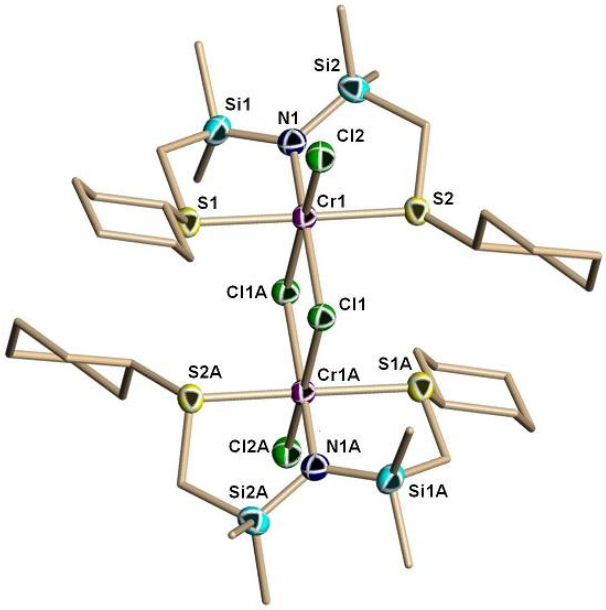


Figure 9.2. Partial thermal ellipsoid plot of **9.2a** with ellipsoids drawn at 50% probability.

Complex 9.3a. The geometry of the chromium center (Figure 9.3) is square pyramidal with the three ligand donor atoms [Cr(1)-S(1) = 2.4890(12) Å; Cr(1)-S(2) = 2.5187(12) Å] and one chlorine [Cr(1)-Cl(1) = 2.4102(12) Å] of an Et_2AlCl_2 unit defining the basal plane [S(1)-Cr(1)-S(2) = 166.71(4)° and N(1)-Cr(1)-Cl(1)=176.01(8)°]. The chromium center shows only little deviation from the basal plane. The protonation of the ligand nitrogen atom in evident from the deviation of the N atom from the trigonal planar geometry and the long Cr-N distance [Cr(1)-N(1) = 2.177(3) Å]. One additional chlorine forming a second Et_2AlCl_2 unit is located on the apical position [N(1)-Cr(1)-Cl(3) = 91.26(8)°, Cl(1)-Cr(1)-Cl(3) = 85.87(3)°, S(1)-Cr(1)-Cl(3) =

99.79(4)°, S(2)-Cr(1)-Cl(3) = 93.01(3)°] forming a substantially longer distance [Cr(1)-Cl(3) = 2.6821(13) Å].

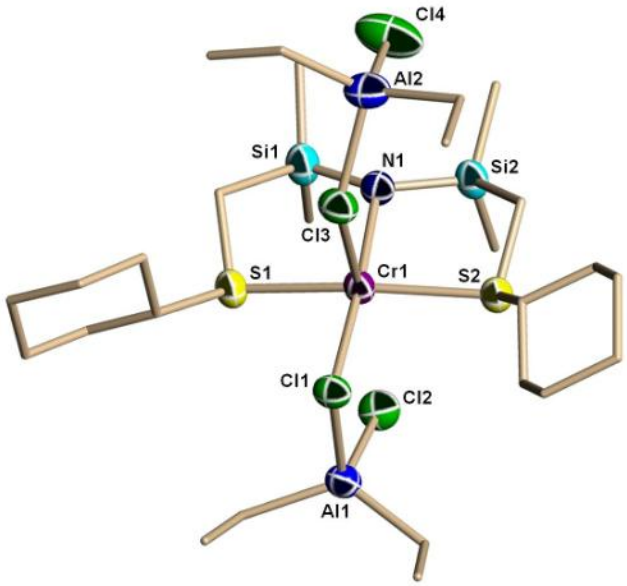


Figure 9.3. Partial thermal ellipsoid plot of **9.3a** with ellipsoids drawn at 50% probability (N-H bond not pictured).

Complexes 9.4a and 9.4b. The two complexes have a very similar arrangement (Figure 9.4) and geometry with only one main difference in the ligand disposition. Both complexes are symmetry generated dimers with the two metals linked by two bridging chlorines of a Cr_2Cl_2 planar core. In **9.4a** the two metals adopted square pyramidal coordination geometry. The two bridging chlorine atoms are respectively located in equatorial and axial positions to respect to each of the two metal centers [Cr(1)-Cl(1) = 2.3679(11) Å; Cr(1)-Cl(1a) = 2.7097(14) Å]. The Cr_2Cl_2 planar core is almost perfectly square planar [Cl(1)-Cr(1)-Cl(1a) = 92.49(3)°; Cr(1)-Cl(1)-Cr(1a) = 87.51(3)°]. The three ligand donor atoms complete, with the equatorial chlorine atom, the basal square plane [Cr(1)-S(1) = 2.4756(12) Å; Cr(1)-S(2) = 2.4788(12) Å, S(1)-Cr(1)-

S(2) = 178.88(3)°]. The Cr-N distance is in the short range [Cr(1)-N(1) = 2.051(2) Å] as normally formed by a deprotonated trigonal planar N atom.

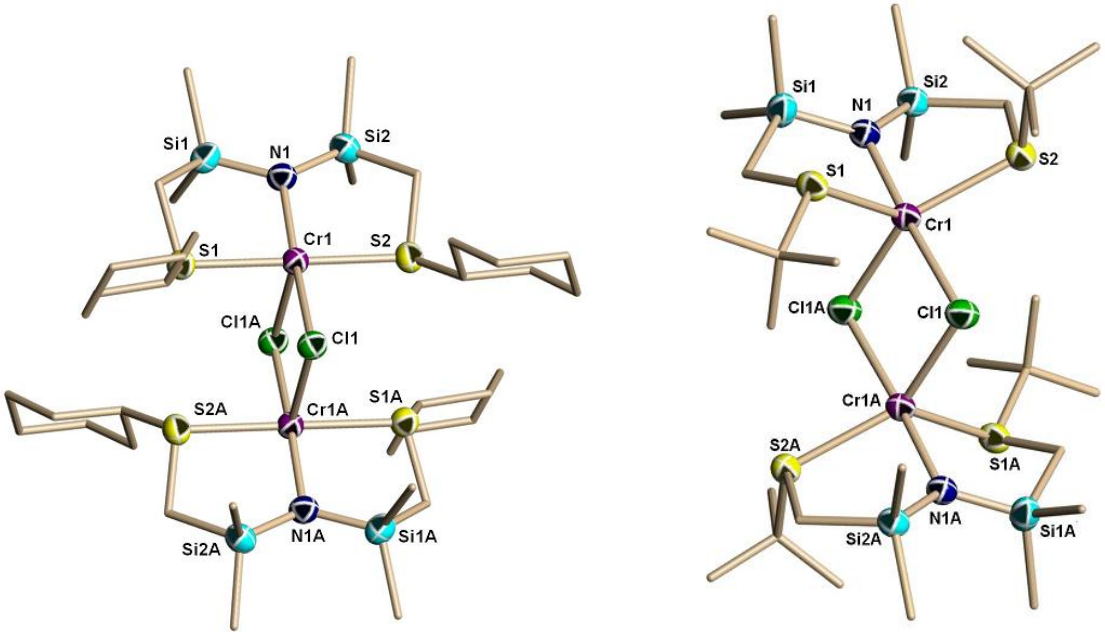


Figure 9.4. Partial thermal ellipsoid plot of **9.4a** and **9.4b** (respectively) with ellipsoids drawn at 50% probability.

Complex **9.4b** has instead the coordination geometry of the two chromium atoms as being better described as trigonal bipyramidal. The two bridging chlorine atoms are axially [N(1)-Cr(1)-Cl(1) = 176.44(8)°] and equatorially [N(1)-Cr(1)-Cl(1a)= 95.53(8)°] located forming comparable Cr-Cl distances [Cr(1)-Cl(1) = 2.4118(9)Å; Cr(1)-Cl(1a) = 2.5079(9)Å]. The trigonal equatorial plane is bound by the two sulfur atoms [Cr(1)-S(2) = 2.5151(9)Å; Cr(1)-S(1) = 2.6466(9)Å] and one of the two chlorines [[S(2)-Cr(1)-S(1) = 123.90(3)°, Cl(1a)-Cr(1)-S(2) = 134.64(3)°, Cl(1a)-Cr(1)-S(1) = 101.36(3)°]. The ligand deprotonated nitrogen atom is located in apical position *trans* to one of the two chlorine atoms forming the expected short distance with the metal center [Cr(1)-N(1) = 2.027(3)Å].

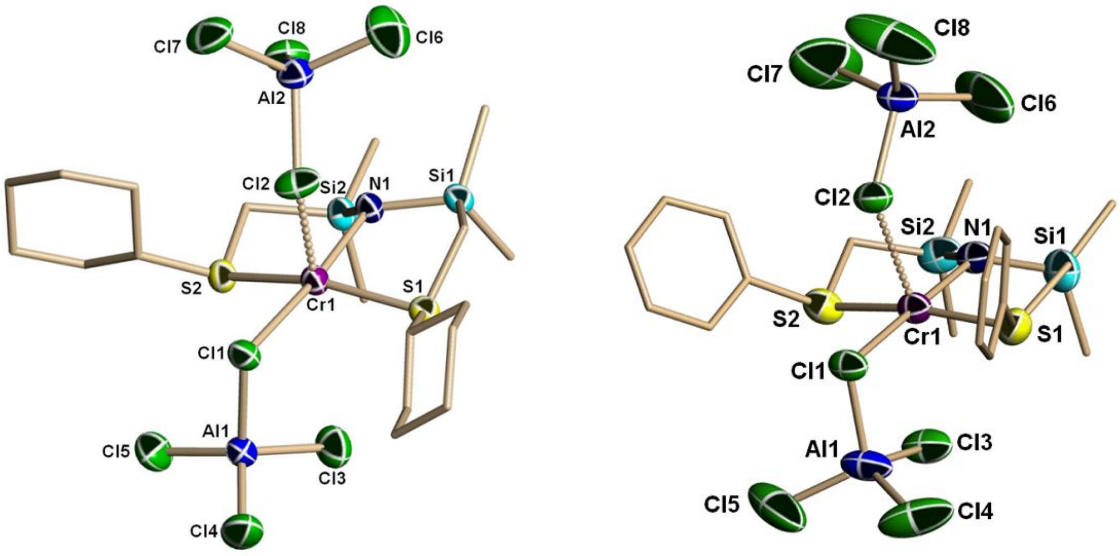


Figure 9.5. Partial thermal ellipsoid plot of **9.5a** and **9.5c** (respectively) with ellipsoids drawn at 50% probability (N-H bonds not pictured).

Complexes 9.5a and 9.5c. The two complexes possess the same structure (Figure 9.5), the only difference consisting of the different substituents attached to the ligand sulfur atoms (cyclohexyl *versus* phenyl). In both cases the coordination geometry of the metal center is square pyramidal with a minor elevation of the metal center over the basal plane. The basal square-plane [N(1)-Cr(1)-Cl(1) = 174.76(13)°, N(1)-Cr(1)-S(1) = 88.42(12)°, N(1)-Cr(1)-S(2) = 88.60(12)°, S(2)-Cr(1)-S(1) = 160.54(6)°] for **9.5a**; S(2)-Cr(1)-S(1) = 169.20(6)° and N(1)-Cr(1)-Cl(1) = 178.96(12)°for **9.5c**] is defined by the protonated ligand's three donor atoms [Cr(1)-S(1) = 2.4706(16) Å ; Cr(1)-S(2) =2.4459(16) Å for **9.5a**; Cr(1)-S(1) = 2.4719(15)Å; Cr(1)-S(2) = 2.4718(15)Å for **9.5c**], and one chlorine atom of a formal $AlCl_4$ anion [Cr(1)-Cl(1) = 2.4371(16) for **9.5a**; Cr(1)-Cl(1) = 2.4448(12)Å for **9.5c**]. The Cr-N distance is in the range formed by a quaternary nitrogen [Cr(1)-N(1) = 2.149(4) Å for **9.5a**; Cr(1)-N(1) = 2.170(4)Å for **9.5c**]. A second chlorine atom of a second $AlCl_4$ anion is located on the apical position [Cl(1)-Cr(1)-Cl(2) = 86.93(6)°, S(1)-Cr(1)-Cl(2) = 88.15(6)°, S(2)-Cr(1)-Cl(2) = 111.10(6)°, N(1)-Cr(1)-Cl(2) =

90.39(13)° for **9.5a**; Cl(1)-Cr(1)-Cl(2) = 84.64(4)°, S(1)-Cr(1)-Cl(2) = 96.94(5)°, S(2)-Cr(1)-Cl(2) = 93.78(5)°, N(1)-Cr(1)-Cl(2) = 95.52(11)° for **9.5c**] forming the usually longer Cr-Cl distance [Cr(1)-Cl(2) = 2.7484(18) Å for **9.5a**; Cr(1)-Cl(2) = 2.7287(14)Å for **9.5c**].

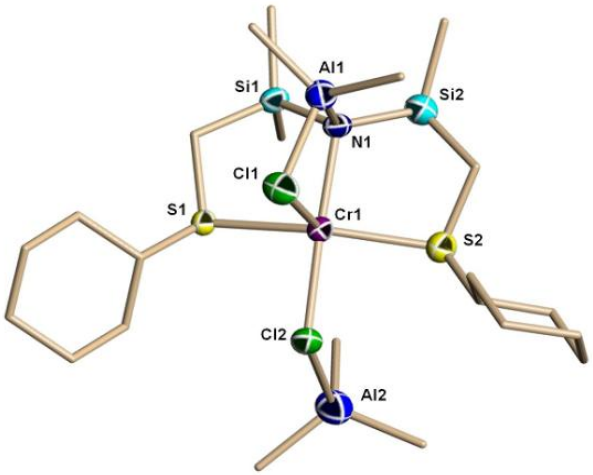


Figure 9.6. Partial thermal ellipsoid plot of **9.6a** with ellipsoids drawn at 50% probability.

Complex 9.6a. The structure of **9.6a** consists of a divalent chromium center in an overall distorted square-pyramidal coordination geometry (Figure 9.6). The three ligand donor atoms [Cr(1)-S(1) = 2.5083(14) Å; Cr(1)-S(2) = 2.4460(14) Å] and one bridging chlorine [Cr(1)-Cl(2) = 2.3723(14) Å] atom of a Me_3AlCl anion define the distorted basal square plane [S(2)-Cr(1)-S(1) = 152.89(5)°; S(2)-Cr(1)-Cl(1) = 114.75(5)°; S(1)-Cr(1)-Cl(1) = 92.18(5)°]. The apical position is occupied by a second chlorine atom [N(1)-Cr(1)-Cl(1) = 84.15(11)°; Cl(2)-Cr(1)-Cl(1) = 93.14(5)°; S(1)-Cr(1)-Cl(1) = 92.18(5)°] of a formally neutral Me_2AlCl unit [Cr(1)-Cl(1) = 2.5825(15) Å] in which the Al atom is bonded to the N atom of the deprotonated ligand [Al(1)-N(1) = 1.990(4) Å]. The ligand N atom is forming with chromium [Cr(1)-N(1) = 2.179(4) Å] a bond distance as expected for a quaternary nitrogen.

Complex 9.7d. The complex is a symmetry-generated dimer (Figure 9.7) with the two metal centers each in a square-pyramidal coordination environment. Two aluminate {$(Al(CH_3)_2Cl)_2(\mu$-

Cl)} counter-anions unconnected with the dicationic dichromium units complete the structure. The bonding between the two metal centers is realized by two bridging chlorine atoms equatorially [N(1)-Cr(1)-Cl(1a) =161.4(2)°] and axially placed [Cl(1a)-Cr(1)-Cl(1)= 90.31(12)°; N(1)-Cr(1)-Cl(1) = 108.3(2)°, S(2)-Cr(1)-Cl(1) = 89.73(10)°, S(1)-Cr(1)-Cl(1) = 90.67(11)°] with respect to each metal atom. The two distances formed by the equatorial and axial chlorine are markedly different [Cr(1)-Cl(1) = 2.655(3) Å; Cr(1)-Cl(1a) = 2.349(4) Å] as is typical of the square-pyramidal coordination geometry of divalent chromium. The basal plane is formed by the two sulfur atoms [Cr(1)-S(1) = 2.476(3) Å; Cr(1)-S(2) = 2.475(3) Å], one quaternary N atom [Cr(1)-N(1) = 2.127(9) Å] and one of the two chlorine atoms. The Cr-N distance is in the usual range for a quaternary N atom bonded to chromium.

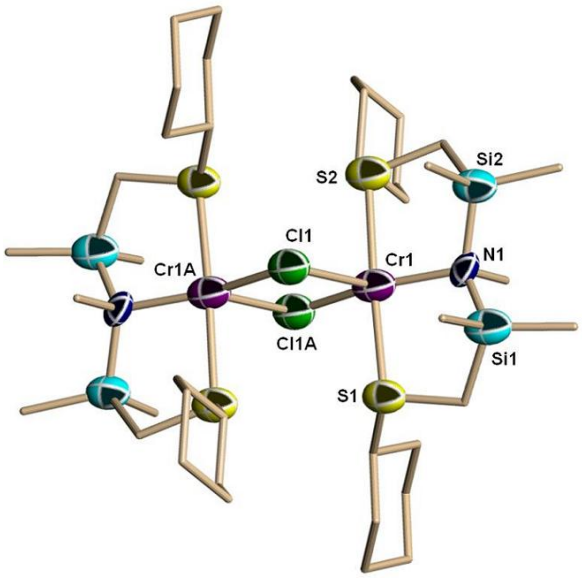


Figure 9.7. Partial thermal ellipsoid plot of **9.7d** with ellipsoids drawn at 50% probability.

9.5 Results and Discussion

The three ligands $CySCH_2Si(CH_3)_2N(H)Si(CH_3)_2CH_2SCy$ (**9.a**), *t*-$BuSCH_2Si(CH_3)_2N(H)Si(CH_3)_2CH_2St$-Bu (**9.b**), and $PhSCH_2Si(CH_3)_2N(H)Si(CH_3)_2CH_2SPh$ (**9.c**) used in this work were readily prepared via direct reaction of the 1,3-bis-chloromethyl-1,1,3,3-tetramethyl-disilazane with the appropriate thiolate anion. The N-methylated derivative of **9.a** $CySCH_2Si(CH_3)_2N(CH_3)Si(CH_3)_2CH_2SCy$ (**9.d**) was prepared via deprotonation followed by reaction with MeI. All the ligands have been reacted with either $CrCl_2(THF)_2$ or $CrCl_3(THF)_3$ but only in the cases where crystalline materials were obtained further investigation and testing was pursued. Oily or ill-characterized organometallic compounds have been discarded due to the lack of reproducibility of their analytical data. Ligand **9.a** in either protonated or deprotonated forms reacted with $CrCl_3(THF)_3$ to afford the corresponding monomeric $[CySCH_2Si(CH_3)_2N(H)Si(CH_3)_2CH_2SCy]CrCl_3$ **9.1a** or dimeric $\{[CySCH_2Si(CH_3)_2NSi(CH_3)_2CH_2SCy]CrCl(\mu\text{-}Cl)\}_2$ **9.2a** (Scheme 9.1).

Scheme 9.1

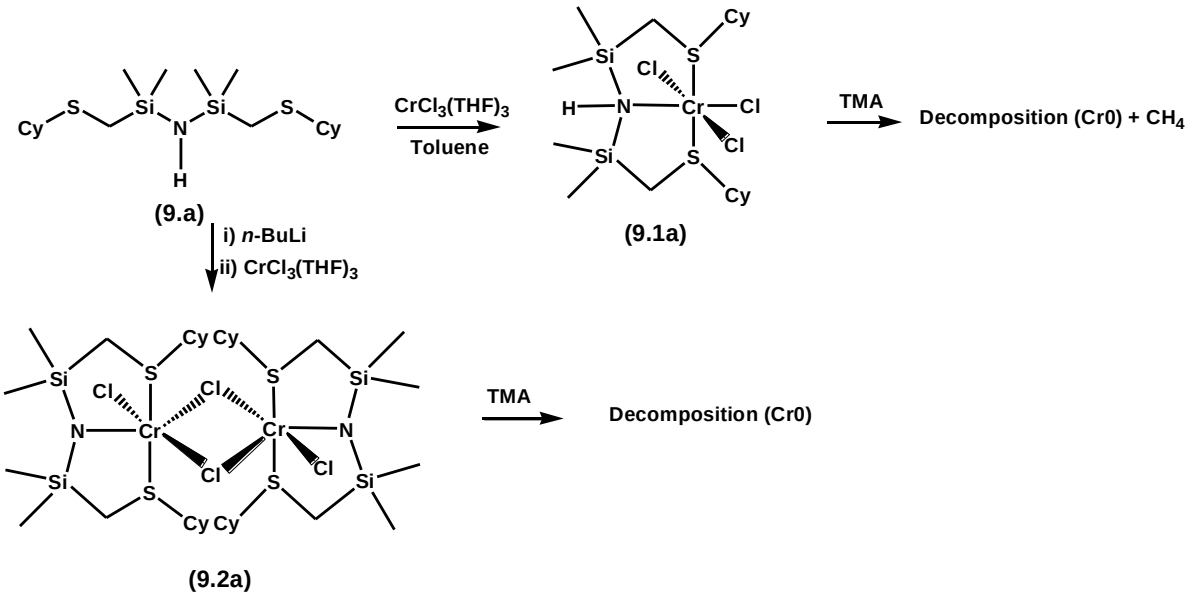


Table 9.2. Oligomerization results.[a]

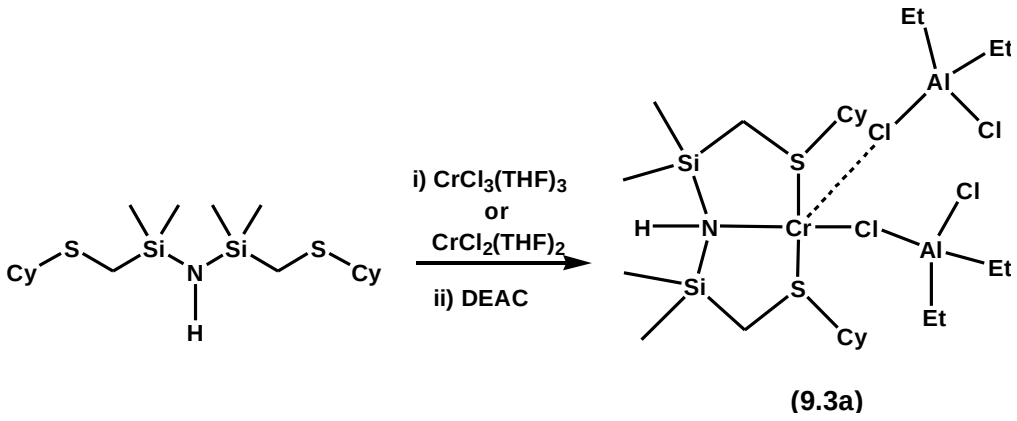
Catalyst	MAO (equiv)	Alkenes (mL)	PE (g)	Activity (g/mmolCr/h)	C6 (mol%)	C8 (mol%)	C10 (mol%)	C12 (mol%)	C14 (mol%)	C16 (mol%)	α_{avg}
(SNS)CrCl$_3$[8a]	1000	13.5	0.08	5824	> 98	traces	traces	traces	traces	traces	-
9.1a	1000	0	0	0	0	0	0	0	0	0	-
9.1a	500	0	0	0	0	0	0	0	0	0	-
9.2a	1000	0	0	0	0	0	0	0	0	0	-
9.2a	500	0	0	0	0	0	0	0	0	0	-
9.3a	0	0	0	0	0	0	0	0	0	0	-
9.3a	500	5	0.41	8970	29	25	18	13	8	7	0.75
9.3a	1000	25	0.25	44900	30	26	17	14	8	5	0.70
9.4a	1000	31	0.3	55600	29	26	18	14	8	5	0.71
9.4a	500	38	0.1	68200	28	25	19	13	9	6	0.73
9.4b	1000	0	0	0	0	0	0	0	0	0	-
9.5a	1000	9	0.2	16200	30	26	19	12	8	5	0.70
9.6a	0	0	0	0	0	0	0	0	0	0	-
9.6a	500	1	0.1	1790	31	27	19	11	8	4	0.67
9.6a	1000	25	0.53	44900	29	27	19	12	7	6	0.74
9.7d	1000	0	0	0	0	0	0	0	0	0	-

[a)] Conditions: 100 mL of toluene, loading 15 μmol of catalyst, 35 bar of ethylene, reaction temperature 60 °C, reaction time 60 min.

Both complexes displayed a disappointing non-catalytic behavior in spite of the close structural relationship of **9.1a** to that of the non-silylated SNS analogue[8a,4a-c] (Table 9.2). Thus, in an attempt to isolate species that could possibly clarify this comportment, both complexes were reacted with stoichiometric amounts of several alkyl aluminum. In the case of R_3Al [R = Me, Et], the reactions afforded separation of metallic chromium thus indicating that catalyst decomposition occurred during the attempted activation process. The extensive reductive decomposition of these two species is surprising. The SNS analogues of **9.1a** are in fact excellent catalyst precursors invariably producing under the same conditions cationic and *trivalent* [SNS-CrRCl]$_2^{(+)}$ derivatives, also catalytically active. Furthermore, these very same *trivalent* species may be also obtained from *divalent* precursors and only slowly decompose to metallic chromium leading to final catalyst deactivation. The decomposition of **9.2a** was also unexpected given that the deprotonated forms of SNS strongly stabilize chromium species, not even allowing reactivity with alkyl aluminum.[8] Instead, a one-pot reaction of **9.a** in the presence of Et_2AlCl with either Cr(III) or Cr(II) chlorides, did not produce metallic chromium but rather afforded the *divalent*

{[$CySCH_2Si(CH_3)_2N(H)Si(CH_3)_2CH_2SCy$]Cr($\mu$-Cl)$_2${$Al(CH_2CH_3)_2Cl$}$_2$ **9.3a** (Scheme 9.2). The noticeable features of these two reactions were that the ligand was not deprotonated by the aluminum alkyl function and that the divalent state was either formed or preserved with no sign of further decomposition to metallic chromium. The formation of **9.3a** from a trivalent precursor seems to be a typical one-electron reductive elimination of an unstable trivalent organochromium intermediate.[7c,10] Accordingly, preparation of **9.3a** from the divalent precursors afforded substantially higher yield.

Scheme 9.2

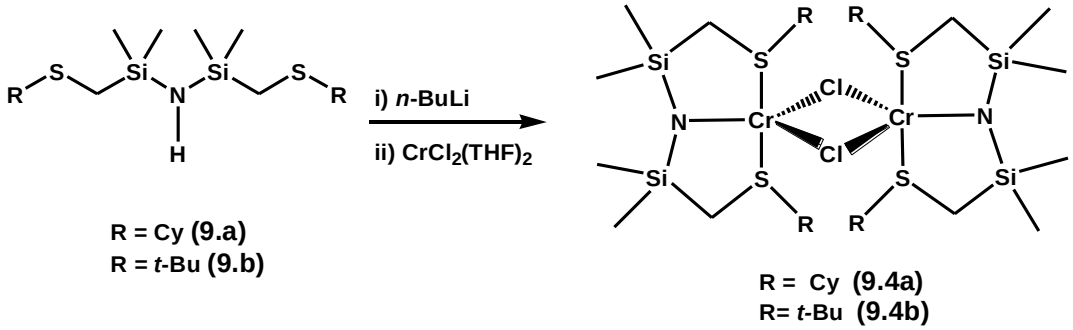


(9.3a)

The key to understand the remarkable selectivity of the standard SNS catalytic systems is the ability of this ligand to effectively support the redox dynamism of the metal center. In other words, the trivalent catalyst precursors may be reduced to Cr(II) and eventually to Cr(I). When further reduction to Cr(0) occurs, metallic chromium separates and the catalyst is deactivated. An enhanced tendency of Cr(II) to return to Cr(III) via disproportionation prevents the formation of S-F distribution of oligomers. Therefore, the overall excellent trimerization activity indicates that during the rapid inter-conversion of the three oxidation states, Cr(I) is the dominant one. In this scenario, our results seem to indicate that the introduction of the silyl moiety in the ligand

scaffold effectively blocks the redox dynamism. In the case of **9.3a**, Cr(III) was irreversibly reduced to Cr(II) which, as indicated by the S-F catalytic behavior, is the dominant oxidation state of the catalytic cycle. This also indicates that no further significant reduction to the monovalent state occurs in this case. When it does, as for **9.1a** and **9.2a**, further rapid decomposition to metallic chromium leads to catalyst deactivation. The puzzling difference in behavior between **9.3a**, **9.1a** and **9.2a** can only be ascribed to the larger content of chlorine in the activator (chlorine effect).

Scheme 9.3



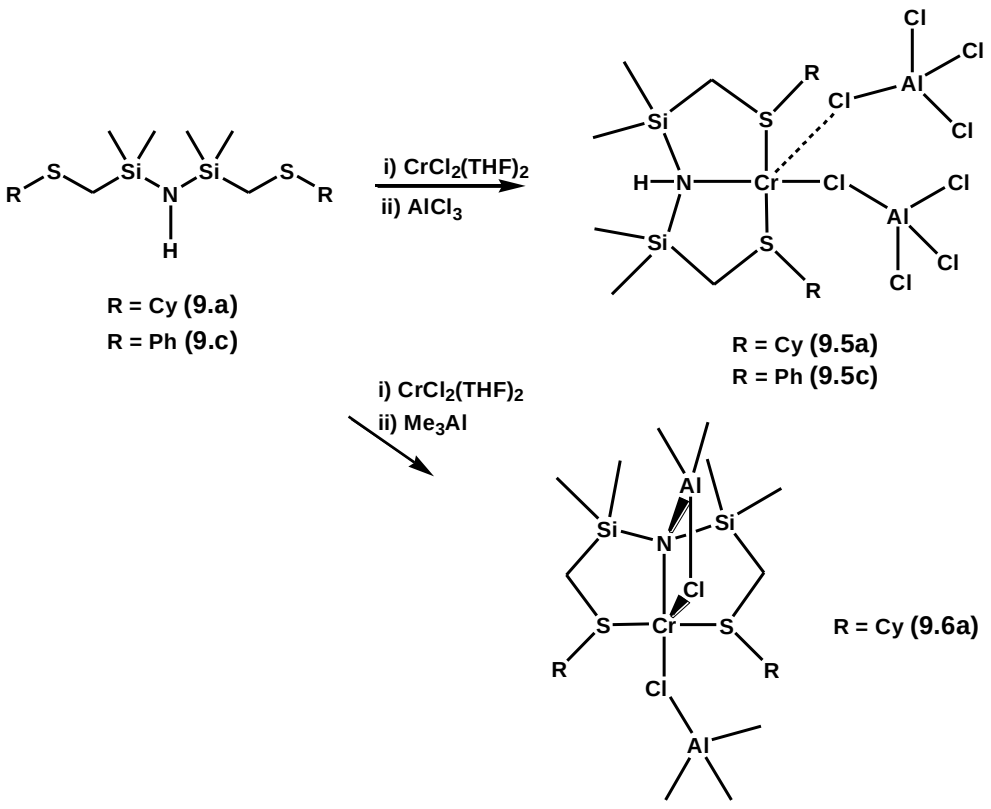
The N-H function of the Si-SNS and SNS ligands also plays a significant role. While in the case of SNS ligands deprotonation afforded stable divalent complexes producing S-F distribution, in the case of the *trivalent* **9.2a**, it gave only extensive decompositions. We have therefore prepared the divalent chromium analogue. The reaction was successful in the case of both **9.a** and **9.b** affording the two nearly iso-structural divalent complexes $\{[CySCH_2Si(CH_3)_2NSi(CH_3)_2CH_2SCy]Cr(\mu\text{-}Cl)\}_2$ (**9.4a**) and $\{[(t\text{-}Bu)S\ CH_2Si(CH_3)_2NSi\ (CH_3)_2CH_2S(t\text{-}Bu)]Cr(\mu\text{-}Cl)\}_2$ (**9.4b**) in crystalline form (Scheme 9.3).

As anticipated, complex $\{[CySCH_2Si(CH_3)_2NSi(CH_3)_2CH_2SCy]Cr(\mu\text{-}Cl)\}_2$ (**9.4a**) gave a very good activity as S-F catalysts therefore indicating that the divalent state was preserved in these cases during the activation process. Therefore, the absence of the amino hydrogen atom

seems to play a particularly important role in stabilizing divalent derivatives and inhibiting further reduction to the seemingly unstable, and yet catalytically active, monovalent state. Complex $\{[(t\text{-Bu})SCH_2Si(CH_3)_2NSi(CH_3)_2CH_2S(t\text{-Bu})]Cr(\mu\text{-Cl})\}_2$ (**9.4b**) produced no activity upon MAO activation possibly due to steric effect of the *t*-Bu groups on sulfur atoms.

To further clarify the interaction of **9.4** with aluminate species we have carried out *in situ* complexation in the presence of either $AlCl_3$ or $AlMe_3$ and using divalent instead of trivalent chromium salts. As mentioned above, trivalent complexes afforded metallic Cr in the case of $AlMe_3$. In the cases of ligands **9.a** and **9.c** and $AlCl_3$, two isostructural complexes $\{[CySCH_2Si(CH_3)_2N(H)Si(CH_3)_2CH_2SCy]Cr(\mu\text{-Cl})_2\}\{AlCl_3\}_2$ **9.5a** and $\{[PhSCH_2Si(CH_3)_2N(H)Si(CH_3)_2CH_2SPh]C(\mu\text{-Cl})_2\}\{AlCl_3\}_2$ **9.5c** have been obtained (Scheme 9.4). The structures of these two species indicate that no disproportionation occurred.

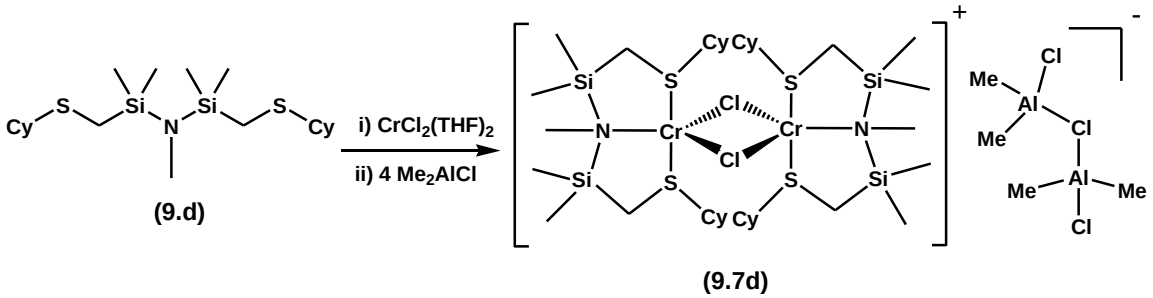
Scheme 9.4



The result of the reaction with $AlMe_3$ affording {[$CySCH_2Si(CH_3)_2N(Al(CH_3)_2$-$\mu$-$Cl)Si(CH_3)_2CH_2SCy]Cr(\mu$-$Cl)$}{$Al(CH_3)_3$} (**9.6a**) was particularly informative, surprisingly showing ligand deprotonation and retention of an aluminate residue bridged to the Cr-N moiety. This structure suggests a possible general pathway for ligand abstraction when catalyst decomposition occurs. The fact that in the case of non-silylated SNS the aluminates are unable to deprotonate the ligand (due to lower acidity) prevents coordination of Al to the N atom and ligand abstraction from the monovalent chromium intermediate becomes more difficult: hence the very high selectivity of that particular catalytic system. In the case of **9.6a** the original divalent state has been preserved during its formation. Given the instability of **9.2a** with the same activator, we must necessarily conclude that, during the attempted activation of trivalent precursors, the divalent state is bypassed when the catalyst is decomposed to metallic chromium.

To further evaluate this point we have also methylated ligand **9.a** at the N atom. The complexation to chromium was successful only in the presence of Me_2AlCl and if a *divalent* chromium precursor was used. The reaction afforded the catalytically inactive divalent {[$CySCH_2Si(CH_3)_2N(CH_3)Si(CH_3)_2CH_2SCy]Cr(\mu$-$Cl)$}$_2${$(Al(CH_3)_2Cl)_2)(\mu$-$Cl)$}$_2$ (**9.7d)** that was isolated in crystalline form and fully characterized (Scheme 9.5). In the case of *trivalent* chromium once again neither clearly defined species nor catalytic activity were obtained.

Scheme 9.5



(9.d) **(9.7d)**

Based on our current understanding of the redox mechanism for chromium-catalyzed tri- and tetramerization, the role of the ligand is of stabilizing the doubly alkylated trivalent chromium species prior to its reductive elimination to the catalytically active monovalent chromium state. This is a crucial step for the effective progression through the catalytic cycle. Without this important effect from the ligand, the alkylated trivalent chromium center will not undergo reductive elimination to form the active monovalent chromium species. Instead, it will initially reduce to the divalent state affording a Schultz-Flory distribution of oligomers or further decompose to the inactive zero-valent chromium state.

9.6 Conclusions

In conclusion, we have herein reported the results of an exploratory study on a modification of the ethylene trimerization SNS ligand system. The introduction of two Me_2Si units in the ligand scaffold and in the positions contiguous to the nitrogen atom resulted in a loss of redox dynamism. Thus, the consequent disappearance of selectivity has to be ascribed to the instability of both the tri- and monovalent states both readily decomposing to metallic chromium. Instead, depending on the conditions it is possible to stabilize divalent species that, by not longer possessing redox dynamism, simply produce the expected S-F distribution of oligomers.

Both work on SNS and the Si-SNS did not allow for the isolation of a single component selective catalysts. Therefore, in the next chapter, we have introduced one more important modification in the ligand frame to introduce better stabilization of critical intermediates.

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Chapter Ten

Publication:

Albahily. K.; Shaikh, Y.; Ahmed, Z.; Korobkov, I.; Gambarotta, S.; Duchateau, R. *Organometallics*. (Submitted)

New Insight into the Ethylene Trimerization Mechanistic Pathway of the Cr-SNS System: Isolation of Unprecedented Single Component Trimerization Catalyst

10.1 Introduction

Current research on ethylene oligomerization is primarily focused on understanding the factors responsible for both activity and selectivity with the ultimate goal of tailoring new and better performing catalysts.[1] The Sasol SNS system [$CySCH_2CH_2N(H)CH_2CH_2SCy$] with its ideal selectivity and activity is one of the most prominent examples of a perfect catalytic system.[2] Since the announcement of its discovery, important mechanistic questions have been raised about the role of ligand geometry, proticity and denticity, and metal oxidation state responsible for the remarkable performance of this system.[3] To address these fundamental questions, we have been interested in isolating and characterizing the catalytically active species generated by the interaction of trivalent catalyst precursors with the aluminate activator.[4] This work has identified chromium redox dynamism in the oligomerization catalytic cycle, readily interconverting the three critical oxidation states (I, II, and III) through a continuous series of dis- and comproportionations as well as reductions. Most of these transformations directly involve alkyl aluminum activators. This work has also required a number of ligand modifications. For example, in order to better understand the role of the N-H in the SNS ligand

and to improve the ability of the ligand to stabilize the catalytically selective monovalent state,[5] we have replaced the N donor atom with a central pyridine ring [pyridine-SNS].[6,4a] Previous catalytic testing[2b,5] of the trivalent derivative of this modified SNS ligand confirmed that the complex is a selective ethylene trimerization catalyst precursor, although its activity was somewhat reduced when compared to the original system. Furthermore, it was possible to conclusively link the chromium divalent state to the appearance of a Schulz-Flory distribution of oligomers.[7] Given the extremely high selectivity of the trivalent precursors as a trimerization catalyst, we were led to believe that the two oxidation states (II and III) are not so readily interchanged in this particular catalytic cycle. In turn, this has prompted the idea that the possibility for introducing selectivity in an oligomerization system may rely on the possibility for the trivalent state to undergo two-electron reduction and form the monovalent state without passing through the divalent state.

Following up the previous work, we have now attempted to generate catalytically active species by reaction of the trivalent precursor pyridine-SNS-$CrCl_3$ with aluminates. Herein we describe our findings.

10.2 Experimental Part

All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried using an aluminum oxide solvent purification system. The liquid product mixtures were analyzed by using a CP 9000 gas chromatograph (GC) equipped with a 30 mL × 0.32 mm id, capillary CP volamine column and a FID detector. All single-point experiments were performed in duplicate. The yield was determined by ^{1}H-NMR spectroscopy (Varian Mercury 400 MHz spectrometer). Samples for magnetic susceptibility were pre-weighed inside a dry box equipped with an analytical balance and measured on a Johnson Matthey Magnetic Susceptibility balance. Elemental analysis

was carried out with a Perkin-Elmer 2400 CHN analyzer. Data for X-ray crystal structure determination (Table 10.1) were obtained with a Bruker diffractometer equipped with a 1K Smart CCD area detector. Trimethylaluminum were purchased from Strem. Methylaluminoxane (MAO, 10% in toluene) was purchased from Aldrich. The ligand (2,6-CH_2S-*t*-Bu)$_2C_5H_5N$ (**10.a**) was prepared according to a literature procedure.[8]

Preparation of (2,6-CH_2S-*t*-Bu)$_2C_5H_5N$ (10.a)

A solution of 2-methyl-2-propanethiol (5.02 g, 55.7 mmol) in THF (10 mL) was combined with a suspension of potassium hydride (2.44 g, 61.0 mmol) in THF (50 mL) at 0 ^oC. The mixture was stirred at room temperature for 2 h. The resulting solution was added at 0 ^oC dropwise over 10 min to a solution of 2,6-*bis*(chloromethyl)pyridine (4.9 g, 27.83 mol) in THF (50 mL), stirred at room temperature for 18 h and subsequently filtered. The solvent was removed *in vacuo* to yield **10.a** (6.8 g, 86 %) as an analytically pure pale yellow powder. ^{1}H-NMR ($CDCl_3$, 300 MHz, 300 K) δ 1.33 (s, 18H, C(*CH*$_3$)$_3$) 3.89 (s, 4H, py-*CH*$_2$-S) 7.28 (d, 2H, *J* = 6 Hz, *pyridine*) 7.57 (t, 1H, *J* = 6 Hz, *pyridine*).^{13}C-NMR ($CDCl_3$, 75 MHz, 300 K) δ 30.97 (C(*CH*$_3$)$_3$) 35.57 (py-*CH*$_2$-S) 43.09 (*C*(CH$_3$)$_3$) 121.18, 136.96, 158.55 (*pyridine*). MS (ESI) *m/z* $(M+H)^+$ = 284.070. El. Anal. Calcd. (found) for $C_{15}H_{25}NS_2$: C 63.55 (63.57), H 8.89 (8.91), N 4.94 (4.95).

Preparation of (2,6-CH_2S-*n*-Decyl)$_2C_5H_5N$ (10.b)

A solution of 1-decanethiol (9.9 g, 56.80 mmol) in THF (100 mL) was combined with a suspension of potassium hydride (2.49 g, 62.48 mmol) in THF (50 mL) at 0 ^oC. The mixture was stirred at room temperature for 2 h. The resulting solution was added at 0 ^oC dropwise over 10 min to a THF (50 mL) solution of 2,6-*bis*(chloromethyl)pyridine (5.0 g, 28.4 mol), stirred at room temperature for 18 h and subsequently filtered. The solvent was removed *in vacuo* to yield

10.b (11.5 g, 89%) as an analytically pure pale yellow powder. ^{1}H-NMR ($CDCl_3$, 300 MHz, 300 K) δ 0.86 (t, 6H, *J* = 6.9 Hz, $S(CH_2)_9\mathit{CH_3}$) 1.15-1.40 (m, 28H, $SCH_2CH_2(\mathit{CH_2})_7CH_3$) 1.45-1.65 (q, 4H, *J* = 7.5 Hz, $SCH_2\mathit{CH_2}(CH_2)_7CH_3$) 2.40-2.55 (t, 4H, *J* = 7.5 Hz, $S\mathit{CH_2}CH_2(CH_2)_7CH_3$) 3.79 (s, 4H, pyridine-$\mathit{CH_2}$-S) 7.22 (d, 2H, *J* = 7.5 Hz, *pyridine*) 7.59 (t, 1H, *J* = 7.5 Hz, *pyridine*).^{13}C-NMR ($CDCl_3$, 75 MHz, 300 K) δ 14.06 ($S(CH_2)_9\mathit{CH_3}$) 22.62, 28.83, 29.18, 29.24, 29.26, 29.48, 29.51, 31.68 ($SCH_2(\mathit{CH_2})_8CH_3$) 31.84 ($S\mathit{CH_2}(CH_2)_8CH_3$) 38.07 (pyridine-$\mathit{CH_2}$-S) 120.89, 137.11, 158.45 (*pyridine*). MS (ESI) *m/z* $(M+H)^+$ = 452.6. El. Anal. Calcd. (found) for $C_{27}H_{49}NS_2$: C 71.77 (71.75), H 10.93 (10.37), N 3.10 (3.11).

Preparation of [(2,6-CH_2S-*t*-Bu)$_2$$C_5H_5N$]$CrCl_3$ (10.1a)

A solution of **10.a** (0.284 g, 1.0 mmol) in toluene (10 mL) was treated with $CrCl_3(THF)_3$ (0.375 g, 1.0 mmol). The mixture was refluxed for 2 h and then allowed to stir at room temperature for 20 h. The insoluble product was filtered and washed with diethyl ether (10 mL). The green powder was dissolved in CH_3CN (3 mL) and then stored in a freezer at -40 ^{o}C for 5 days. The resulting green crystals were filtered and washed with cold hexanes (10 mL) and dried *in vacuo* affording **10.1a** (0.239 g, 0.54 mmol, 54 %). μ_{eff} = 3.85 μ_B. El. Anal. Calcd. (found) for $C_{15}H_{25}Cl_3CrNS_2$: C 40.77 (40.62), H 5.70 (5.65), N 3.17 (3.11).

Preparation of [(2,6-CH_2S-*n*-decyl)$_2$$C_5H_5N$]$CrCl_3$ (10.1b)

A solution of **10.b** (0.452 g, 1.0 mmol) in toluene (10 mL) was treated with $CrCl_3(THF)_3$ (0.375 g, 1.0 mmol). The mixture was refluxed for 1 h and then allowed to stir at room temperature for 20 h. The suspension was centrifuged and the supernatant concentrated and stored in a freezer at -40 ^{o}C for 4 days. The resulting product was filtered and washed with cold hexanes (10 mL) and dried *in vacuo* affording **10.1b** as green crystalline material (0.128 g, 0.21

mmol, 21%). μ_{eff} = 3.81 μ_B. El. Anal. Calcd. (found) for $C_{27}H_{49}Cl_3CrNS_2$: C 53.15 (53.11), H 8.09 (8.10), N 2.30 (2.31).

Preparation of [(2,6-CH_2S-*t*-Bu)$_2C_5H_5N$]$CrCl_2$(THF) (10.2a)

A solution of **10.a** (0.283 g, 1.0 mmol) in THF (10 mL) was treated with $CrCl_2(THF)_2$ (0.268 g, 1.0 mmol). The mixture was refluxed for 10 minutes and then stirred at room temperature for 20 h. The resulting suspension was centrifuged and the supernatant concentrated and stored in a freezer at -40 ^oC for 7 days. The resulting brown crystalline **10.2a** was filtered and washed with cold hexanes (10 mL) and dried *in vacuo* (0.244 g, 0.51 mmol, 51%). μ_{eff} = 4.95 μ_B. El. Anal. Calcd. (found) for $C_{19}H_{33}Cl_2CrNOS_2$: C 47.69 (47.77), H 6.95 6.94), N 2.93 (2.91).

Preparation of {[2,6-CH_2S(*t*-Bu)]$_2C_5H_5N$}CrMe(μ-Cl-$AlMe_3$)$_2$ (10.3a).

A solution of **10.a** (0.283 g, 1.0 mmol) in toluene (10 mL) was treated with $CrCl_3(THF)_3$ (0.375 g, 1.0 mmol). The mixture was refluxed for 10 minutes and then stirred at room temperature for 4 h. After cooling to -40 ^oC, trimethyl aluminum (0.720 g 10.0 mmol) was added dropwise and the mixture stirred for 30 minutes. The suspension was centrifuged and the supernatant concentrated and then layered with hexanes (3 mL) and stored in a freezer at -40 ^oC for 3 days. The resulting green crystals were filtered, washed with cold hexanes (10 mL) and dried *in vacuo* affording **10.3a** (0.231 g, 0.41 mmol, 41%) as green crystals. μ_{eff} = 3.88 μ_B. El. Anal. Calcd. (found) for $C_{22}H_{46}Al_2Cl_2CrNS_2$: C 46.72 (46.75), H 8.20 (8.23), N 2.48 (2.50).

10.3 X-ray Data

Table 10.1. Crystal Data and Structure Analysis Results of Complexes **10.1a-10.3a**.

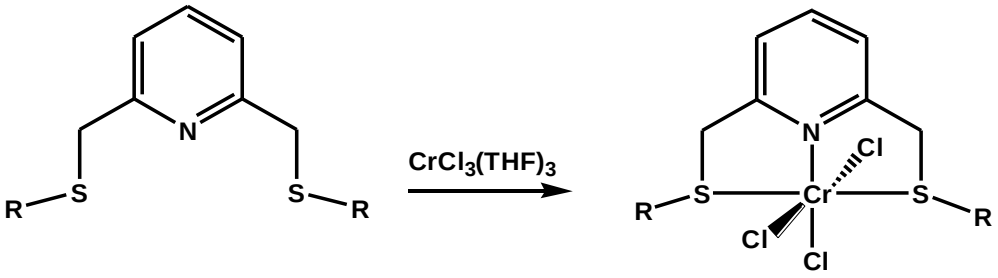
	10.1a	**10.1b**	**10.2a**	**10.3a**
formula	$C_{17}H_{28}Cl_3CrN_2S_2$	$C_{27}H_{49}Cl_3CrNS_2$	$C_{19}H_{33}Cl_2CrNOS_2$	$C_{44}H_{92}Al_4Cl_4Cr_2N_2S_4$
Mw	482.88	610.14	478.48	1131.16
space group	Monoclinic, P2(1)/c	Monoclinic, P2(1)/c	Monoclinic ,P2(1)/c	Triclinic , P-1
***a* (Å)**	9.0956(3)	16.353(3)	11.9048(14)	9.2413(11)
***b* (Å)**	13.9065(4)	13.518(2)	12.2321(14)	18.245(2)
***c* (Å)**	17.8684(5)	14.550(2)	17.021(2)	21.310(3)
***α*, (deg)**	90	90	90	112.897(2)
***β*, (deg)**	92.4240(10)	101.877(4)	107.792(2)	100.925(2)
***γ*, (deg)**	90	90	90	90.513(2)
***V* (Å^3)**	2258.11(12)	3147.6(9)	2360.0(5)	3236.4(7)
Z	4	4	4	2
radiation(Å)	0.71073	0.71073	0.71073	0.71073
***T* (K)**	200(2)	200(2)	203(2)	210(2)
D_{calcd} (g cm$^-$)	1.420	1.288	1.347	1.161
μ_{calcd} (mm^{-1})	1.050	0.767	0.897	0.712
***F*$_{000}$**	1004	1300	1008	1204
***R*, *Rw*^{2a}**	0.0346,0.0786	0.0698, 0.1551	0.0551, 0.1181	0.0700, 0.1847
GoF	1.011	1.072	0.968	1.022

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

10.4 Results and Discussion

Treatment of $CrCl_3(THF)_3$ with $(2,6\text{-}CH_2SR)_2C_5H_5N$ [R = *t*-Bu (**10.a**), *n*-decyl (**10.b**)] afforded the corresponding $[(2,6\text{-}CH_2SR)_2C_5H_5N]CrCl_3$ [R = *t*-Bu (**10.1a**), *n*-decyl (**10.1b**)] (Scheme 10.1). The purpose of the *n*-decyl groups was to improve the generally poor solubility of these catalyst precursors.

Scheme 10.1



R = *t*-Bu (10.a)
***n*-decyl (10.b)**

R = *t*-Bu (10.1a)
***n*-decyl (10.1b)**

The structure of **10.1a** (Figure 10.1) shows a distorted octahedral [S(2)-Cr(1)-S(1) = 167.10(2)°; N(1)-Cr(1)-Cl(1) = 88.45(5)°; Cl(2)-Cr(1)-S(1) = 95.47(2)°] trivalent chromium center surrounded by the three meridionally-oriented donor atoms of the ligand [Cr(1)-N(1) = 2.0724(17) Å; Cr(1)-S(1) = 2.4460(6) Å; Cr(1)-S(2) = 2.4277(6) Å]. The three chlorine atoms occupy the three remaining meridional positions [Cr(1)-Cl(1) = 2.3072(6) Å; Cr(1)-Cl(2) = 2.2921(6) Å; Cr(1)-Cl(3) = 2.3242(6) Å]. The distortion of the coordination octahedron is probably caused by the compression of bond angles introduced by both Cr and S in each of the two five-member cycles formed by the two sulfur and pyridine N atoms.

The structure of **10.1b** (Figure 10.2) shows a distorted octahedral [S(2)-Cr(1)-S(1) = 162.4(3)°; N(1)-Cr(1)-Cl(1)= 90.03(16)°; Cl(2)-Cr(1)-S(1) = 97.11(19)°] trivalent chromium center surrounded by the three meridionally-oriented donor atoms of the ligand [Cr(1)-S(1) =

2.476(7) Å; Cr(1)-S(2) = 2.379(9) Å; Cr(1)-N(1) = 2.066(6) Å]. The three chlorine atoms occupy the three remaining meridional positions [Cr(1)-Cl(1) = 2.293(2) Å; Cr(1)-Cl(2) = 2.282(2) Å; Cr(1)-Cl(3) = 2.319(14) Å]. Similar to **10.1a,** the distortion of the coordination octahedron is probably caused by the same reason.

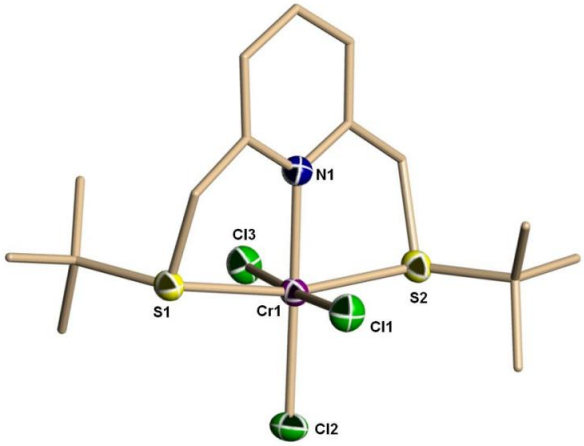


Figure 10.1. Partial thermal ellipsoid plot of **10.1a** with ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (°): Cr(1)-N(1) = 2.0724(17), Cr(1)-Cl(2) = 2.2921(6), Cr(1)-Cl(1) = 2.3072(6), Cr(1)-Cl(3) = 2.3242(6), Cr(1)-S(2) = 2.4277(6), Cr(1)-S(1) = 2.4460(6), N(1)-Cr(1)-Cl(2) = 178.77(5), N(1)-Cr(1)-Cl(1) = 88.45(5), Cl(2)-Cr(1)-Cl(1) = 90.88(2), N(1)-Cr(1)-Cl(3) = 89.01(5), Cl(2)-Cr(1)-Cl(3) = 91.69(2), Cl(1)-Cr(1)-Cl(3) = 177.04(2), N(1)-Cr(1)-S(2) = 83.85(5), Cl(2)-Cr(1)-S(2) = 97.26(2), Cl(1)-Cr(1)-S(2) = 98.67(2), Cl(3)-Cr(1)-S(2) = 79.55(2), N(1)-Cr(1)-S(1) = 83.43(5), Cl(2)-Cr(1)-S(1) = 95.47(2), Cl(1)-Cr(1)-S(1) = 83.13(2), Cl(3)-Cr(1)-S(1) = 98.08(2), S(2)-Cr(1)-S(1) = 167.10(2).

Divalent analogues were also prepared but successful crystallization was possible only in the case of the *t*-Bu derivative {[2,6-CH_2S(t-Bu)]$_2C_5H_5N$}$CrCl_2$(THF) (**10.2a**) (Scheme 10.2), the *n*-decyl derivative only forming oily materials. The divalent chromium atom displays the axially distorted octahedral geometry not infrequently observed with d^4 species (Figure 10.3). The equatorial square plane around the divalent chromium center [N(1)-Cr(1)-Cl(1) = 91.85(9) Å; N(1)-Cr(1)-Cl(2) = 91.53(9) Å, O(1)-Cr(1)-N(1) = 179.2(3) Å, O(1)-Cr(1)-Cl(1) = 88.0(4) Å, O(1)-Cr(1)-Cl(2) = 88.7(4) Å] is defined by the two chlorines [Cr(1)-Cl(1) = 2.4096(13) Å; Cr(1)-Cl(2)= 2.3882(14) Å], the N atom of the pyridine ring [Cr(1)-N(1) = 2.160(3) Å], and the

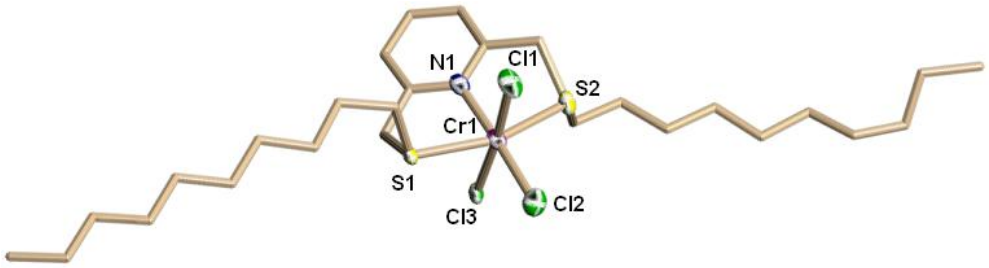
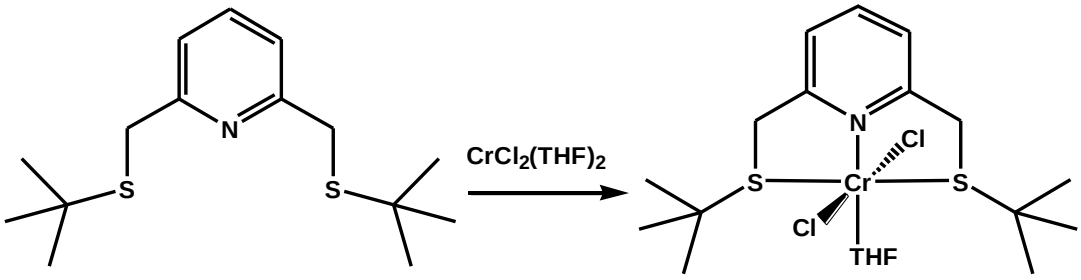


Figure 10.2. Partial thermal ellipsoid plot of **10.1b** with ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (°): Cr(1)-N(1) = 2.066(6), Cr(1)-Cl(1) = 2.293(2), Cr(1)-Cl(2) = 2.282(2), Cr(1)-Cl(3) = 2.319(14), Cr(1)-S(1) = 2.476(7), Cr(1)-S(2) = 2.379(9), N(1)-Cr(1)-Cl(1) = 90.03(16), Cl(2)-Cr(1)-Cl(1) = 91.41(8), Cl(2)-Cr(1)-S(2) = 100.4(3), Cl(2)-Cr(1)-S(2) = 100.4(3), Cl(2)-Cr(1)-S(2) = 100.4(3), Cl(3)-Cr(1)-S(2) = 95.9(9), N(1)-Cr(1)-S(1) = 80.9(2), Cl(2)-Cr(1)-S(1) = 97.11(19), Cl(1)-Cr(1)-S(1) = 91.30(16), Cl(3)-Cr(1)-S(1) = 85.0(9), S(2)-Cr(1)-S(1) = 162.4(3).

coordinated THF molecule [Cr(1)-O(1) = 2.069(9) Å]. The two sulfur atoms are located on the perpendicular axis of the ideal octahedron [S(1)-Cr(1)-S(2) = 157.90(4)°] centered on chromium. The Jahn-Teller axial distortion is clearly emphasized by the long Cr-S distances at the edge of the bonding range [Cr(1)-S(1) = 2.7420(13) Å; Cr(1)-S(2) = 2.7654(13) Å].

Scheme 10.2



(10.a) **(10.2a)**

The catalytic activity of the three complexes is well comparable to those of the Ph and Cy derivatives of the same ligand frame with the trivalent derivatives **10.1a** and **10.1b** selectively

affording 1-hexene with moderate/good activity and high purity (Table 10.2). The higher activity of **10.1b** is likely to be ascribed to its higher solubility. As expected, the divalent derivative **10.2a** only produces a S-F distribution of LAO. Small amounts of polymer were also ubiquitously present.

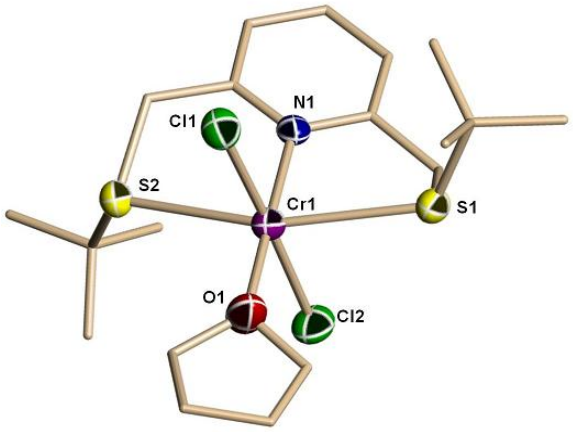


Figure 10.3. Partial thermal ellipsoid plot of **10.2a** with ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (°): Cr(1)-O(1) = 2.069(9), Cr(1)-N(1) = 2.160(3), Cr(1)-Cl(2) = 2.3882(14), Cr(1)-Cl(1) = 2.4096(13), Cr(1)-S(1) = 2.7420(13), Cr(1)-S(2) = 2.7654(13), N(1)-Cr(1)-Cl(1) = 91.85(9), N(1)-Cr(1)-S(1) = 79.40(9), O(1)-Cr(1)-S(1) = 99.9(3), Cl(1)-Cr(1)-S(1) = 99.48(4), N(1)-Cr(1)-S(2) = 78.54(9), Cl(2)-Cr(1)-Cl(1) = 176.59(5), Cl(1)-Cr(1)-S(2) = 82.55(4), O(1)-Cr(1)-Cl(1) = 88.0(4), Cl(2)-Cr(1)-S(1) = 81.64(4), O(1)-Cr(1)-Cl(2) = 88.7(4), O(1)-Cr(1)-N(1) = 179.2(3), S(1)-Cr(1)-S(2) = 157.90(4).

The distinctive difference in catalytic behavior between the two oxidation states further reiterates that in the quest for trimerization catalysts the divalent state must be avoided. It also reiterates that the divalent state is unlikely to play any role in the ring-expansion redox mechanism responsible for the selective formation of 1-hexene. The small excess of 1-hexene observed in the S-F distribution of oligomers generated by **10.2a** indicates that a small extent of reduction is also afforded by the divalent precursor.

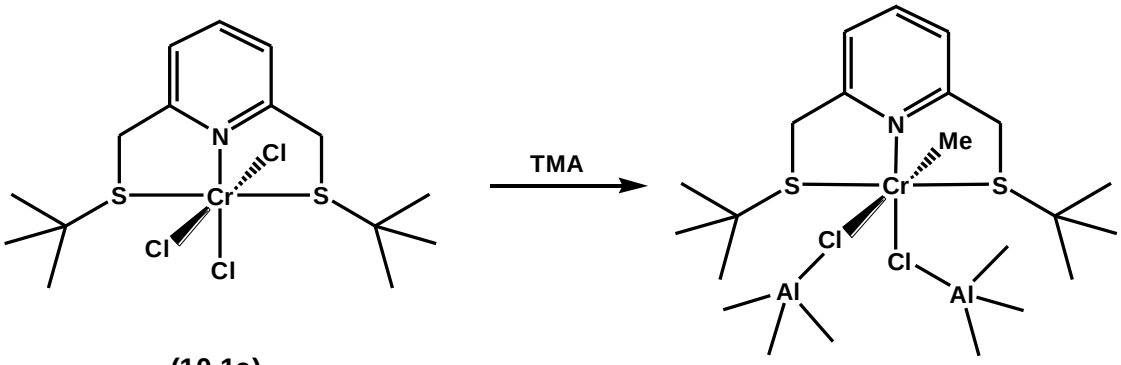
Table 10.2. Oligomerization results.[a]

Catalyst	MAO (equiv)	Alkenes (mL)	PE (g)	Activity (g/mmolCr/h)	C6 (mol%)	C8 (mol%)	C10 (mol%)	C12 (mol%)	C14 (mol%)	C16 (mol%)
(SNS)CrCl3	1000	13.5	0.08	308	> 98	traces	traces	traces	traces	traces
10.3a	0	2	0.4	59	99.99	0	0	0	0	0
10.1a	1000	6.5	1.2	187	99.99	0	0	0	0	0
10.1b	1000	8	1.1	217	99.99	0	0	0	0	0
10.2a	1000	5	0.96	149	47	26	16	7	3	1

[a)] Conditions: 100 mL of toluene, loading 30 μmol of catalyst, 35 bar of ethylene, reaction temperature 60 °C, reaction time 60 min.

The reactivity of the three complexes was examined with a variety of aluminum alkyls. The results were rather discouraging since only oily or ill-defined materials have been systematically obtained. However, in the case of the reaction of **10.1a** with TMA it was possible to isolate a new complex {[2,6-CH_2S(*t*-Bu)]$_2C_5H_5N$}CrMe(μ-Cl-$AlMe_3$)$_2$ (**10.3a**) in crystalline form (Scheme 10.3).

Scheme 10.3



(10.1a) **(10.3a)**

The structure of the complex shows a trivalent chromium atom in a distorted octahedral geometry (Figure 10.4) [S(1)-Cr(1)-S(2) = 158.99(6)°; C(16)-Cr(1)-Cl(1) = 178.10(19)°; [N(1)-Cr(1)-Cl(2) = 175.56(13)°]. The coordination polyhedron is defined by the three donor atom of the meridionally arranged ligand system forming bond distances in the expected range [Cr(1)-

S(1) = 2.4385(18) Å; Cr(1)-S(2) = 2.4386(17) Å; Cr(1)-N(1) = 2.061(14) Å]. The remaining three meridional coordination sites are occupied by one carbon atom of a terminally bonded Me group [Cr(1)-C(16) = 2.070(6) Å] and two *cis*-positioned chlorine atoms [Cr(1)-Cl(1) = 2.5399(6) Å; Cr(1)-Cl(2) = 2.3378(16) Å] each bridging one of the Al atoms of the two Me_3Al residues.

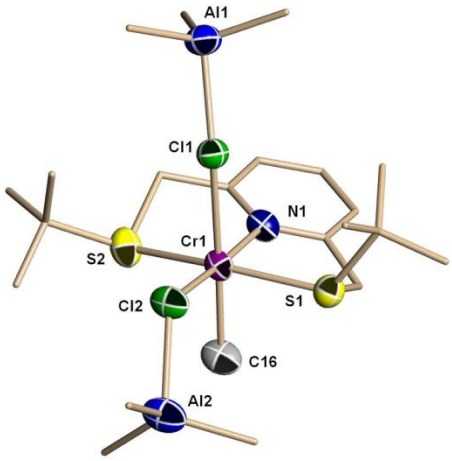
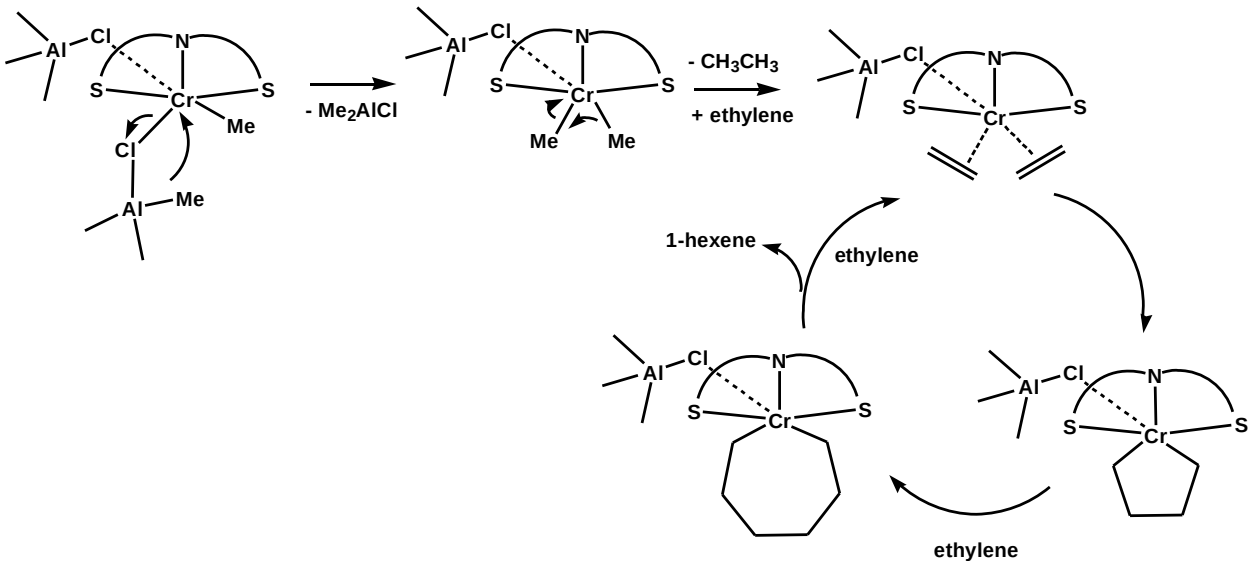


Figure 10.4. Partial thermal ellipsoid plot of **10.3a** with ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (°):Cr(1)-N(1) = 2.061(4), Cr(1)-C(16) = 2.070(6), Cr(1)-Cl(2) = 2.3378(16), Cr(1)-S(1) = 2.4385(18), Cr(1)-S(2)= 2.4386(17), Cr(1)-Cl(1) = 2.5399(16), N(1)-Cr(1)-C(16) = 92.0(2), N(1)-Cr(1)-Cl(2) = 175.56(13), C(16)-Cr(1)-Cl(2) = 92.43(18), N(1)-Cr(1)-S(1) = 79.59(14), C(16)-Cr(1)-S(1) = 85.5(2), Cl(2)-Cr(1)-S(1) = 101.27(7), N(1)-Cr(1)-S(2) = 83.04(14), C(16)-Cr(1)-S(2) = 83.4(2), Cl(2)-Cr(1)-Cl(1) = 86.07(5), S(1)-Cr(1)-S(2) = 158.99(6), N(1)-Cr(1)-Cl(1) = 89.53(13), C(16)-Cr(1)-Cl(1) = 178.10(19), S(1)-Cr(1)-Cl(1) = 93.69(6).

Complex **10.3a** is a single-component self-activating trimerization catalyst requiring no further activation to produce highly pure 1-hexene. Furthermore the structure of **10.3a** gives some hint about the activation pathways clearly emphasizing the two primary functions of the aluminate activators as both alkylating agents and Lewis acids. The fact that no reduction has been observed at this stage is not surprising since trivalent organo-chromium complexes of both the modified and regular SNS systems have been already previously isolated starting from either tri- a well as divalent precursors.[4a,5] Yet, the single component trimerization activity indicates

that a two-electron reduction must necessarily occur under the thermal conditions required by the reaction. Scheme 10.4 offers a possible rationalization for the self-activation pathway. If one assumes dissociation of a Me_2AlCl residue (incidentally similar to those observed in pyrrolato chemistry), followed by reductive elimination of the corresponding dialkyl species, the Cr(I) catalytically active species may be readily generated. The retention of the second aluminate might be particularly beneficial for either complete or partial cationization of the metal center.

Scheme 10.4



Not in disagreement with these hypotheses, activation of **10.3a** with 1000 equiv. of MAO doubled the catalytic activity given the larger availability of alkyl functions and increased presence of Lewis acidic centers

10.5 Conclusions

In conclusion, we have isolated and characterized the first single-component self-activating catalyst of a highly selective SNS trimerization system. Technically, complex **10.3a** is not the

catalytically active species since it has chromium resting in its trivalent state. However, the situation is conceptually not much different from $[(Me_4C_4NAlR_3)Cr(\mu\text{-}Me)]_2$ that, while possessing chromium in the divalent state, is still one of the best performing trimerization catalysts. The reason for this seemingly contradictory behavior is that the self activation proceeds via heterolytic cleavage forming a monovalent species (catalytically active) and a trivalent dialkyl that undergoes further two-electron reduction to the catalytically active monovalent complex. In the case of **10.3a**, the trivalent species may self-activate by simple dissociation of a neutral aluminate residue with concomitant alkyl transfer. The following two-electron reductive elimination gives direct accessibility to the monovalent catalytically active species. The completely unselective catalytic behavior of the divalent analogue **10.2a** reiterates once again that bypassing this oxidation state is central to obtain a selective oligomerization system. Simple divalent organochromium complexes are obviously far more stable than the trivalent ones and show little inclination towards spontaneous reduction.

10.6 References

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Chapter Eleven

Conclusions

There is some truly new information that has been generated by this thesis work and that we believe will be important to guide the future quests for new and better performing catalysts.

Firstly, we have confirmed that monovalent chromium is responsible for the selectivity of the oligomerization cycle. This is true even in the case of the tetramerization system that is not proceeding through a ring expansion mechanism, but through a "dimetallic" pathway. In turn this has conclusively proven the suspected non-ability of divalent chromium to trigger any metallacycle mechanism. Divalent chromium simply does not have sufficient reducing power to couple two ethylene molecules. Also the stability of the divalent oxidation state requires the development of two-electron reducing systems capable of bypassing this oxidation state. Finally, we have also confirmed the existence of the chromium redox dynamism through which the three critical oxidation states readily interconvert via reductions and disproportionations.

Secondly, the findings of previous work on pyrrolato system about the ability of divalent complexes to work as a single component polymerization system might have been in fact misleading. We have produced conclusive evidence that divalent chromium produces only non-selective oligomerization possibly via the Cossee mechanism. In the process we have identified one of the best performing and cleanest non-selective trimerization catalysts producing large amounts of LAO not accompanied by polymer formation.

Thirdly, we have identified in the oxidative coupling of vinyl anions a new pathway to monovalent chromium species with consequent formation of single component catalysts. The

future challenge in this chemistry will be the mobilization of the butadiene residue to increase the catalytic activity while preserving the excellent selectivity of these new systems.

Finally, in all this work we have both confirmed and produced more evidence for the ability of alkyl aluminum to reduce the metal center and to trigger re-oxidation. Boosting the alkylating ability of the activator is central to obtaining the two-electron reduction necessary to bypass the thermodynamic sink of the divalent state. Although our arguments are reasonable, confirming literature data and exploring the behaviour of our discoveries, we must admit that a large body of work is yet to be carried out to fully rationalize the role of the activators.

APPENDIX A

General Oligomerization procedure

A Parr reactor was dried in an oven at 115 °C overnight prior to each run and then placed under vacuum for 1 h at 120 °C. The reactor was then cooled to the desired temperature and charged with the solvent and co-catalyst with stirring. After 10 min the catalyst was injected into the reactor under a stream of N_2 and then the reactor was immediately pressurized with ethylene (600 psi). The reaction was allowed to run for 30 min or 1 h while the temperature remained stable. The temperature was then rapidly reduced to 5 °C with an ice bath; the reactor was slowly depressurized and a mixture of MeOH/HCl conc. (45ml/5ml) was injected to quench the reaction. The organic phase was separated from the aqueous phase and analysis and yield of oligomers were obtained respectively by GC, by using calibrated standard solutions, and by ^{1}H-NMR. Precautions were taken to maintain the temperature as low as possible during the workup to minimize loss of volatiles.

APPENDIX B

X-ray crystallography

Suitable crystals were selected, mounted on a thin, glass fiber with paraffin oil, and cooled to the data collection temperature. Data were collected on a Bruker AXS SMART 1 k CCD diffractometer. Data collection was performed with three batch runs at phi = 0.00 deg (600 frames), at phi = 120.00 deg (600 frames), and at phi = 240.00 deg (600 frames). Initial unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied. The systematic absences and unit-cell parameters were consistent for the reported space groups. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on *F*2. All non-hydrogen atoms were refined with anisotropic displacement parameters. When it was not possible to locate them, the hydrogen atoms were treated as idealized contributions.