Towards Selective Ethylene Tetramerization

Yacoob Shaikh

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Abstract

There is an increasing trend towards advancing the understanding and development of ethylene oligomerization catalysts, both in academia and industry. The metal of choice in this chemistry is invariably chromium, which has shown great versatility in selective trimerization/tetramerization, non-selective oligomerization and polymerization of ethylene. While much success has been achieved in ethylene trimerization, the same con not be said about tetramerization catalysis. Aminophosphine based ligands have demonstrated their ability towards selective 1-octene production, however, the popular PNP catalyst is able to achieve only 70% selectivity. In order to explore the possibility of developing and enhancing the selectivity of chromium based ethylene tetramerization catalyst, this thesis work was undertaken.

The ligand systems we chose for our work were bidentate aminophosphine based ($PN(CH_2)_nNP$), which has yielded interesting selective oligomerization. Subtle modifications were found to result in drastic changes in selectivity, from tetramerization ($PN(CH_2)_3NP$) to trimerization ($PN(CH_2)_2NP$). We managed to successfully develop the first truly selective (over 90%) 1-octene catalyst with polymer-free behavior. Further modifications on the ligand framework, where one atom of Si was used to link the two NP units, resulted in non-selective oligomerization, in which case we determined that the oxidation-state of chromium is a key player.

We explored other modifications on our selective ligands in which one of the arms on the bidentate ligand was replaced with a base-donor amine, phosphine or pyridine, and resulted in interesting selectivity changes. The final modification that we tested was a novel $N(CH_2)_2P$ ligand and found it to be a highly active, non-selective oligomerization catalyst.

I would like to dedicate this thesis to my parents, Bilal Shaikh and Aisha Shaikh, for their perseverance and loving support throughout my academic endeavors.

Acknowledgements

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Publications related to thesis work

[1] **Shaikh, Y**.; Albahily, K.; Sutcliffe, M.; Fomitcheva, V.; Gambarotta, S.; Korobkov, I.; Duchateau, R. *Angew. Chem., Int. Ed.* **2012**, *51*, 1366.

[2] **Shaikh, Y**.; Gurnham, J.; Gambarotta, S.; Korobkov, I. *Organometallics* (Submitted).

[3] **Shaikh, Y**.; Vidjaycoumar, B.; Gambarotta, S.; Korobkov, I. *Organometallics* (Submitted).

[4] **Shaikh, Y**.; Gambarotta, S.; Korobkov, I. *Organometallics* (Submitted).

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

[6] Albahily, K.; Fomitcheva, V.; **Shaikh, Y**.; Sebastiao, E.; Gambarotta, S.; Korobkov, I.; Duchateau, R. *Organometallics*, **2011**, *30*, 4201.

[7] Albahily, K.; **Shaikh, Y**.; Zeeshan, A.; Korobkov, I.; Gambarotta, S.; Duchateau, R. *Organometallics* **2011**, *30*, 4159.

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List of Abbreviations

BP	British Petroleum
BuAO	butylaluminoxane
CCD	charge coupled detector
CHN	carbon, nitrogen, hydrogen analyzer
DEAC	diethylaluminum chloride
DMAO	depleted methylaluminoxane
DME	1,2-dimethoxyethane
DMP	2,5-dimethylpyrrole
EA	elemental analysis
EPR	electron paramagnetic resonance
ESI-MS	electrospray ionization mass spectrometry
GC-MS	gas chromatography mass spectrometry
HDPE	high density polyethylene
IR	infrared spectroscopy
LAO	linear alpha olefin
LDPE	low density polyethylene
LLDPE	linear low density polyethylene
MAO	methylaluminoxane
MeCy	methylcyclohexane
MMAO	modified methylaluminoxane
NHAO	*n*-hexylaluminoxane
NMR	nuclear magnetic resonance
PE	polyethylene
S-F	Schulz-Flory

SHOP	Shell higher olefin process
SK-Energy	South Korean Energy
TEAL	triethylaluminum
THF	tetrahydrofuran
TMA	trimethylaluminum
Z-N	Zieglar-Natta

Introduction

1.1 Overview

Polymers have played a key role in modernizing our society and enriching our standards of living. With the advancements in science and technology, we are able to mimic naturally found polymers, such as DNA, cellulose, sugars, starch, natural rubber, silk, proteins, etc., and make synthetic polymers like plastics, elastomers, nylon, Teflon, Kevlar, silicone, fabrics and so on.

From the strictly chemical point of view, polymerization makes new covalent bonds between adjacent monomer units, where these monomers can be the same or different depending on the desired property. The most common monomers are linear alpha-olefins (LAO's), which are organic molecules with alkene functionality in the alpha position. Polyolefins can be thought of as large assemblies of smaller repeating units, like ethylene or propylene, which are linked by reducing the sp^2 carbon centers to sp^3 hybridized carbons, thereby forming adjacent new single bonds. The petrochemical industry has developed an entire family of organometallic catalysis for manufacturing these large molecules.

The advent of engineering science and technology has made a significant contribution to the development of the chemistry of polymers. Physical and mechanical characterization, rheological studies and advances in engineering technology have made it possible to expand the practical applications of polymers in daily life. As a result there has been a constant increase of necessity to improve the chemistry and understanding of polymer synthesis.

Polymers can be classified into three major types; thermoplastics, thermosets and elastomers. Thermoplastics are the most common polymer type and can be conveniently melted and reused. They are made most commonly from ethylene, the simplest of α-olefins, giving rise to polyethylene (PE). PE has a vast array of applications including various packaging materials, insulation materials, cushioning, pipes and much more. PE can be made highly dense (high density PE (HDPE)) which has a high degree of branching, or less dense (low density PE (LDPE)) by the addition of co-monomers during the polymerization process. LDPE has an ever-growing demand because it is used in the manufacture of plastic bags, plastic wraps, toys, lids, pipes, containers, cable coverings and many more related essential commodities. The co-monomers for making LDPE (along with ethylene) are light LAO's, commonly 1-butene, 1-hexene or 1-octene. Although ethylene comes directly as a by-product of other petrochemical processes and therefore is available in large quantity and reasonable price, LAO's are much less available. These are either distilled from crude petroleum sources, which is an energy intensive process and therefore not cost effective, or more efficiently obtained from oligomerization of ethylene.

Oligomerization is a truncated polymerization process, where a few ethylene monomers are joined to make a LAO (generally ranging from C_4 to C_{20}), having a carbon-carbon double bond in the α-position. These LAO's have applications not only as co-monomers for manufacturing LDPE, but also for the production of surfactants, lubricants, alcohols, waxes, plasticizers and many more. Although being similar to a polymerization, an oligomerization follows a slightly different mechanism where the LAO are being eliminated from the transition metal center at a much earlier stage. This subtlety is attributed to the effect of the ligand which controls the steric and electronic environment of the transition metal involved.

Ethylene oligomerization is classified as either a selective or a non-selective process. When the process is non-selective, a distribution of oligomers (LAO's) results in the range C_4-C_{20+}. The desired fragments are then separated using fractional distillation. Different fractions are used for different applications, depending on the market demands. Because the market application distribution is constantly shifting, non-selective oligomerization often results in 'unwanted' LAO's. A solution to this problem is to develop selective oligomerization. Selective di-, tri- and tetramerization of ethylene do exist with 1-butene, 1-hexene or 1-octene each having its own applications. Once again, this selective behavior is attributed completely to the underlying chemistry of the process. Of all the poly-/oligomerization processes described thus far, selective tri- and tetramerization are the most challenging.

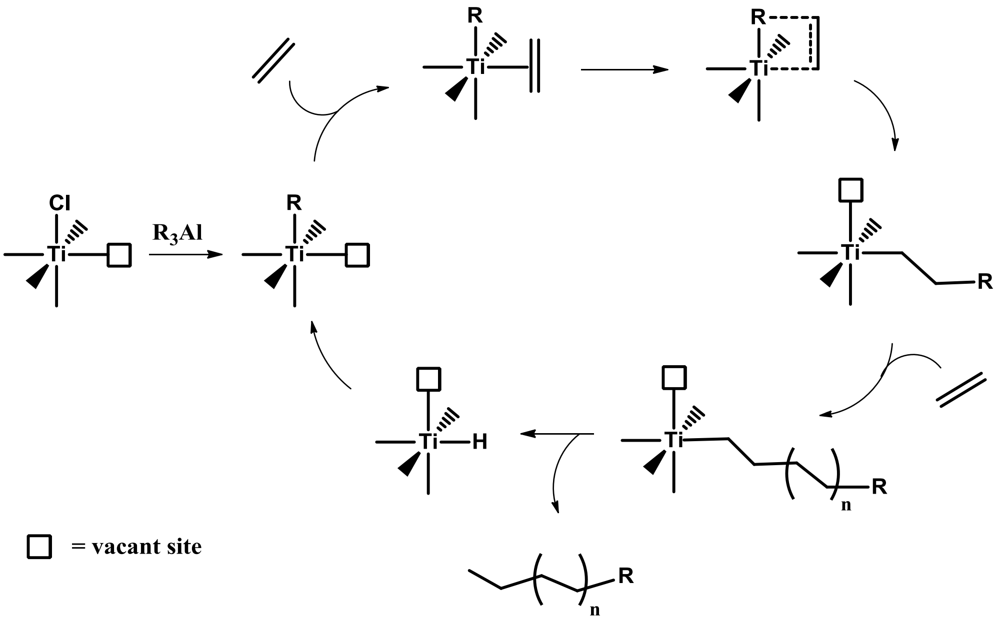
A few transition metals have been established to be capable of performing selective ethylene oligomerization. The most versatile element to this end remains chromium.

1.2 Ethylene Polymerization

Each year over 50 million tons of polyolefins are produced. Polyolefins have a rapidly growing demand due to the fact that they only contain carbon and hydrogen, and hence they are inert and recyclable.[1] In 1953 Karl Ziegler succeeded in polymerizing ethylene into HDPE at standard pressure and room temperature.[2] Soon after, Giulio Natta discovered an efficient catalyst for polymerization of propylene into polypropylene.[3] For their tremendous contributions, they shared the Nobel Prize for Chemistry in 1963. Classical *homogeneous* Zieglar-Natta (Z-N) systems are based on Ti,[4] V,[5] Cr[5a,6] and Zr[7] metal salts; these catalysts have been extensively studied and provide understanding of the elementary steps in polymerization.

The term 'Ziegler-Natta catalysts' in the context of polymerization is used for processes utilizing Titanium or Vanadium metal ions,[8] and alkyl-Aluminum compounds as co-catalysts.[9] Alkyl-Al serves the purpose of alkylating the metal center which becomes the active site for monomer insertion and subsequent chain elongation, leading to polymerization.[10] Cossee-Arlman chain growth mechanism has been widely accepted for Z-N polymerization (Scheme 1.1) consisting of an endless repetitive insertion of ethylene molecules into a preformed M-C bond.[11] The octahedral transition metal center is first alkylated by alkyl-Al, whereby the alkyl group on Al exchanges with chloride on the metal ion. Next, ethylene coordinates (at the vacant site) to the metal center in a π-bonding manner followed by insertion into the metal-alkyl bond, regenerating the vacancy for another molecule of ethylene to coordinate and propagate the process. The insertion reactions are migratory, therefore the growing polymer chain exchanges position with the coordination vacancy. The growing of the polyethylene chain terminates via β-hydride elimination, resulting in a metal-hydride which can also allow ethylene insertion and consequent restart of the cycle.

Scheme 1.1



With a thorough understanding of the factors contributing to the polymerization process, it has been possible to advance the chemistry of polymers into new and exciting frontiers. Oligomerization and especially slctive tri- and tetramerization remain a challenge. Below there will be a brief description of non-selective ethylene oligomerization, followed by an account of the quest for the highly sought selective tri- and tetramerization processes.

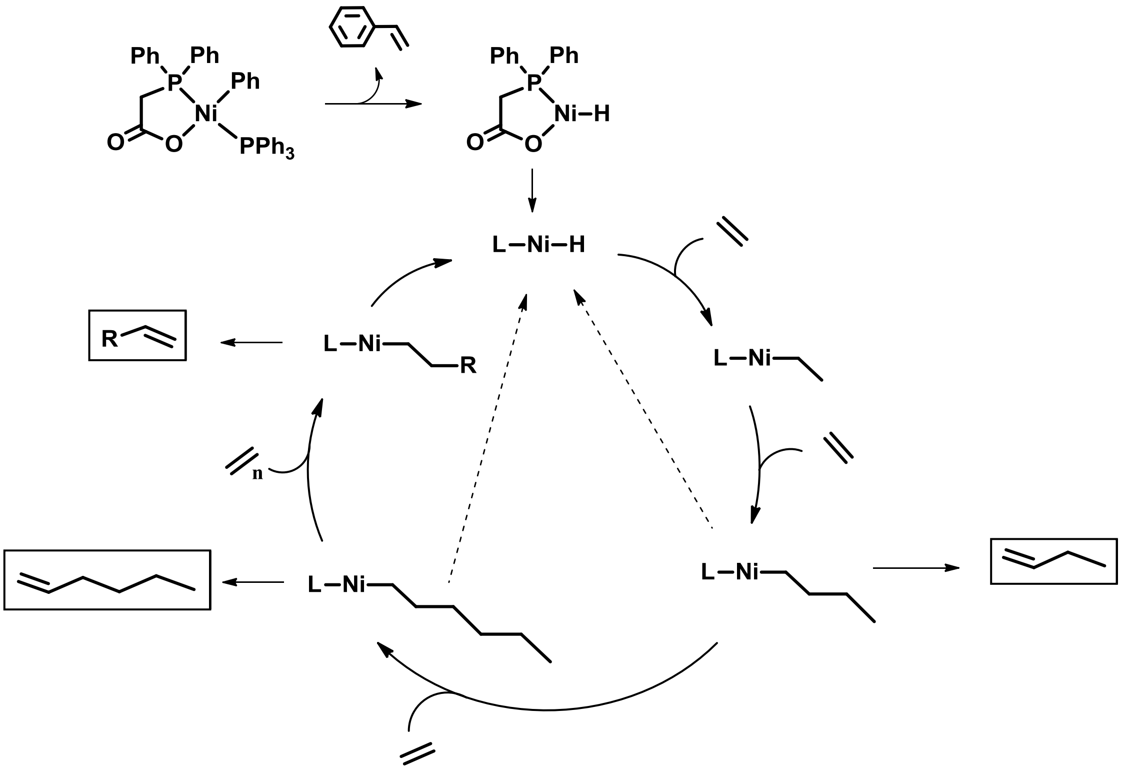
1.3 Non-Selective Ethylene Oligomerization

In the mid 1950's it was discovered that alkyl-aluminum-catalyzed ethylene oligomerization, as pioneered by Karl Ziegler,[12,2] is significantly enhanced in the presence of nickel salts.[13] This led to the development of the Shell higher olefin oligomerization process (SHOP), which today produces almost one-half of the linear alpha-olefins (LAO's) worldide, amounting to nearly 1 million tons per year.[14] Other processes for making LAO's are paraffin wax-cracking, paraffin dehydrogenation and alcohol dehydration, but because of the high product quality and good ethylene availability, the production of LAO's by oligomerization remains the most convenient route.[14]

Different LAO's have their own specific applications. Poly-1-butene is made from C_4 α-olefin units; C_4-C_8 are used in the production of linear low density polyethylene (LLDPE), high density polyethylene (HDPE) as well as being used as plasticizers in polyethylene; C_6-C_{10} are used as plasticizers; C_{12}-C_{20} are used for surfactants and biodegradable detergents. Other equally important applications include intermediates in the production of oxo-alcohols, mercaptans, synthetic fatty acids, organo-aluminum compounds, synthetic lubricants, amines, epoxide intermediates, alkylated aromatics and wax lubricants.[14] By introducing LAO's as polymerization co-monomers, polymer rheology can be controlled which results in polymers with different properties.

The SHOP process uses a nickel chloride salt ligated to a diorganophosphino acid derivative, which upon reduction to Ni-H, starts the oligomerization process.[15] The catalytic cycle follows the Cossee-Arlman chain growth mechanism and results in a statistical distribution of even numbered carbon olefins, called the Schulz-Flory distribution.[16] For the economy of the SHOP process, it is important to control the Schulz-Flory distribution by controlling the geometric α-olefin chain growth factor K.[17] This is done by varying the catalyst composition, and typically $K = 0.75$-0.80 are regarded as desirable for an industrial process. Keim and co-workers have investigated the mechanistic aspects of SHOP oligomerization in detail,[18] and found that it is no different from polymerization. The only difference between the two is that chain termination occurs at an early stage *via* β-H elimination. Scheme 1.2 illustrates the generally accepted mechanism for non-selective oligomerization, also called the chain growth mechanism. The initiation step is the formation of nickel-hydride species (it occurs at high temperature and ethylene pressure in toluene), followed by ethylene insertion to form the metal-alkyl which eliminates an α-olefin *via* β-H elimination, regenerating the metal-hydride. The metal oxidation state does not change throughout the cycle. The SHOP process is attractive because it does not require a co-catalyst for activation, and thus is very cost effective. Metals that are popularly used for other non-selective, homogeneous oligomerization processes include Ti, Zr, Ni, Ru, Hg, Pd and Al.[19]

Scheme 1.2



This process results in a statistical distribution of α-olefins which are separated by fractional distillation, adding cost to an otherwise very economical process. As an alternative approach, selective trimerization or tetramerization system can be utilized in order to get the highly desired C_6 and C_8

fractions respectively.[20] With the successful commercialization of Schulz-Flory based non-selective oligomerization catalysis, developing selective tri-/tetramerization systems and commercializing them is the next challenge for the petrochemical industry.

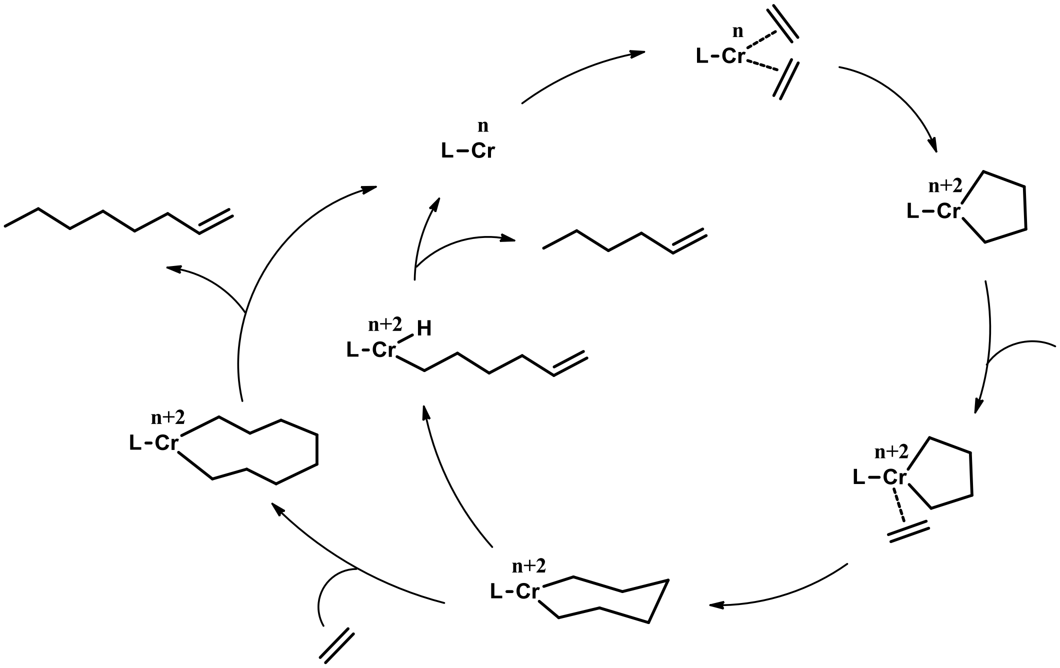
1.4 Selective Ethylene Trimerization: Mechanistic Aspects

To satisfy the steadily increasing market demand for lighter LAO's, a different reaction mechanistic pathway needs to be utilized. Namely a redox mechanism, involving the intermediate formation of metallacyclic intermediates, is today commonly regarded as responsible for selective oligomerization to 1-hexene and even 1-octene.[21] Since the discovery of metallacycles in the early 1970s,[22] they have been proposed as intermediates in selective oligomerization of ethylene. With regards to ethylene dimerization, the metallacycle route was proposed to be feasible for the commercial Alphabutol process developed by Institut Francais du Petrole (French Institute of Petroleum), which produces over half-million tons of 1-butene per year.[23,14,21a] However, recent mechanistic investigations, H/D scrambling experiments and theoretical calculations strongly support the Cossee-Arlman chain growth mechanism.[24]

The first examples of selective ethylene trimerization systems producing 1-hexene, were based on Chromium.[21b] Although other transition metal catalytic systems do exist for selective ethylene oligomerization, trivalent chromium is by far the most versatile,[25] producing the best performing trimerization and tetramerization catalysts and accounting for over 90% of the existing systems for oligomerization.[26] This special behavior can be attributed to the underlying mechanism responsible for selectivity.

Manyik and co-workers were the first to propose the so-called ring expansion mechanism for Cr based trimerization,[27] a generalized mechanism of which is shown in Scheme 1.3. The process is initiated by the oxidative coupling of two ethylene molecules to produce a metallacyclopentane complex. Further insertions of ethylene produce larger ring metallacycles, which decompose via β-H elimination, followed by reductive elimination, to linear α-olefins. The selectivity of the process is therefore controlled by the relative stability of the metallacycles. This is a redox process which is highly dependent on the ligand's ability to stabilize low-valent oxidation states of the metal catalyst.[28,25j-m] The ring expansion mechanism is very well accepted in the field of selective trimerization and tetramerization.[29]

Scheme 1.3



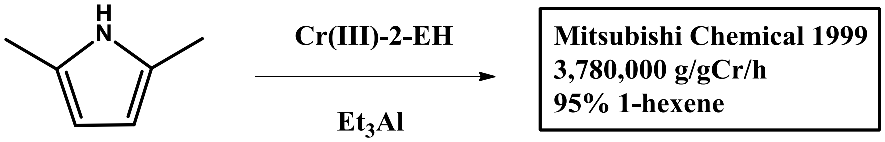
Extensive amount of experimental work has been done to determine *the* oxidation state responsible for selective behavior of chromium. It is generally accepted that the redox couple of Cr(I)/Cr(III) gives rise to the metallacycles mechanism (Scheme 1.3).[30] It is the features of the ligands that allow for this redox dynamism to take place, particularly the capacity to support monovalent Cr.[31] As a synthetic strategy, therefore, monovalent Cr can be generated *in situ, via* two-electron reduction pathways starting from trivalent Cr, bypassing the divalent oxidation state which has been demonstrated to be responsible for non-selective behavior.

1.5 Chromium based Ethylene Trimerization

Since 1991, selective ethylene trimerization systems for the production of high purity 1-hexene have attracted greater commercial attention.[25a,b,e,21b] The first breakthrough was made by Phillips Petroleum (and further developed by Chevron-Phillips) with the 2,5-dimethylpyrrole (DMP) and Cr-based catalytic systm,[25a] which produces over 50,000 tons of 1-hexene per year. Mitsubishi Chemical Corporation made notable improvements to the Phillips DMP catalyst by using the non-coordinating Lewis acid $B(C_6F_5)_3$, along with Cr(III)-2-EH (ethylhexanoate), DMP and triethylaluminum with significantly improved activity and selectivity (from 0.15 to 3.78 × 10^6 g/gCr/h).[32]

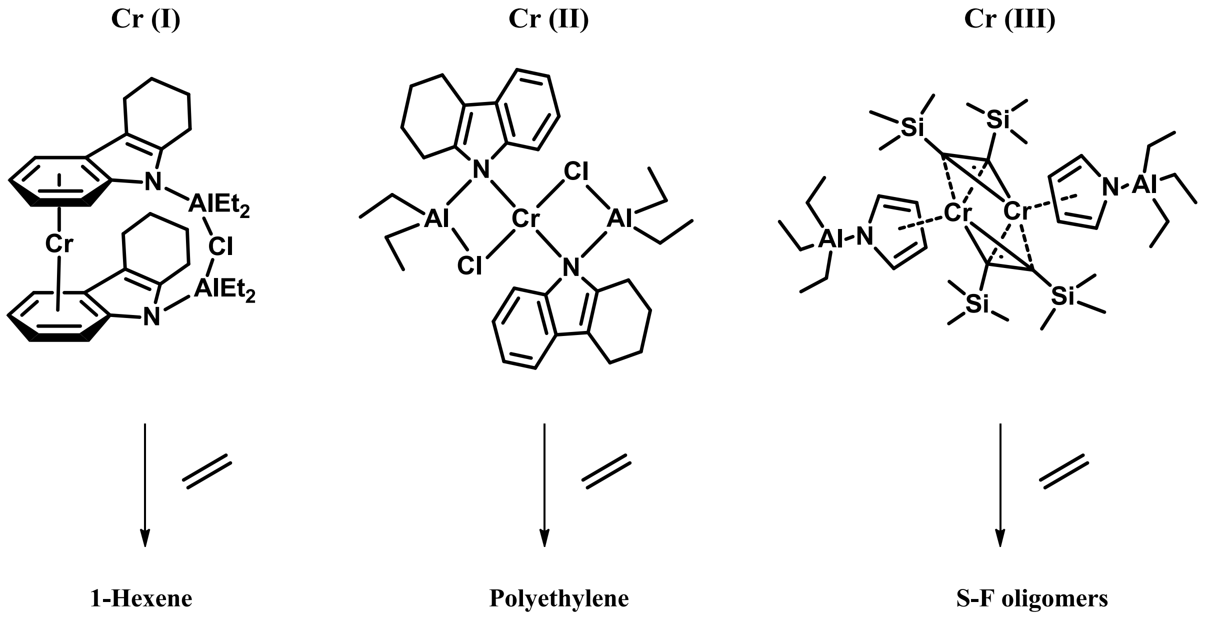
Scheme 1.4

1



Recent work by our group has shed light on the mechanism responsible for the selective behavior of pyrrole based oligomerization.[30a,b] By isolating the catalytically active species in mono-, di- and trivalent oxidation states, the different behaviors in terms of selectivity were identified (Scheme 1.5).[30a] This evidence supports the Cr(I)/Cr(III) ring expansion mechanism responsible to selective trimerization, which was further supported by spectroscopic EPR work by Talsi.[33]

Scheme 1.5

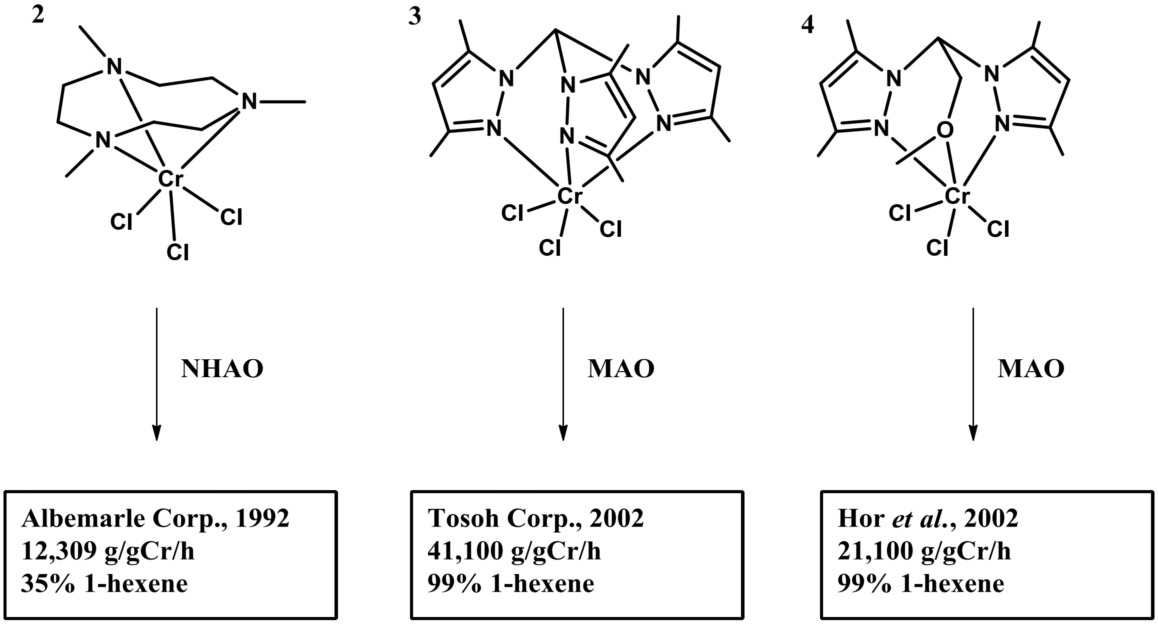


Tridentate facial ligands have been studied for Cr based oligomerization and trimerization (Scheme 1.6). Wu and co-workers at Albemarle Corporation developed 1,4,7-trimethyl-1,4,7-triazacyclononane (**2**) which was found to be active in the presence of *n*-hexylaluminoxane (NHAO), resulting in a Schulz-Flory distribution of α-olefins, enriched in 1-hexene,.[34] Further work on this ligand demonstrated that the alkyl substitutions on nitrogen were essential for preventing polymerization. When the triazacyclohexane analogue of the aforementioned ligand was tested with ethylene, it proved to be an active polymerization catalyst.[35] However, as a side feature these triazacyclohexane complexes of Cr(III) were found to be capable of trimerizing higher α-olefins like propene, 1-hexene and styrene.[36]

Another ligand with similar geometric properties to **2** is tris(pyrazolyl)methane (**3**) as developed by Tosoh Corporation.[25m] It was found to be highly active and selective towards 1-hexene, upon activation with methylaluminoxane (MAO).[25m] Hor and co-workers made interesting variations to the pyrrolyl based framework by replacing one of the arms with a pendant donor; either ether or thioether.[28b]

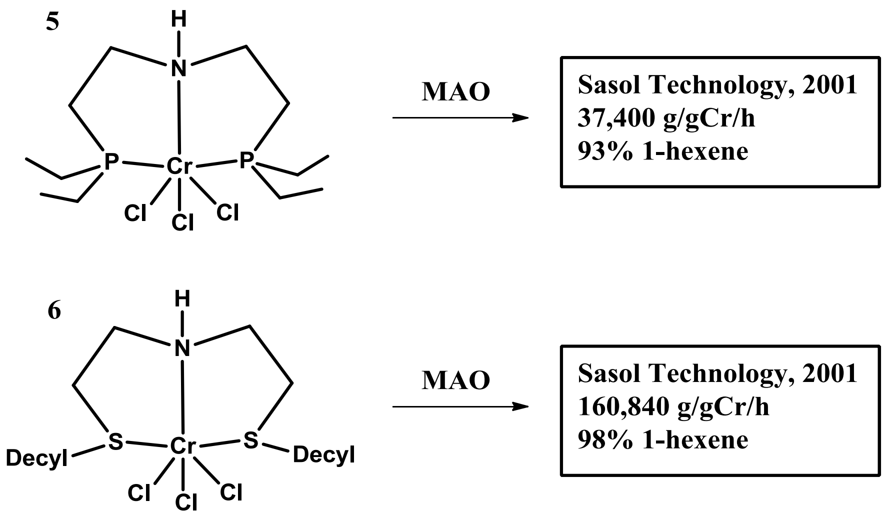
When ether was used as the pendant arm (**4**) in the presence of MAO, high selectivity towards 1-hexene was observed, although activity was reduced.

Scheme 1.6



Sasol Technology's bis(phosphino)amine[37,28a] and bis(sulfanyl)amine[38] ligands have made a significant contribution to the Cr based selective ethylene oligomerization (Scheme 1.7). Their tridentate $R_2PCH_2CH_2N(H)CH_2CH_2PR_2$ ligand complexes with $CrCl_3(THF)_3$ to form an octahedral geometry with meridional arrangement of the ligand. In the case when R = Et (**5**), which is more basic and less sterically demanding compared to Ph, a highly selective trimerization system resulted upon activation with MAO in toluene.[37,28a] Replacing the P-based donor ligand with a S-based one (**6**), an even higher activity and selectivity towards 1-hexene was obtained.[25e,1]

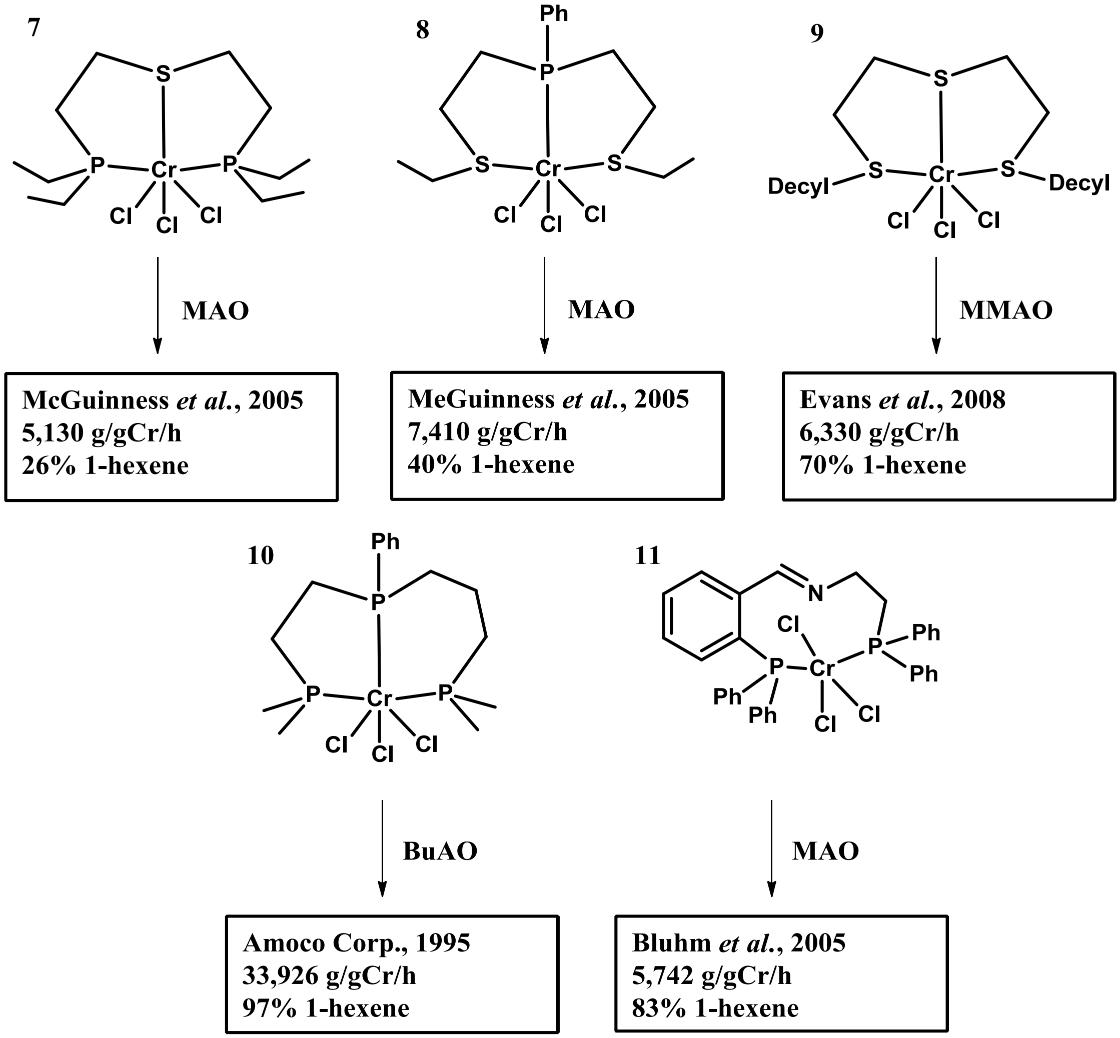
Scheme 1.7



A summary of other tridentate Cr based selective ethylene trimerization catalysts is shown in Scheme 1.8. McGuinness *et al.* modified Sasol's patented ligands **5** and **6**, by preparing PSP and SPS variations (**7** and **8**).[251] However, neither of these modifications proved to be an improvement over the original ligand framework. Evans and co-workers made further modifications by having all the heteroatoms as sulfur (**9**).[38] When activated with modified methylaluminoxane (MMAO) selectivity improved but the activity remained lower. Finally, Amoco Corporation developed the PPP ligand **10** which had much higher selectivity and activity when activated with butylaluminoxane (BuAO).[39] The major factors preventing Amoco from commercializing this ligand were the high cost coupled with difficult synthesis.[39]

Bluhm and co-workers tested ligands with the tridentate backbone **11**, the best of which were ones that had imino nitrogen and phosphorus as a pendant donor instead of sulfur.[40] Upon activation with MAO, low activity but high selectivity for 1-hexene was achieved, although a significant amount of unwanted polyethylene was produced as a byproduct.

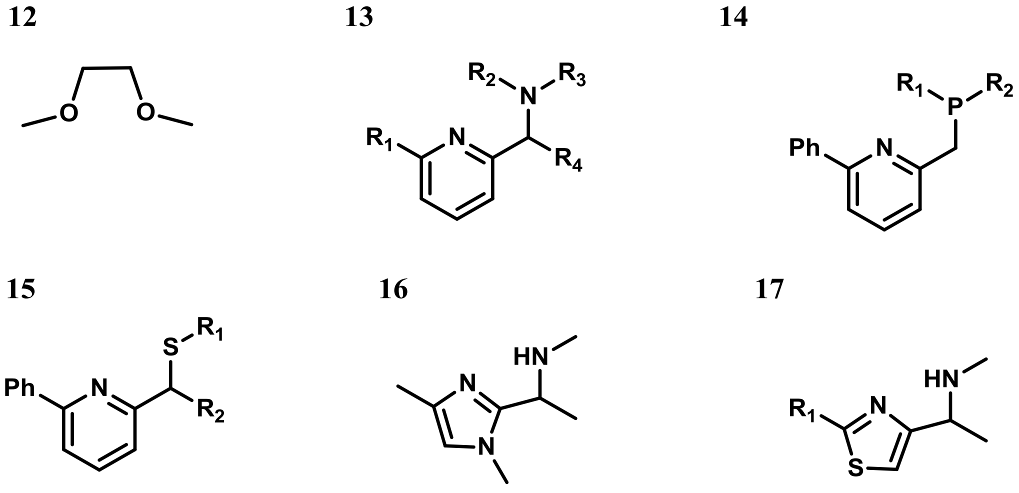
Scheme 1.8



In addition to the extensive amounts of tridentate trimerization ligands presented, there also exists a number of bidentate ones (Scheme 1.9). The simplest of these was developed by Briggs and co-workers of the Long Range Catalyst Group of Union Carbide Corporation.[41] Dimethoxyethane (DME) was used as a simple donor ligand (**12**), and in combination with Cr tris(adamantanecarboxylate), aluminum *t*-butoxide and triisobutylaluminum, moderate selectivities and low activities prevented them from commercializing their catalyst.

A large range of other bidentate ligands were developed by Exxon-Mobil, a few of which are shown in Scheme 1.9 (**13** through **17**). These ligands were screened with various Cr sources in combination with MAO, and led to mixed results for ethylene tri- and tetramerization. A common feature of these ligands was the presence of unwanted polyethylene side products which fouled the reactor, prevented commercialization.[43]

Scheme 1.9



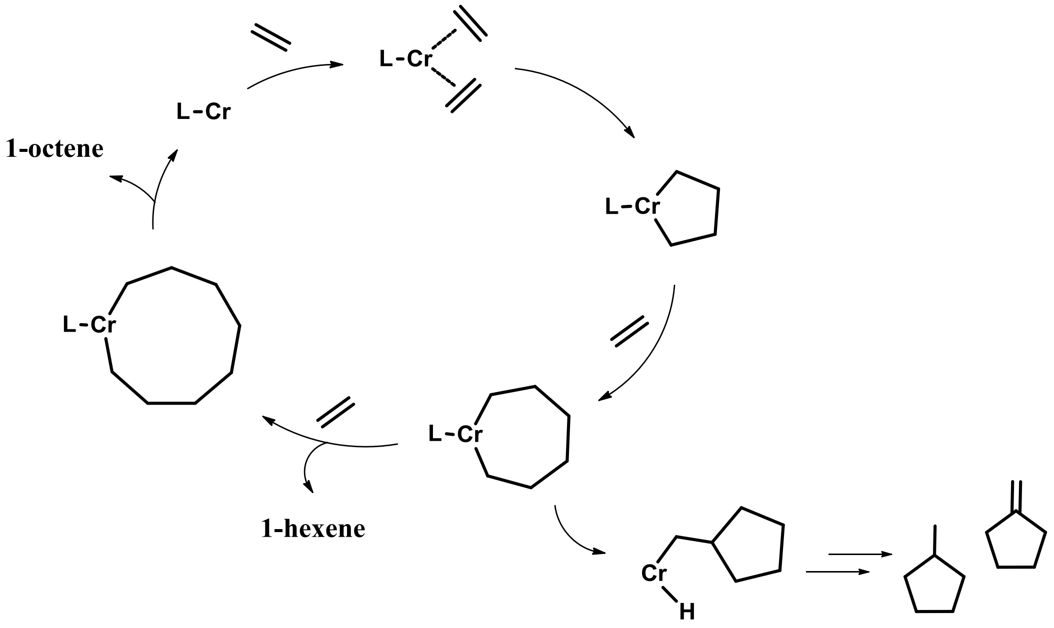
Thus far, much work has been done on Cr based ethylene trimerization systems and much success achieved. The increasing intellectual challenge for researchers in the field is to develop a viable tetramerization system with sufficient selectivity and purity for commercialization.

1.6 Selective Ethylene Tetramerization: Mechanistic Aspects

From the discussions thus far, it becomes clear that achieving a truly selective ethylene trimerization catalyst is no longer a major challenge unless record activity is being sought. On the other hand, a highly selective tetramerization system (>90% selective towards 1-octene) has mostly been elusive, with the exception of recent discoveries made by our group (see Section 1.7), where the 90% barrier has been overcome.[30c,44]

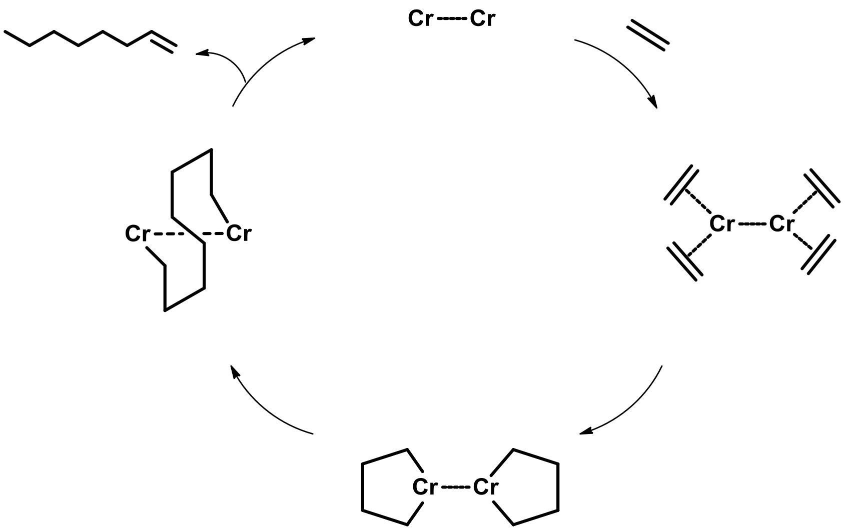
The tetramerization mechanism has been extensively studied,[45] and there is a general consensus by researchers in the field that a modified metallacycle mechanism is at play (Scheme 1.10). It is suggested that in the case of tetramerization, the 7-membered species is more inclined to further expansion than towards 1-hexene reductive elimination. As a result, the 9-membered ring is accessible which eliminates 1-octene. An unwanted consequence of this more stable 7-membered ring is the formation of cyclic C_6 by-products, which are proposed to be obtained *via* rearrangement of the ring.[46,45a] A fine balance must therefore be struck in order to favor tetramerization over trimerization if the ring expansion mechanism is followed.

Scheme 1.10



It can be argued that if the 7-membered ring is capable of expanding into the 9-membered ring, it can also undergo further expansion.[47] Therefore, a distribution of α-olefins may be expected, where 1-octene may dominate but not be the exclusive product. This problem was first addressed by Rosenthal and co-workers,[48] who proposed an alternative bimetallic mechanism for high selectivity towards tetramerization (Scheme 1.11). The hypothesis suggests that two low valent Cr centers that are unlinked but in close proximity, may independently form metallacycles with 5-membered rings. These rings would then cooperatively eliminate 1-octene *via* reductive elimination. It must be emphasized that the details of such a coupling and elimination process were not explicitly mentioned, and there has been no direct experimental observation to support this idea. Further experimental work needs to be undertaken in order to support this idea of a bi-metallic mechanism.

Scheme 1.11

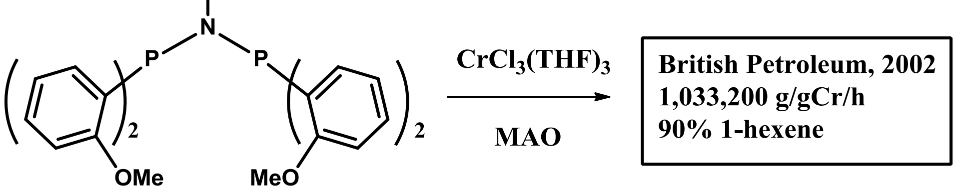


1.7 Chromium based Ethylene Tetramerization

The first truly selective tetramerization system started with the discovery of a highly active trimerization system. Researchers at British Petroleum (BP) reported the PNP ligand (**17**), when combined with Cr and MAO, produces over 1 million g/gCr/hr of 1-hexene (Scheme 1.12).[25d,k] The pendant coordination of the *ortho*-methoxy substituents was determined to stabilize low valent Cr, which is responsible for the metallacycle mechanism.[21b,c,25g,f,29b] Bercaw and co-workers conclusively identified that the ring expansion mechanism proceeds *via* Cr(I)/Cr(III) redox.[49,29b]

Scheme 1.12

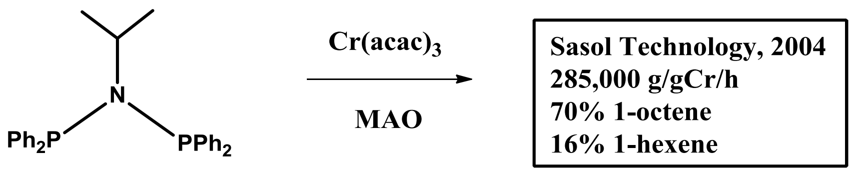
17



Further investigation into the *ortho*-Me-PNP of BP by Sasol Technology led to a remarkable breakthrough in the field. Sasol researchers removed the *ortho*-substitution from the phenyl groups and made their own PNP ligand (**18**) which was the first example of a highly active tetramerization system with high selectivity for 1-octene (up to 70%) (Scheme 1.13).[25i] The major by-product of this PNP system was 1-hexene, with significant amounts of methylcyclopentane and methylenecyclopentane also formed. This is consistent with the well-established metallacycle ring-expansion mechanism (see Scheme 1.10). The major factor contributing to the C_6/C_8 control is the steric interactions of the bulky *ortho*-substitution of phenyl rings of **17**, which restrict the expanding ring from growing beyond the 7-membered stage.[45b] Similar switch in selectivity is also observed when the pendant donor ether atom is on the nitrogen backbone of PNP (**19**).[28h]

Scheme 1.13

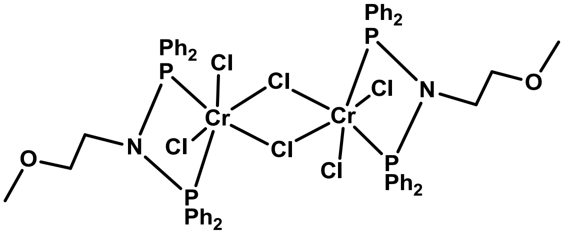
18



Because of the significance of this discovery on tetramerization, a large amount of work has been carried out where the alkyl substituent on the nitrogen has been altered in a broad series of ligands of general formula $Ph_2PN(R)PPh_2$ (Scheme 1.14).[50] The most dominant parameter in these substitution studies was that steric bulk, and not basicity, on nitrogen affects 1-octene selectivity.[30f] Bulky alkyl substitutions, like **20** and **21**, lower 1-octene selectivity. The same is true for aromatic R groups like **22**.

Scheme 1.14

19



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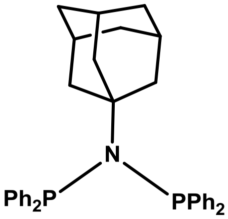

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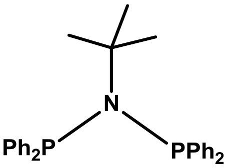
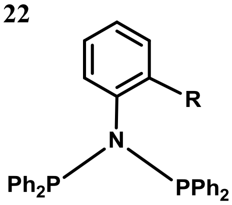
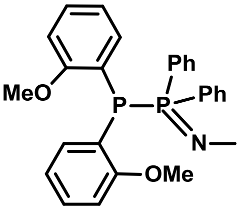


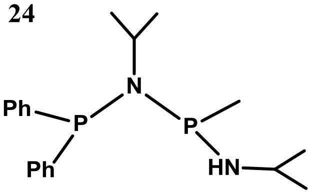
22



23



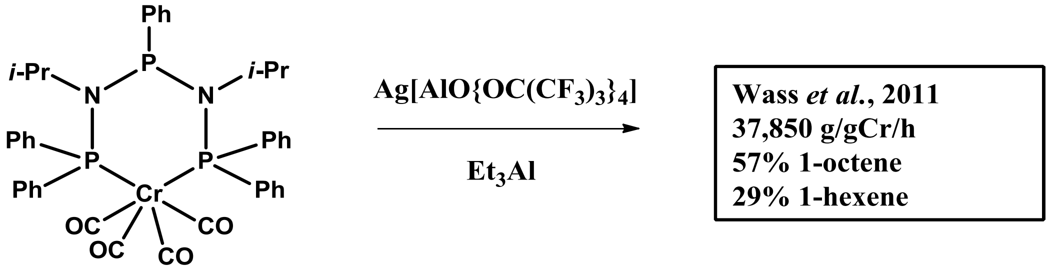
24



Shell chemicals modified the PNP tetramerization catalyst by using iminodiphosphine ligand (**23**) and upon activation with Cr/MAO obtained an active tri-/tetramerization catalyst.[51] Rosenthal and group further modified it to PNPN system (**24**), which in the presence of Cr source and Et_3Al as activator, has been shown to be selective towards 1-octene with a moderate activity.[52] Wass extended Rosenthal's work by the synthesis of a symmetric PNPNP ligand (**25**), which was followed by complexing PNPNH to $Cr(CO)_6$ and then treatment with MeLi and Ph_2PCl. This non-trivial method had to be employed because of the inaccessibility of the N-H proton, which is shielded by the phenyl group on phosphorus, preventing the direct reaction of PNPNH with Ph_2PCl.[53] This 'metal templating' strategy allowed the synthesis of complex **25** where Cr is in zero-valent oxidation state. This catalyst was activated by using an oxidizing agent in order to generate the mono-valent Cr needed for tri-/tetramerization. Although the activity and selectivity towards 1-octene is poor, it is valuable due to the scarcity of tetramerization systems (Scheme 1.15). The activation was done by using a Lewis acid activator $Ag[AlO\{OC(CF_3)_3\}_4]$, along with Et_3Al in chlorobenzene.[53]

Scheme 1.15

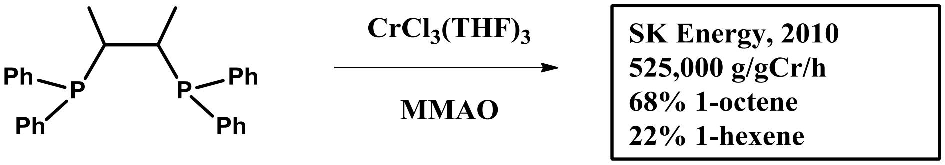
25



SK-Energy's contribution to ethylene tetramerization chemistry is their diphenylphosphinoethane (dppe) ligand, having alkyl substituents on the backbone (**26**).[54] When activated with modified methylaluminoxane (MMAO) in presence of a Cr(III) source, the catalyst produces 68% 1-octene with high activity (Scheme 1.16).[54c] Remarkably, only the S,S- and R,R- forms were effective at tri-/tetramerization, whereas the *meso*-stereoisomer gave only polyethylene. Similar selectivity was observed when a cyclohexyl backbone was used (**27**), but with *ortho*-substituted phenyl phosphines (**28**), the selectivity switches to 1-hexene exclusively. This is similar to the pendant donor effect of *ortho*-Me-PNP of British Petroleum (see Scheme 1.12).

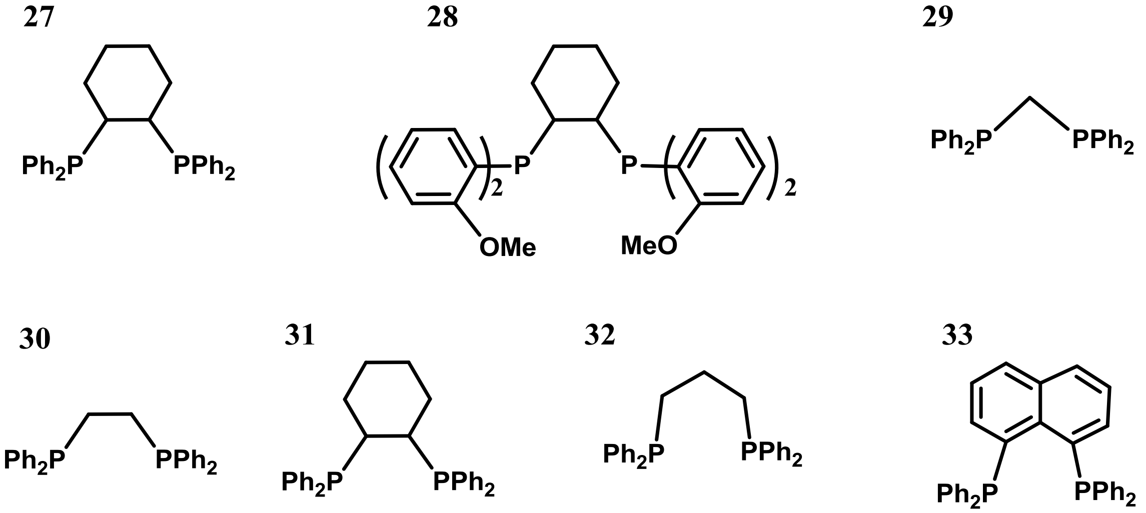
Scheme 1.16

26



A large range of diphosphine type ligands were surveyed by Sasol researchers,[55] a few of which are shown in Scheme 1.17. The ligand most similar to the tetramerization PNP is PCP (**29**), which behaves in a non-selective manner giving a Schulz-Flory distribution of oligomers. The acidic methylene protons in the backbone can be removed upon activation of the catalyst and results in a different reactivity. The ligands **30** through **33** which have a longer carbon bridge were also active tri-/tetramerization catalysts,[55] with the general trend that the smaller the P-Cr-P bite angle, the higher the C_8/C_6 ratio. Selectivity in the case of ethylene tetramerization is highly influenced by minor changes in ligand electronics and sterics.

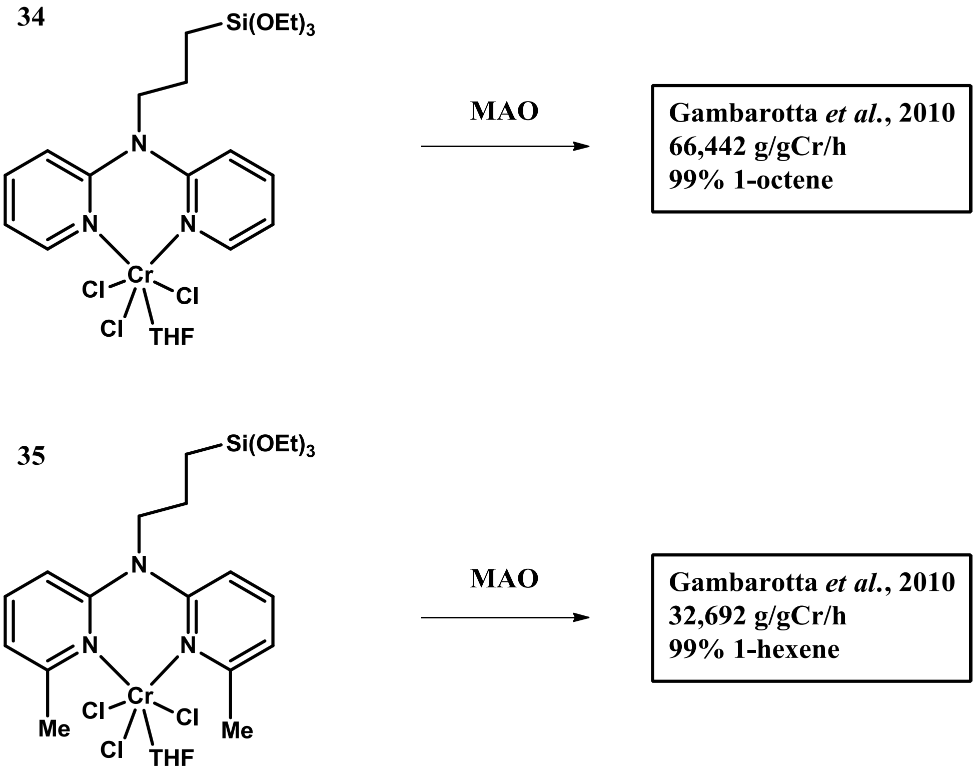
Scheme 1.17



For the purpose of ethylene tetramerization our group developed the bispyridine ligand, which is the only system in current literature and patents that produces 99% 1-octene, albeit with a large amount of wax (low molecular weight polyethylene) (Scheme 1.18).[30c] The presence of bulky R group on the bridging nitrogen atom aids in the solubility of the precatalyst. Selective tetramerization is observed in the case when Cr(III) is used as a chromium source, whereas Cr(II) results in the formation of unwanted waxes only. Therefore in the case of the selective catalyst, these waxes result from the formation of a divalent complex at low temperatures in the reaction mixture.[30c]

To further explore the mechanistic aspect of this unique system, a modification to the original ligand was done with methyl substitutions at the *ortho* positions of the pyridine rings (Scheme 1.18, **35**). The selectivity switched completely towards 1-hexene (with the formation of waxes alongside), which led to the conclusion that although ring expansion could produce an excess of 1-octene, it is highly unlikely to offer 99% selectivity towards tetramerization. On the other hand, it is highly likely that because of the weakly binucleating nature of the ligand, an assembly of non Cr-Cr ligated dinuclear Cr(I) species might be responsible for selective 1-octene formation. This is in agreement to the bimetallic mechanism for tetramerization (see Scheme 1.11).[48] This hypothesis explains the observation where the introduction of steric constraints in the case of **35**, results in exclusive 1-hexene formation (following a mono-metallic ring expansion mechanism). The methyl substituents would prevent the formation of the hypothetic dinuclear Cr(I), which would allow two neighbouring chromacyclopentane units to couple and eliminate 1-octene.[30c]

Scheme 1.18



There seems to be two alternative mechanistic approaches to developing a selective ethylene tetramerization system. The 'classical' ring expansion mechanism works quite nicely for trimerization, but when it comes to tetramerization it cannot be expected to be highly selective towards 1-octene. On the other hand, the newly hypothesized bimetallic mechanism offers a possible alternative towards ligand design, although much work needs to be done in order to establish this.

A few concluding remarks have to be added to the significance of the co-catalyst in order to make this introduction comprehensive. In almost all the catalytic systems mentioned thus far, a co-catalyst has been used, usually alkyl-Aluminum based since these systems are in essence Zeigler-Natta based. The most common activator is MAO (methylaluminoxane), which is made by controlled hydrolysis of Me_3Al.

MAO plays two major roles as a co-catalyst activator; alkylation and enhancing the Lewis acidity of the metal centre. Following alkylation, abstraction and cationization make the metal center electrophilic towards ethylene coordination. Commercial MAO is available as a dilute solution in toluene. In order to be able to use an aliphatic solvent (like methylcyclohexane), we have devised a method whereby simple removal of solvent (at elevated temperatures) allowed us to use MAO, which then becomes depleted-MAO, in aliphatic solvents. As we discovered using DMAO (depleted-MAO) in methylcyclohexane switches the non-selective Schulz-Flory catalyst into a selective trimerization or tetramerization catalyst.

Other commercially available co-catalysts have different properties in terms of their alkylating ability, Lewis acidity, solubility in solvents, and cost. Solvent also plays a significant role in this chemistry, as we note that the choice of the right solvent will determine the stabilization of active intermediates, which will result in different mechanistic pathways, and eventually selective *vs*. non-selective oligomerization.

1.8 Thesis Aim

While there is a plethora of catalysts for ethylene trimerization that are both highly selective and active, some of which have been successfully commercialized, there seems to be a scarcity of tetramerization catalysts with comparable selectivity. Among the few Cr based catalysts available for ethylene tetramerization, the most successful ones are based on amino-phosphine ligands. However, much more work needs to be done in improving the selectivity towards 1-octene and that forms the essence of this thesis work. We focused on a variety of novel bidentate ligands based on N and P donor atoms, and were successful in developing the first truly selective (polymer-free) 1-octene catalyst. Other ligand modifications allowed us to determine the prerequisites for selectivity, and in doing so we discovered a highly active, non-selective catalyst as well.

1.8.1 Chapter 2

One of the most selective ligands available towards ethylene tetramerization based on chromium, prior to our work, was the commercially developed PNP ligand discovered by Sasol. In that case, the highest selectivity achieved was merely 70%. Hence in order to break that barrier, we embarked on the development of our own ligand system which proved to be highly selective towards 1-octene (> 90%). The ligands that we studied had the motif of $PN(CH_2)_nNP$ where n = 2 or 3. In doing so, we also discovered that the reaction solvent has a remarkable ability of switching the selectivity and we also popularized the use of DMAO as a co-catalyst for oligomerization. We propose an alternative mechanism to the well accepted ring-expansion one; our proposal follows a bi-metallic metallacycle.

1.8.2 Chapter 3

Given the success of the ligands $PN(CH_2)_nNP$ where n = 2 or 3, we embarked on further studying the framework by linking the NP units with a one-atom bridge and investigating their behavior on Cr oligomerization of ethylene. We therefore synthesized the ligand with the motif of PNSiNP and in this work we isolated a vast number of complexes upon Al-alkyl treatments and noticed a general trend; the complex forms a dimeric aggregate with Al-bridging the two Cr metal centers. The catalytic activity of the catalyst was also analyzed.

1.8.3 Chapter 4

In keeping with the amino-phosphine based ligands, we designed ligands with the framework of $PN(CH_2)_2X$, where X was a pendant base donor group either an amine, a phosphine or a pyridine. The different base donors behaved in a different manner, resulting from selective to non-selective oligomerization when tested with Cr. Isolation of complexes was successful and an explanation on the catalytic behaviors is presented.

1.8.4 Chapter 5

The final modification that we naturally tried was to synthesize the $N(CH_2)_2P$ ligand frame. This ligand proved to be capable of stabilizing di-valent chromium and as a result yielded a highly active oligomerization catalyst. Furthermore, the catalytic performance was not fouled by the presence of unwanted polymers. Isolation of active catalytic intermediate was achieved by treatment with Me_3Al affording a complex that helped us to present a mechanism.

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A Highly Selective Ethylene Tetramerization Catalyst

2.1 Introduction

The issue of selectivity has been the most challenging aspect of ethylene oligomerization since its discovery.[1] In the last three decades trimerization systems of high selectivity have been discovered,[2] but tetramerization catalysts of high selectivity remain elusive.[3] Central to the future success of this endeavor is understanding the factors responsible for the selectivity of the process that proceeds through a metallacycle mechanism.[4]

Trivalent chromium complexes are the catalyst precursors most commonly used for these transformations. In the presence of alkyl aluminum activators these precursors are reduced to the divalent state (responsible for non-selective oligomerization and/or polymerization) or the monovalent state (responsible for selective behavior).[5] To complicate the scenario, there is also the possibility for these monovalent and divalent species to undergo disproportionative redox processes that yield inactive, zero valent chromium together with higher-valent species ready for further cycles of reduction/reoxidation.[6] Due to the presence of such a redox dynamism in the catalytic cycle, the ancillary ligand system determines the selectivity by preferentially stabilizing one particular oxidation state over another. For example, when highly reactive monovalent species are stabilized for a sufficient amount of time, selective oligomerization is initiated via the so-called redox/ring-expansion mechanism.[2,5,7]

Despite advancement in research, selective ethylene tetramerization remains exceedingly rare. Maximum activity obtained to date is around 77% in the case of SK-Energy process,[3d] and while selectivity is definitely good it remains far from the levels obtained with the trimerization systems. In addition, the unavoidable formation of polymer that accompanies the catalytic processes, poses serious reactor fouling problems which complicate industrial application. The same redox/ring expansion mechanism that accounts for the selectivity of the trimerization cycle has also been utilized for rationalizing of the tetramerization processes.[3b,8] However, in accordance with this mechanism, it is deduced that high selectivity cannot be achieved via this cycle. The selectivity in this mechanism is determined by the rate of the reduction/elimination step compared to the rate of further ring expansion. If the seven-membered ring is readily capable of expanding into the nine-membered ring, it is hard to imagine why additional expansion should not occur equivalently as fast.[9] Ultimately, a distribution of oligomers should be expected where 1-octene may be a dominant product.

Rosenthal[10] first recognized these considerations and postulated an alternative mechanism for highly selective formation of 1-octene. According to his hypothesis, a dimetallic system, with two low-valent chromium centers held at a non Cr-Cr bonding distance, may independently form two five-membered metallacycles. Further, cooperative dimetallic reductive elimination selectively affords 1-octene. It is by following this fascinating hypothesis that we have recently observed for the first time the formation of 1-octene uncontaminated by other olefins.[3e] Albeit a step forward, this particular system also produced large amounts of waxes, possibly as a result of incomplete reduction of the precatalyst to the monovalent state.

The combination of N and P donor atoms on an ancillary ligand system has successfully produced selective oligomerization systems.[3,11] Recent studies in our lab on chromium complexes stabilized by a simple monoanionic $[Ph_2PN(R)]^-$ ligand system illustrated its versatility for assembling polymetallic structures and self-activating species occasionally showing selective catalytic behavior.[12,13] To study how the nuclearity of the catalysts may affect the catalytic behavior, we have now linked two NP-units with both ethylenic and propylenic bridges in order to stimulate the formation of dimetallic species.

2.2 Experimental Part

Reactions were carried out under inert atmosphere in Schlenk glassware or in a purified nitrogen-filled drybox. Solvents were dried using a purification system composed of aluminum oxide. All chemical reagents were purchased from commercial sources and used as received. Diethyl aluminum chloride, trimethyl aluminum, triethyl aluminum, tri-isobutyl aluminum and diethyl zinc were purchased from Strem and used as received. Methylaluminoxane (MAO, 20% in toluene) was purchased from Albemarle Corporation. TMA-depleted methylaluminoxane (DMAO) was prepared by removing all the volatiles from MAO *in* vacuo (2 mmHg) and with moderate heating (40 °C) for 6 hours. GC-MS analysis of the oligomers was done with a Hewlett-Packard HP 5973 gas chromatograph using an Agilent DB1 column. Elemental analysis was carried out with a Perkin-Elmer 2400 CHN analyzer. Magnetic susceptibility measurements were performed with a Johnson Matthey Magnetic Susceptibility balance at room temperature; the samples were weighed inside a drybox and transferred to sealed and calibrated tubes for measurements. X-ray crystal data were determined using a Bruker diffractometer equipped with a Smart CCD area detector and with Bruker Kappa APEXII CCD diffractometer. NMR spectra were recorded on Bruker Avance 300 MHz spectrometer at 300 K. Oligomerization reactions were carried out under pressure in a 300 mL Parr reactor equipped with stirrer and temperature control.

2.2.1 Synthesis of Ligands

Preparation of $Ph_2PN(Me)(CH_2)_2N(Me)PPh_2$ (a-Me)

A solution of N,N'-dimethylethane-1,2-diamine (4 mL, 40 mmol) in THF (100 mL) was treated with Et_3N (14 mL, 100 mmol). The solution was cooled to 0°C and chlorodiphenylphosphine (14 mL, 80 mmol) was slowly added. Formation of a white salt was observed within a few hours. The solution was heated to 70 °C for 96 hours and then filtered. The clear filtrate was heated *in vacuo* to remove the solvent and a white solid residue of **a-Me** was obtained. The sample did not require further purification (16.0 g, 35 mmol, 88%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.33 (m, 20H), 3.17 (m, 4H), 2.50 (d, J = 5.8 Hz, 6H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 139.3, 131.8, 128.4, 128.0, 55.1, 37.2. ^{31}P NMR (300 MHz, $CDCl_3$) δ: 61.92 (s).

Preparation of $Ph_2PN(Me)(CH_2)_3N(Me)PPh_2$ (b-Me)

A solution of N,N'-dimethylpropane-1,3-diamine (5 mL, 48 mmol) in THF (90 mL) was treated with Et_3N (16 mL, 112 mmol), cooled to 0°C, and added dropwise with chlorodiphenylphosphine (17 mL, 97 mmol). After similar treatment as above, a colorless oil of **b-Me** sufficiently pure for further use was obtained (14 g, 29 mmol, 61%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.31 (m, 20H), 3.05 (m, 4H), 2.47 (d, J = 6.1 Hz, 6H), 1.68 (m, 2H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 139.2, 131.8, 128.3, 128.0, 54.4, 37.0, 28.4. ^{31}P NMR (300 MHz, $CDCl_3$) δ: 61.19 (s).

Preparation of $Ph_2PN(Et)(CH_2)_3N(Et)PPh_2$ (b-Et)

A solution of N,N'-diethylpropane-1,3-diamine (10 mL, 63 mmol) in THF (180 mL) was treated with Et_3N (20 mL, 145 mmol), cooled to 0°C, and added with chlorodiphenylphosphine (22 mL, 126 mmol) dropwise. After similar treatment as above, **b-Et** was isolated as a slightly yellow oil of sufficient purity for further use (25 g, 50 mmol, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.28 (m, 20H), 2.94 (dq, J = 9.5, 7.1 Hz, 4H), 2.85 (q, J = 8.9 Hz, 4H), 1.36 (m, 2H), 0.83 (t, J = 7.0 Hz, 6H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 140.1, 132.0, 128.2, 128.0, 48.1, 45.1, 28.4, 14.4. ^{31}P NMR (300 MHz, $CDCl_3$) δ: 61.19 (s).

Preparation of $Ph_2PN(\textit{i}\text{-}Pr)(CH_2)_3N(\textit{i}\text{-}Pr)PPh_2$ (b-^{i}Pr)

A solution of N,N'-diisopropylpropane-1,3-diamine (3 mL, 16 mmol) in THF (100 mL) was treated with Et_3N (5 mL, 36 mmol), cooled to 0°C and added dropwise with chlorodiphenylphosphine (6 mL, 32 mmol). After similar treatment as above, **b-^{i}Pr** was isolated as a thick yellow oil of sufficient purity for further use (6 g, 12 mmol, 72%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.28 (m, 20H), 3.04 (sep, J = 6.7 Hz, 2H), 2.53 (m, 4H), 1.03 (d, J = 6.6 Hz, 12H), 0.99-0.91 (overlapped, 2H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 140.4, 132.2, 128.0, 127.9, 51.5, 46.8, 31.2, 23.4. ^{31}P NMR (300 MHz, $CDCl_3$) δ: 42.85 (s).

Preparation of *i*Pr$_2$PN(Me)(CH$_2$)$_3$N(Me)P*i*Pr$_2$ (b-P^{i}Pr)

A solution of N,N'-dimethylpropane-1,3-diamine (6 mL, 50 mmol) was treated with Et_3N (16 mL, 115 mmol) in THF (130 mL), cooled to 0°C and added drop-wise with chlorodiisopropylphosphine (16 mL, 100 mmol). After similar treatment as above, **b-P^{i}Pr** was isolated as a yellow liquid of sufficient purity for further use (12 g, 36 mmol, 71%). ^{1}H [^{31}P] NMR (300 MHz, $CDCl_3$) δ: 2.82 (t, J = 7.4 Hz, 4H), 2.46 (s, 6H), 1.73 (sep, J = 7.0 Hz, 4H), 155 (m, 2H), 0.94 (dd, J = 4.4, 7.1 Hz, 24H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 55.7, 36.7, 28.8, 26.2, 19.4. ^{31}P NMR (300 MHz, $CDCl_3$) δ: 82.28 (s).

2.2.2 Synthesis of Complexes

Preparation of (a-Me)CrCl$_3$(THF)

A suspension of $CrCl_3(THF)_3$ (0.19 g, 0.50 mmol) in toluene (5 mL) was treated with **a-Me** (0.23 g, 0.50 mmol). The suspension changed color to brown and stirring was continued for 4 hours. A small amount of insoluble material was eliminated by centrifugation and the resulting solution was layered with hexane affording **(a-Me)CrCl$_3$(THF)** at room temperature as a brown microcrystalline solid (0.24 g, 0.35 mmol, 70%). Elemental Analysis % calculated for $C_{32}H_{38}P_2N_2CrCl_3O$ (Found): C 55.93 (55.91), H 5.53 (5.50), N 4.08 (4.10). ESI-MS *m/z* = 686.27 $(M+H)^+$

Identical procedure and amount as above were used for the preparation of the following complexes for the purpose of ethylene oligomerization:

Preparation of (a-Me)$CrCl_2$

A brown solid (0.14 g, 0.24 mmol, 48%). E.A. calculated for $C_{28}H_{30}P_2N_2CrCl_2$ (Found): C 58.03 (58.07), H 5.18 (5.12), N 4.83 (4.79); ESI-MS *m/z* = 579.35 $(M+H)^+$

Preparation of (b-Me)$CrCl_3$(THF)

A brown solid (0.23 g, 0.33 mmol, 66%). E.A. calculated for $C_{33}H_{40}P_2N_2CrCl_3O$ (Found): C 56.53 (56.49), H 5.71 (5.80), N 4.00 (4.11); ESI-MS *m/z* = 700.42 $(M+H)^+$

Preparation of (b-Me)$CrCl_2$

A brown solid (0.15 g, 0.26 mmol, 52%). E.A. calculated for $C_{29}H_{32}P_2N_2CrCl_2$ (Found): C 58.78 (58.69), H 5.40 (5.49), N 4.07 (4.09); ESI-MS *m/z* = 593.01 $(M+H)^+$

Preparation of (b-Et)$CrCl_3$(THF)

A brown solid (0.28 g, 0.39 mmol, 77%). E.A. calculated for $C_{35}H_{44}P_2N_2CrCl_3O$ (Found): C 57.66 (57.81), H 6.08 (5.92), N 3.84 (3.79); ESI-MS *m/z* = 728.29 $(M+H)^+$

Preparation of (b-^{i}Pr)$CrCl_3$(THF)

A brown solid (0.17 g, 0.22 mmol, 44%). E.A. calculated for $C_{37}H_{48}P_2N_2CrCl_3O$ (Found): C 58.70 (58.92), H 6.39 (6.42), N 3.70 (3.80); ESI-MS *m/z* = 755.98 $(M+H)^+$

Preparation of (b-P^{i}Pr)$CrCl_3$(THF)

A brown solid (0.17 g, 0.29 mmol, 59%). E.A. calculated for $C_{21}H_{48}P_2N_2CrCl_3O$ (Found): C 44.65 (44.54), H 6.39 (6.38), N 3.70 (3.66); ESI-MS *m/z* = 564.17 $(M+H)^+$

Preparation of Complex 2.1

A solution of **a-Me** (0.23 g, 0.5 mmol) in toluene (3 mL) was treated with $CrCl_3(THF)_3$ (0.19 g, 0.5 mmol). The suspension was stirred overnight affording a brown suspension. To this, Et_2AlCl (0.30 g, 2.5 mmol) was slowly added, and the resulting greenish blue solution was stirred for 1 hour and then centrifuged. The supernatant was layered with hexanes (1 mL) and stored at -30 °C for 3 days. Teal blue crystals of **2.1** were filtered and washed with cold hexanes (2 mL) and dried *in vacuo* (0.54 g, 0.3 mmol, 76%). $\mu_{eff} = 5.09\ \mu_B$. ESI-MS *m/z* = 1243.16 (**2.1**+H)$^+$

Preparation of Complex 2.2

A suspension in toluene (3 mL) of **a-Me** (0.23 g, 0.5 mmol) and $CrCl_3(THF)_3$ (0.19 g, 0.5 mmol) was stirred overnight to afford a brown suspension. After cooling to -30 °C, Me_3Al (0.11 g, 1.5 mmol) was added dropwise and under stirring for 10 min. A dark green solution was obtained that was then centrifuged. Blue crystals of **2.2** formed upon slow evaporation of the supernatant over a period of 3 days. The crystals were filtered and washed with cold hexanes (2 mL) and dried *in vacuo* (0.12 g, 0.1 mmol, 19%). $\mu_{eff} = 4.69\ \mu_B$. MS (ESI) *m/z* = 1123.10 (**2.2**+H)$^+$

2.3 X-Ray Data

Table 2.1. Table of crystal data and refinements for **2.1** and **2.2**.

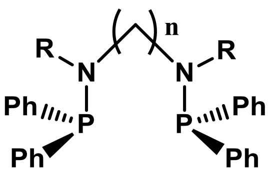
	2.1	**2.2**
Formula	$C_{134.5}H_{162}Al_4Cl_{14}Cr_4N_8P_8$	$C_{58}H_{66}AlCl_5Cr_2N_4P_4$
Mw	2950.70	1251.26
Space group	Triclinic, P-1	Triclinic, P-1
a **(Å)**	11.9044(2)	14.467(2)
b **(Å)**	19.7633(4)	14.571(2)
c **(Å)**	20.3439(4)	15.578(3)
α, (deg)	78.534(1)	107.124(4)
β, (deg)	81.279(1)	97.457(3)
γ, (deg)	79.365(1)	90.184(4)
V **(Å^3)**	4577.28(15)	3108.7(9)
Z	2	2
Radiation	0.71073	0.71073
T (K)	200(2)	200(2)
D_{calcd} **(g cm^{-3})**	1.313	1.337
μ_{calcd} **(mm^{-1})**	0.790	0.721
F_{000}	1878.0	1296.0
R, Rw^{2a}	0.0473, 0.1350	0.0538, 0.1596
GoF	1.012	1.021

[a] $R = \Sigma jFoj - jFcj/\Sigma jFj$. $Rw = [\Sigma(jFoj - jFcj)2/\Sigma wFo2]^{1/2}$

2.4 Results and Discussion

The $Ph_2PN(R)(CH_2)_nN(R)$ PPh_2 (**a-Me**: $n = 2$, R = Me; **b-Me**: n = 3, R = Me; **b-Et**: n = 3, R = Et; **b-*i*Pr**: n = 3, R = *i*-Pr) (Scheme 2.1) ligands were synthesized by the condensation of the appropriate diamine with chlorodiphenylphosphine. These ligands do not react with chromium salts in THF. Nonetheless, they readily ligate trivalent chromium salts in toluene as indicated by color change and dissolution upon mixing. Complexes were isolated as microcrystalline materials from toluene solutions after centrifugation and upon layering with hexane. Analytical and ESI-MS data were in agreement with simple ligand coordination.

Scheme 2.1



a-Me: n = 2, R = Me

b-Me: n = 3, R = Me

b-Et: n = 3, R = Et

b-*i*Pr: n = 3, R = *i*Pr

In the case of the reaction of $CrCl_3(THF)_3$ with **a-Me** the precipitated complex was isolated, re-suspended in toluene and subsequently treated with aluminum alkyl reagents. When Et_2AlCl (DEAC) and Me_3Al (TMA) were used as aluminum alkyls, two crystalline products were obtained. The formulations as $(\{[Ph_2PN(Me)(CH_2)_2N(Me)PPh_2]Cr(\mu\text{-}Cl)\}_2[(\mu\text{-}Cl)_2(AlEt_2)])^+(EtAlCl_3)^-.(toluene)_{1.5}$ (**2.1**) and $[\{[Ph_2PN(Me)(CH_2)_2N(Me)PPh_2]\ Cr\}(\mu\text{-}Cl)_3]^+[AlMe_2Cl_2]^-$ (**2.2**) were deduced by X-ray crystal structure determinations (Figure 2.1 and 2.2 respectively).

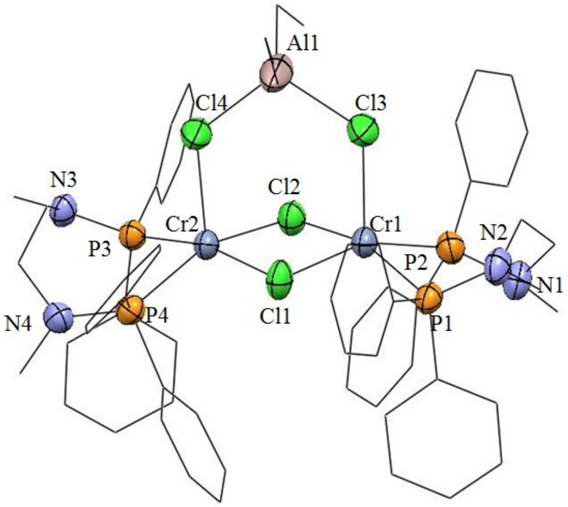


Figure 2.1. Partial thermal ellipsoid drawings for **2.1** at 50% probability. The $EtAlCl_3$ counteranion has been omitted for clarity. Select bond lengths (Å) and angles (deg) of **2.1**: Cr1-Cl1 2.3593(15), Cr1-Cl2 2.4031(15), Cr1-Cl3 2.5967(17), Cr1-P1 2.4701(17), Cr1-P2 2.4934(16), Cl1-Cr1-Cl2 89.39(5), Cl1-Cr1-P1 150.54(6), Cl2-Cr1-P2 85.93(5), Cl1-Cr1-Cl3 98.64(6).

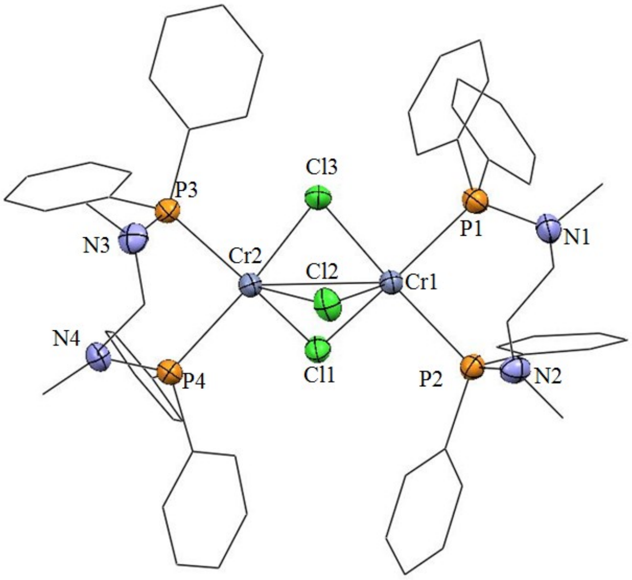


Figure 2.2. Partial thermal ellipsoid drawings for **2.2** at 50% probability. The Me_2AlCl_2 counteranion has been omitted for clarity. Select bond lengths (Å) and angles (deg) of **2.2**: Cr1-P1 2.5148(11), Cr1-P2 2.4732(12), Cr1-Cll 2.3973(10), Cr1-Cl2 2.5550(11), Cr1-Cl3 2.3930(11), Cr1-Cr2 2.9714(8), P1-Cr1-P2 91.01(4), Cl2-Cl1-Cl3 87.41(4), Cr1-Cl1-Cr2 76.53(3), Cr1-Cl2-Cr2 71.34(3), Cr1-Cl3-Cr2 76.34(3), P1-Cr1-Cl1 162.19(4), P1-Cr1-Cr2 109.20(4), P1-Cr1-Cl3 89.06(4).

Both complexes showed similar dinuclear structures where each ligand chelates a single chromium atom with the two phosphorus donors. The Cr..N distances are well beyond the bonding range, varying between 3.419 and 3.618 Å. The dimetallic structures are formed by either two bridging chlorines and one bridging $(\mu\text{-Cl})_2AlEt_2$ unit (**2.1**), or by three bridging chlorines (**2.2**). In either case, $EtAlCl_3^-$ or $Me_2AlCl_2^-$ counter anions, unconnected with the dimetallic frame, are also part of the ionic structure. In both complexes the chromium centers are divalent. As expected, reduction of the metal center is often observed when trivalent chromium precursors are treated with aluminum alkyls.[6,14]

The catalytic activity of complexes **2.1** and **2.2** is low due to their poor solubility in both methylcyclohexane (MeCy) and toluene. Test reactions carried out on the precipitated ligand-$CrCl_3$ adducts showed no difference in catalytic behavior in comparison with the *in situ* generated species. Therefore, extensive catalytic testing was probed with *in situ* generated complexes, conveniently obtained by mixing either $CrCl_3(THF)_3$ or $CrCl_2(THF)_2$ with the appropriate ligand, activator and solvent in the reactor pressurized with ethylene. The reactions carried out in toluene using MAO as cocatalyst produced S-F distributions of oligomers albeit with high activity. Interestingly though, it must be noted that the product mixtures were polymer-free (Table 2.2). Conversely, when MeCy was used as solvent and TMA-depleted MAO (DMAO) as cocatalyst, a reasonably selective oligomerization catalyst was obtained. The reason for using DMAO was that MAO is available in a toluene solution, and hence in order to perform oligomerization tests in MeCy using MAO, it must be dried completely (in doing so, depleting free TMA that it contains).

Although the catalytic activity, when the oligomerization tests are carried out in MeCy using DMAO, is significantly lower than for the MAO- activated system in toluene, the product distributions were interesting. The mixtures consisted exclusively of 1-hexene and 1-octene. Generally 1-hexene was the dominant product, except for the cases when $CrCl_2(THF)_2$ was substituted for $CrCl_3(THF)_3$, and when a mixture of DMAO and Et_3Al was employed as a cocatalyst. The moderate predominance of ethylene tetramerization observed with the **a-Me**/$CrCl_3(THF)_3$/DMAO complex prompted us to modify the ligand further.

Table 2.2. Ethylene oligomerization results of **a-Me**/$CrCl_3(THF)_3$ and **2.1**.[a]

catalyst	co-catalyst (equiv)	α-olefins (mL)	PE (g)	activity (g/g Cr . h)	Mol % C_6	Mol % C_8	Mol % $C_{10\text{-}18}$
a-Me[b]	MAO (500)	97	0	88,917	28	26	46
a-Me[c]	DMAO (500)	6	1.1	6,910	70	31	0
a-Me[c,d]	DMAO (500)	3	0	2,750	40	60	0
a-Me[c]	DMAO/Me_3Al (500/100)	3	0	2,750	50	50	0
a-Me[c]	DMAO/Et_3Al (500/100)	3	0	2,750	37	61	2
a-Me[c]	DMAO/*i*Bu_3Al (500/100)	1	0	917	56	44	0
2.1[b]	MAO (500)	50	0	45,833	17	23	60
2.1[c]	DMAO (500)	-	-	-	-	-	-

[a]Conditions: ligand (30 μmol), [$CrCl_3(THF)_3$] (30 μmol), solvent (100 mL), 80 ˚C, ethylene (40 bar), 30 min. [b]Toluene as solvent. [c]MeCy as solvent. [d][$CrCl_2(THF)_2$]. PE = polyethylene.

The simple introduction of an additional methylene group into the ethylenic bridge linking the two NP units (**b-Me**)had a remarkable impact on catalytic behavior (Table 2.3). Even in this case the microcrystalline adducts with chromium salts displayed the same catalytic behavior as *in situ* generated species. However, the use of MAO and DMAO in toluene with the new complex resulted in a S-F distribution of oligomers, albeit with good activity and no polymer formation, whereas switching to MeCy as solvent produced a highly selective and reasonably active ethylene tetramerization system. Even more interestingly, the product mixtures were polymer-free with the only byproduct being 1-hexene. Increasing the temperature up to 100 °C had a positive effect on the selectivity towards 1-octene whilst the activity remained the same. As observed for **a-Me**, using $CrCl_2(THF)_2$ as catalyst precursor helps to increase the selectivity towards 1-octene with the selectivity reaching a record high of 91%. The addition of organoaluminum or organozinc activators to DMAO considerably improved the outcome of the catalytic runs in terms of both activity and selectivity. Adding Et_3Al, in particular peaked the activity of 1-octene while maintaining good selectivity, although some polymer was also produced as a function of the amount of Et_3Al added. Other additives such as *i*-Bu_3Al or Et_2Zn also displayed good selectivity for 1-

octene but resulted in somewhat lower activity and also produced small amounts of polymer. The introduction in the molecular scaffold of bulkier groups at either the N (**b-Et, b-^{i}Pr**) or P atoms (**b-P^{i}Pr)** of the ligand decreased both activity and selectivity. Changing the Cr/ligand ratio also negatively affected the activity and the selectivity. Variation of overall catalyst loading dramatically affects the selectivity (Table 2.3, entries 2 and 9-13). The overall behavior has a non-straightforward interpretation clearly showing the existences of two parallel trends. After the initial rise of octene concentration as function of the loading, the selectivity switches towards 1-hexene to fall then into a S-F distribution at the highest loadings. Because of this dependence of selectivity on the catalyst concentration, it is assumed as an indication for the presence of multiple equilibria in the catalytic mixture.

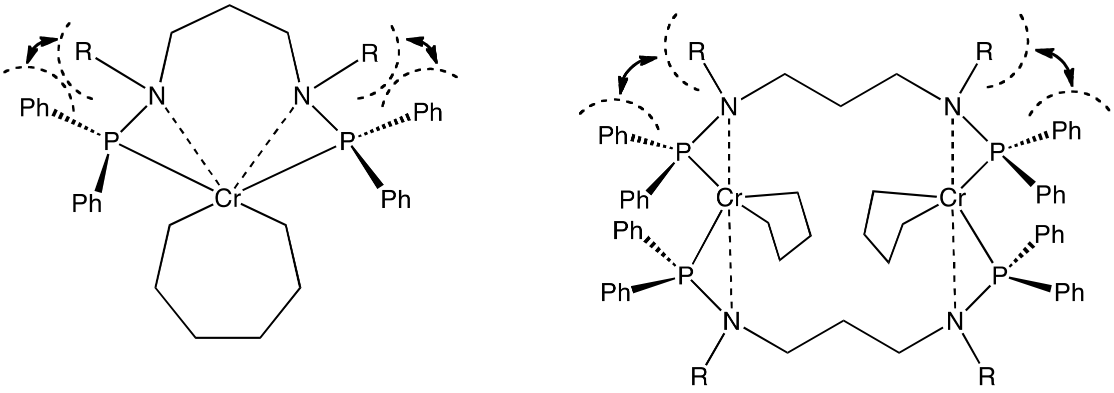
Table 2.3. Ethylene oligomerization results of various ligands.[a]

catalyst	co-catalyst (equiv)	α-olefins (mL)	PE (g)	activity (g/g Cr . h)	Mol % C_6	Mol % C_8	Mol % C_{10-18}
b-Me[e]	MAO (500)	18	0	16,500	35	30	35
b-Me[e]	DMAO (500)	22	0	11,000	15	26	59
b-Me[f]	DMAO (500)	8	0	7,333	19	81	0
b-Me[f,h]	DMAO (500)	6	1.0	6,621	31	69	0
b-Me[f,i]	DMAO (500)	3	3.0	6,012	33	67	0
b-Me[b,f]	DMAO (500)	8	0	7,333	29	68	4
b-Me[c,f]	DMAO (500)	8	0	7,333	15	85	0
b-Me[d,f]	DMAO (500)	2	0	1833	9	91	0
b-Me[f,j]	DMAO (500)	1	0	555	35	65	0
b-Me[f,k]	DMAO (500)	5	0.7	5,480	28	72	0
b-Me[f,l]	DMAO (500)	11	1.1	11,494	27	67	6
b-Me[f,m]	DMAO (500)	21	2.6	22,186	59	15	24
b-Me[f,n]	DMAO (500)	18	3.0	20,346	27	17	56
b-Me[f]	DMAO/Me_3Al (500/100)	12	0	11,000	25	75	0
b-Me[f]	DMAO/Et_3Al (500/25)	13	0.7	12,814	18	77	5
b-Me[f]	DMAO/Et_3Al (500/100)	22	4.1	25,424	11	88	1
b-Me[f,g]	DMAO/Et_3Al (500/100)	10	0.2	9,424	23	77	0
b-Me[f]	DMAO/Et_3Al (500/250)	5	0.4	5,096	24	72	4
b-Me[f]	DMAO/$i$$Bu_3Al$ (500/100)	7	0.6	7,186	10	89	1
b-Me[f]	DMAO/Et_2AlCl (500/100)	1	1.1	2,326	53	36	11
b-Me[f]	DMAO/Et_2Zn (500/100)	2	0	1,834	12	87	1
b-Et[f]	DMAO/Et_3Al (500/100)	8	0.9	8,488	33	67	0
b-*i*Pr[f]	DMAO (500)	4	1.6	5,718	59	41	0
b-*i*Pr[f]	DMAO/Et_3Al (500/100)	6	0.4	6,012	73	27	0
b-P*i*Pr[f]	DMAO (500)	3	2.5	5,956	41	59	0

[a]Conditions: ligand (30 µmol), $[CrCl_3(THF)_3]$ (30 µmol), solvent (100 mL), 80 ˚C, ethylene (40 bar), 30 min. [b]60 ˚C. [c]100 ˚C. [d]$[CrCl_2(THF)_2]$. [e]Toluene as solvent. [f]MeCy as solvent. [g]Ethylene (20 bar). [h]Ligand (60 µmol), $[CrCl_3(THF)_3]$ (30 µmol). [i]Ligand (30 µmol), $[CrCl_3(THF)_3]$ (60 µmol). [j]Catalyst (15 µmol). [k]Catalyst (22 µmol). [l]Catalyst (45 µmol). [m]Catalyst (60 µmol). [n]Catalyst (90 µmol).

Given the close similarity between **a-Me** and **b-Me** (ethylenic *vs.* propylenic bridge between the two NP units), the switch of selectivity from 1-hexene to 1-octene cannot possibly be understood on the ground of differences in electronic features. Therefore, the longer $N(CH_2)_3N$ chain of **b-Me** remains the sole factor responsible for the unique selectivity towards ethylene tetramerization. Although we have no conclusive data, we speculate that such a remarkable sensitivity could perhaps be explained in terms of monomer *versus* dimer formation (Scheme 2.2). In fact, the formation of dichromium systems (both mono and divalent) is indeed highly dependent on steric interactions within the ligand scaffold.[15] Thus, if we assume that monomeric and dimeric structures may co-exist and that each of the two arrangements is responsible for either 1-hexene or 1-octene formation, it is natural that changes on the ligand scaffold may lead the catalytic cycle into either direction of product formation. Given that the ligand system is neutral, the formation of a dimeric structure may or may not require reversible dissociation of one ligand. The marked dependence on the nature of the activator may be difficult to rationalize and yet, it may contribute to the same working hypothesis. This is to say that, it must be assumed that the aggregation with alkyl aluminum is also affecting the sterics of the catalytically active species (see for example the structure of **2.1**). However, even in the case that a dimetallic mechanism would be followed, it would not necessarily deliver bimetallic reductive elimination.

Scheme 2.2



The selective behavior in any event is provided by a monovalent chromium, as the only oxidation state so far shown capable of performing the initial reductive coupling of the two ethylene molecules.[5] Unlike Sasol's PNP- and SK Energy's PC_2P-based catalysts,[3a,b] the current system shows a strong solvent and cocatalyst dependence. So far, selective ethylene tetramerization has only been observed in MeCy. In toluene invariably S-F distributions of α-olefins were obtained.

2.5 Conclusion

We have herein reported the first tetramerization catalyst capable of producing 1-octene with high purity, and moderate activity with little to no polymer produced as a byproduct. Both solvent and cocatalyst have a dramatic impact on the selectivity. In a previous study,[3e] we have observed a tetramerization system producing 1-octene at greater than 99% selectivity, along with the formation of a large amount of wax. With this work, we have been able to advance further in developing a potentially useful tetramerization system of high selectivity and low byproduct formation, as demonstrated.. Whether the present catalytic system may or not be linked to Rosenthal's dimetallic hypothesis is not yet clear. The remarkable change in catalytic behavior upon such a minor modification on the ligand framework as going from **a-Me** to **b-Me** (ethylenic *vs.* propylenic bridge between the two NP units) is puzzling, to say the least. Regrettably, the transition species responsible for such selectivity have so far eluded crystallographic characterization that possibly could have conclusively supported the link between nuclearity and tetramerization behavior. Nonetheless, the fact that we are able to observe a tetramerization system of such high selectivity (up to 91%) is encouraging. Further attempts to isolate self-activating catalytically active species as well as improving catalyst performance will be carried out.

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Ethylene Oligomerization Study of Si(NP)$_2$ Ligand on Chromium

3.1 Introduction

Ethylene oligomerization is a highly relevant catalytic process particularly important for the petrochemical industry.[1] In particular, the high demand for 1-hexene and 1-octene for their large scale use as co-monomers in polyethylene industry, as well as for the manufacture of lubricants, surfactants and alcohols, continuously stimulate research in both industrial and academic sectors for finding new and better performing catalysts.[2] Over the past decades, there have been significant advances in this field with particular accent on addressing the selectivity issue. As a result, several catalytic systems have been developed almost exclusively with the employment of chromium complexes.[3] Today, trivalent chromium based ethylene trimerization systems are very well established and have proven to be quite selective (99%) and highly active towards 1-hexene production.[4] There have also been reports of selective tetramerization catalysts based on trivalent chromium,[5] albeit the selectivity and activity achieved in this case, curiously, remains far from that of the trimerization catalysts. The reason for this discrepancy is likely to be found in mechanistic reasons. The selective transformation of ethylene to 1-hexene or 1-octene is believed to follow a so-called ‘ring-expansion’ mechanism involving metallacycles.[6] It is a redox process where the Cr(III) pre-catalyst is first reduced to Cr(I). These highly reactive intermediates oxidatively add two ethylene molecules, forming a 5-membered metallacycle. This ‘ring’ expands upon further ethylene insertion and eventually reductively eliminates 1-hexene or 1-octene and reforms Cr(I).

However, there has been recent debates arguing that the selective formation of 1-octene may follow an alternative, bi-metallic mechanism. Such an argument remains yet to be proven.[7]

The most favored synthetic strategy towards designing a selective ethylene oligomerization catalyst is to generate mono-valent chromium upon *in-situ* reduction of tri-valent chromium starting materials.[8] This reduction has to by-pass the di-valent oxidation state which is more resilient to reduction and is instead responsible for non-selective oligomerization with high activity.[9] In fact, there have been a significant number of *non-selective* ethylene oligomerization catalysts based on Cr(II)[9] and whose catalytic mechanism is conceptually different from that of the selective oligomerization.[4u,6] Di-valent chromium follows a standard, non-redox, chain growth mechanism[10] affording a statistical distribution of oligomers called a Schulz-Flory distribution (S-F).

The ligand's geometric and electronic properties, once it is bound to a metal center, are very important factors in determining the catalytic behavior. The intellectual challenge to achieve selective behavior consists of the design of an appropriate ligand system allowing a synchronous two-electron reduction of Cr(III) to the catalytically active monovalent state bypassing the divalent one. To explore this possibility, we have previously worked on $PN(CH_2)_nNP$ ligand framework in combination with Cr(III) precursors and discovered that the number of methylene groups in the bridge connecting the two NP functions ($n = 2, 3$) determines the type of selectivity of the catalytic cycle (formation of 1-hexene, versus 1-octene). In particular, the very high selectivity for the formation of 1-octene (> 90% selectivity) was the prompted us to propose two separate mechanisms for the selective tri- and tetramerization.[7c] Since the $PN(CH_2)_nNP$ ligand has demonstrated its potential to promote selective catalytic behavior, we were led to believe in its ability to support mono-valent chromium during the catalyst activation conditions. Being puzzled by the remarkable switch of selectivity from 1-hexene to 1-octene as a function of the absence/presence of one sole methylene function in the ethylene bridge, we have now modified the ligand framework by introducing a silylated linker. Herein we describe our results.

3.2 Experimental Part

Reactions were carried out under inert atmosphere using Schlenk techniques or in a purified nitrogen-filled drybox. Solvents were dried using a purification system composed of aluminum oxide. All chemical reagents were purchased from commercial sources and used as received. Diethyl aluminum chloride, trimethyl aluminum, triethyl aluminum and tri-isobutyl aluminum were purchased from Strem and used as received. Methylaluminoxane (MAO, 20% in toluene) was purchased from Albemarle Corporation. TMA-depleted methylaluminoxane (DMAO) was prepared by removing all the volatiles from MAO *in* vacuo (2 mmHg) and with moderate heating (40 °C) for 6 hours. GC-MS analysis of the oligomers was done with a Hewlett-Packard HP 5973 gas chromatograph using an Agilent DB1 column. Elemental analysis was carried out with a Perkin-Elmer 2400 CHN analyzer. Magnetic susceptibility measurements were performed with a Johnson Matthey balance at room temperature; the samples were powdered and weighed inside a drybox and transferred to sealed and calibrated tubes for measurements. X-ray crystal data were determined using a Bruker diffractometer equipped with a Smart CCD area detector and with Bruker Kappa APEXII CCD diffractometer. NMR spectra were recorded on Bruker Avance 300 MHz spectrometer at 300 K. Oligomerization reactions were carried out under pressure in a 300 mL Parr reactor equipped with stirrer and temperature control.

3.2.1 Synthesis of Ligands

Preparation of $SiMe_2(N(tol)PPh_2)_2$ [$Si(NP)_2$]

The synthesis was performed by following an established literature procedure.[11] Solid NH_2tol (*p*-toluidine) (10.00 g, 93.3 mmol) was treated with Ph_2PCl (8.60 mL, 46.6 mmol) in THF (150 mL) at 0 °C and the solution was stirred overnight at room temperature. The solid material was eliminated by filtration and the solution dried *in vacuo* to afford a white solid identified as $NH(tol)PPh_2$ (11.13 g, 38.2 mmol, 82%). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.62-6.82 (m, 14H (P-Ph and N-Ph H's)), 4.42 (br, 1H), 2.22 (b, 3H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 144. 9, 140.1, 133.2, 129.8, 129.0, 128.9, 128.2, 115.9, 21.2. ^{31}P NMR (300 MHz, $CDCl_3$) δ: 25.5 (s).

The isolated NH(tol)PPh_2 (11.13 g, 38.2 mmol) was dissolved in THF and added to a toluene and THF mixture (60 mL + 80 mL) and subsequently treated with *n*-BuLi (2.5 M, 15.28 mL, 38.2 mmol) at -30 °C. The resulting mixture was stirred for 2 hr at room temperature and $SiMe_2Cl_2$ (2.30 mL, 129.1 mmol) was added. The solution was then allowed to stir at 60 °C for 24 hrs, the volatiles were then removed *in vacuo*, and the residue was extracted with CH_2Cl_2. The liquid phase was concentrated and layered with hexanes and allowed to stand at -30 °C for 2 days. The white precipitate was collected, washed with Et_2O, dried *in vacuo* and identified as $SiMe_2(N(tol)PPh_2)_2$ (7.19 g, 11.3 mmol, 59%). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.42-6.52 (m, 28H (P-Ph and N-Ph H's)), 2..46 (s, 6H), 0.57 (s, 6H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 142. 6, 139.1, 134.0, 133.8, 130.9, 128.6, 128.3, 127.2, 20.3, 3.0. ^{31}P NMR (300 MHz, $CDCl_3$) δ: 49.4 (s).

3.2.2 Synthesis of Complexes

Preparation of Complex 3.1

A solution of the ligand **$Si(NP)_2$** (0.32 g, 0.5 mmol) in toluene (3 mL) was treated with $CrCl_3(THF)_3$ (0.19 g, 0.5 mmol) and the resulting suspension heated for 5 minutes at 120 °C whereupon the solution turned dark-green. The solution was centrifuged to separate the insoluble precipitate. Upon solvent removal *in vacuo* from the clear solution, the green microcrystalline powder was isolated, washed with hexanes (3 x 3 mL) and used for characterization and oligomerization testing (0.38 g, 0.4 mmol, 87%). $\mu_{eff} = 3.82\ \mu_B$. Elemental Analysis % calculated for $C_{44}H_{48}Cl_3CrN_2OP_2Si$ (Found): C 60.80 (60.62), H 5.57 (5.41), N 3.22 (2.97).

Preparation of Complex 3.2

Method A: A solution of **Si(NP)$_2$** (0.32 g, 0.5 mmol) in toluene (3 mL) was treated with $CrCl_3(THF)_3$ (0.19 g, 0.5 mmol). The suspension was stirred for 2 hours whereby a bluish green color was observed. To this, Et_3Al (0.28 g, 2.5 mmol) was added drop-wise at −30 °C, and the resulting turquoise blue solution was stirred for 10 mins and then centrifuged. The supernatant was layered with hexanes (1 mL) and stored at -30 °C for 3 days. Teal blue X-ray suitable crystals of **3.2** were isolated, filtered and washed with cold hexanes (2 mL) and dried *in vacuo* (0.64 g, 0.3 mmol, 68%). $\mu_{eff} = 6.02\ \mu_B$ per dimeric unit. Elemental Analysis % calculated for $C_{96}H_{120}Al_3Cl_5Cr_2N_4P_4Si_2$ (Found): C 61.58 (61.59), H 6.46 (6.42), N 2.99 (2.82).

Method B: By following the identical procedure as above using **Si(NP)$_2$** (0.32 g, 0.5 mmol), $CrCl_2(THF)_2$ (0.135 g, 0.5 mmol) and Et_3Al (0.28 g, 2.5 mmol) at −30 °C, blue crystalline **3.2** was obtained (0.43 g, 0.2 mmol, 46%).

Preparation of Complex 3.3

Method A: A suspension in toluene (3 mL) of **Si(NP)$_2$** (0.32 g, 0.5 mmol) and $CrCl_3(THF)_3$ (0.19 g, 0.5 mmol) was stirred for 2 hours affording a blue-green suspension. Neat Et_2AlCl (0.30 g, 2.5 mmol) was added dropwise at −30 °C and stirring continued for 10 min. The resulting dark-green solution was centrifuged. Blue crystals of **3.3** formed upon layering the toluene solution with hexanes (1 mL) and storing at -30 °C for 3 days. The crystals were filtered and washed with cold hexanes (2 mL) and dried *in vacuo* (0.54 g, 0.3 mmol, 62%). $\mu_{eff} = 6.16\ \mu_B$ per dimeric formula. Elemental Analysis % calculated for $C_{86}H_{95}Al_2Cl_7Cr_2N_4P_4Si_2$ (Found): C 58.33 (58.79), H 5.41 (5.81), N 3.16 (3.66).

Method B: Following the identical procedure as above using **Si(NP)$_2$** (0.32 g, 0.5 mmol), $CrCl_2(THF)_2$ (0.135 g, 0.5 mmol) and Et_2AlCl (0.30 g, 2.5 mmol) at –30 °C, the blue-green crystalline **3.3** was obtained (0.35 g, 0.2 mmol, 39%).

Preparation of Complex 3.4

A suspension of **Si(NP)$_2$** (0.32 g, 0.5 mmol) and $CrCl_3(THF)_3$ (0.19 g, 0.5 mmol) was prepared in hexanes (7 mL) and *i*-Bu_3Al (0.49 g, 2.5 mmol) was added. The pale-blue suspension turned dark blue upon stirring for 3 hours at room temp. After that time the solution was centrifuged and the insoluble material separated. The supernatant was allowed to stand at room temperature for 2 days. Dark blue crystals of **3.4** were isolated and used for X-ray analysis. The crystals were isolated and dried *in vacuo* (0.54 g, 0.3 mmol, 52%). μ_{eff} = 6.20 μ_B per dimeric formula. Elemental Analysis % calculated for $C_{108}H_{143}Al_3Cl_6Cr_2N_4P_4Si_2$ (Found): C 62.51 (61.78), H 6.95 (6.55), N 2.70 (2.44).

Preparation of Complex 3.5

A suspension of **Si(NP)$_2$** (0.32 g, 0.5 mmol) and $CrCl_3(THF)_3$ (0.19 g, 0.5 mmol) was prepared in toluene (3 mL). The suspension was cooled to –30 °C and Me_3Al (0.18 g, 2.5 mmol) was added over a 10 min period (with intermittent cooling to -30 °C) in a drop-wise manner. The green solution formed was stirred at room temperature for 5 min, and then centrifuged to separate insoluble materials. The solution was separated, layered with hexanes (1 mL) and placed at -30 °C for 3 days. Green crystals of **3.5** were isolated, washed with cold hexanes (2 mL) and used for X-ray analysis. The crystals were then dried *in vacuo* (0.31 g, 0.2 mmol, 37%). μ_{eff} = 5.52 μ_B per dimeric unit. Elemental Analysis % calculated for $C_{85}H_{94}Al_2Cl_5Cr_2N_4P_4Si_2$ (Found): C 60.52 (60.85), H 5.62 (5.72), N 3.32 (3.56).

Preparation of Complex 3.6

Method A: To a suspension of **Si(NP)$_2$** (0.32 g, 0.5 mmol) and CrCl$_3$(THF)$_3$ (0.19 g, 0.5 mmol) in toluene (3 mL), Me$_3$Al was added (0.36 g, 5.0 mmol) drop-wise. The dark blue solution formed was stirred for 15 min, after which time it was centrifuged and the supernatant solution layered with hexanes (1 mL) and stored at -30 °C for 3 days. Blue crystals of **3.6** were collected, filtered and washed with cold hexanes (2 mL) prior to X-ray collection. The crystals were then dried *in vacuo* (0.28 g, 0.2 mmol, 32%). μ_{eff} = 5.98 μ_B per dimeric unit. Elemental Analysis % calculated for $C_{87}H_{101}Al_3Cl_6Cr_2N_4P_4Si_2$ (Found): C 58.69 (58.40), H 5.72 (5.39), N 3.15 (2.94).

Method B: Following identical procedure as above using **Si(NP)$_2$** (0.32 g, 0.5 mmol), CrCl$_2$(THF)$_2$ (0.135 g, 0.5 mmol) and Me$_3$Al (0.18 g, 2.5 mmol) at –30 °C, blue-green crystalline **3.6** was obtained (0.20 g, 0.1 mmol, 23%).

Preparation of Complex 3.7

A suspension of **Si(NP)$_2$** (0.32 g, 0.5 mmol) and CrCl$_3$(THF)$_3$ (0.19 g, 0.5 mmol) was prepared in toluene (3 mL). AlCl$_3$ (0.33 g, 2.5 mmol) was added and a dark brown suspension formed over 30 mins of stirring. Upon centrifugation, a dark brown solution was separated from insoluble materials. The solution was layered with hexanes (1 mL) and left undisturbed for 7 days. Brown block-like crystals of **3.7** were isolated, washed with cold hexanes (2 mL) and used for X-ray analysis. The crystals were dried *in vacuo* (0.56 g, 0.2 mmol, 38%). μ_{eff} = 5.96 μ_B per dimeric unit. Elemental Analysis % calculated for $C_{80}H_{80}Al_{12}Cl_{41}Cr_2N_4P_4Si_2$ (Found): C 30.42 (30.48), H 2.55 (2.55), N 1.77 (1.73).

3.3 X-Ray Data

Table 3.1. Table of crystal data and refinements for **3.2** – **3.7**.

	3.2	**3.3**	**3.4**
Formula	$C_{99.5}H_{122}Al_3Cl_5Cr_2N_4P_4Si_2$	$C_{86}H_{95}Al_2Cl_7Cr_2N_4P_4Si_2$	$C_{106}H_{138.5}Al_3Cl_{6.5}Cr_2N_4P_4Si_2$
Mw	1916.26	1770.83	2064.13
Space group	Triclinic, P-1	Triclinic, P-1	Triclinic, P-1
***a* (Å)**	16.7867(5)	14.0494(6)	14.1701(7)
***b* (Å)**	18.5634(5)	18.7554(8)	20.7331(10)
***c* (Å)**	20.0861(6)	21.3390(8)	21.8217(11)
α, (deg)	82.923(2)	107.504(2)	73.640(3)
β, (deg)	71.588(2)	104.069(2)	72.893(3)
γ, (deg)	63.546(2)	93.035(2)	70.142(3)
V (Å^3)	5315.8(3)	5153.1(4)	5664.0(5)
Z	2	2	2
Radiation	0.71073	0.71073	0.71073
T (K)	200(2)	200(2)	200(2)
D_{calcd} (g cm^{-3})	1.197	1.141	1.215
μ_{calcd} (mm^{-1})	0.481	0.534	0.492
F_{000}	2014.0	1840.0	2176.0
R, Rw^{2a}	0.0617, 0.1906	0.0669, 0.2244	0.0780, 0.2386
GoF	1.012	1.036	1.033

	3.5	**3.6**	**3.7**
Formula	$C_{99}H_{110}Al_2Cl_5Cr_2N_4P_4Si_2$	$C_{90}H_{103.5}Al_3Cl_6Cr_2N_4P_4Si_2$	$C_{82.8}H_{83.2}Al_{5.8}Cl_{26.6}Cr_2N_4P_4Si_2$
Mw	1871.18	1818.97	2517.85
Space group	Triclinic, P-1	Triclinic, P-1	Triclinic, P-1
***a* (Å)**	15.6998(9)	13.4437(3)	14.2770(5)
***b* (Å)**	18.2348(12)	20.2261(5)	18.7128(7)
***c* (Å)**	20.5740(12)	21.1738(5)	28.1865(9)
α, (deg)	69.707(3)	63.493(2)	87.624(2)
β, (deg)	86.292(3)	77.005(2)	78.338(2)
γ, (deg)	81.232(4)	79.213(2)	80.926(2)
V (Å^3)	5459.4(6)	4995.3(2)	7282.3(4)
Z	2	2	2
Radiation	0.71073	0.71073	0.71073
T (K)	200(2)	200(2)	200(2)
D_{calcd} (g cm^{-3})	1.138	1.209	1.148
μ_{calcd} (mm^{-1})	0.460	0.535	0.765
F_{000}	1958.0	1897.0	2543.0
R, Rw^{2a}	0.0773, 0.2506	0.0640, 0.1784	0.0771, 0.2688
GoF	1.034	1.051	1.045

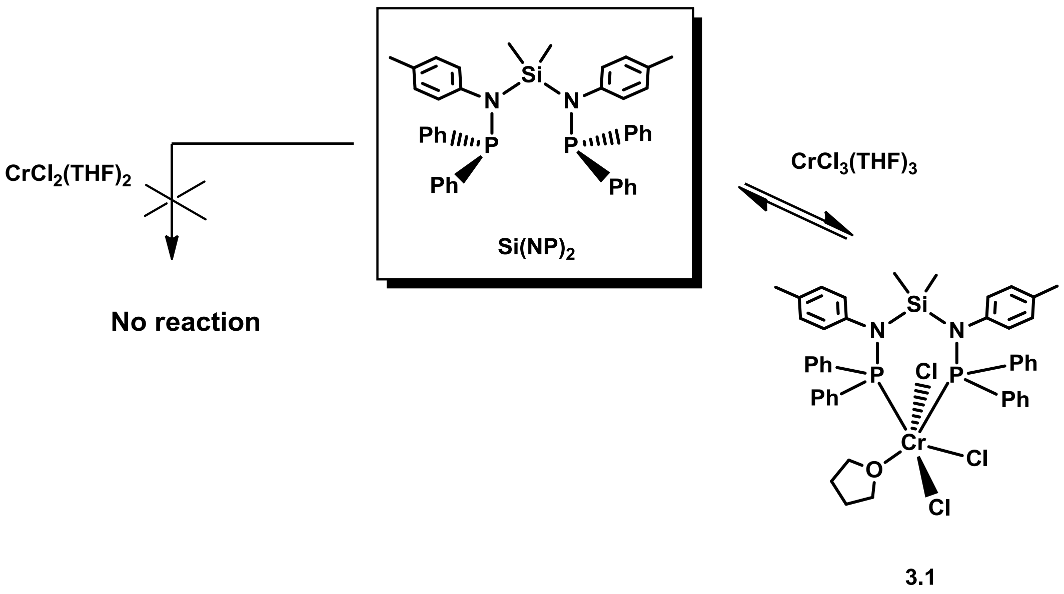
[a] $R = \Sigma jFoj - jFcj/\Sigma jFj$. $Rw = [\Sigma(jFoj - jFcj)2/\Sigma wFo2]^{1/2}$

3.4 Results and Discussion

In order to link two NP units with a one carbon bridge, attempts were made to synthesize $Ph_2PN(Me)CH_2N(Me)PPh_2$ by treating $HN(Me)CH_2N(Me)H$ with Ph_2PCl in the presence of Et_3N. The synthesis proved unsuccessful due to the fact that the protons on the bridging methyl are too acidic and therefore addition of the phosphine at that position becomes possible thus resulting in unwanted mixtures. A solution to this problem was to use Si as the linker, and thus the synthesis of $SiMe_2[N(tol)PPh_2]_2$ (**Si(NP)₂**) was followed according to the established literature procedure.[11]

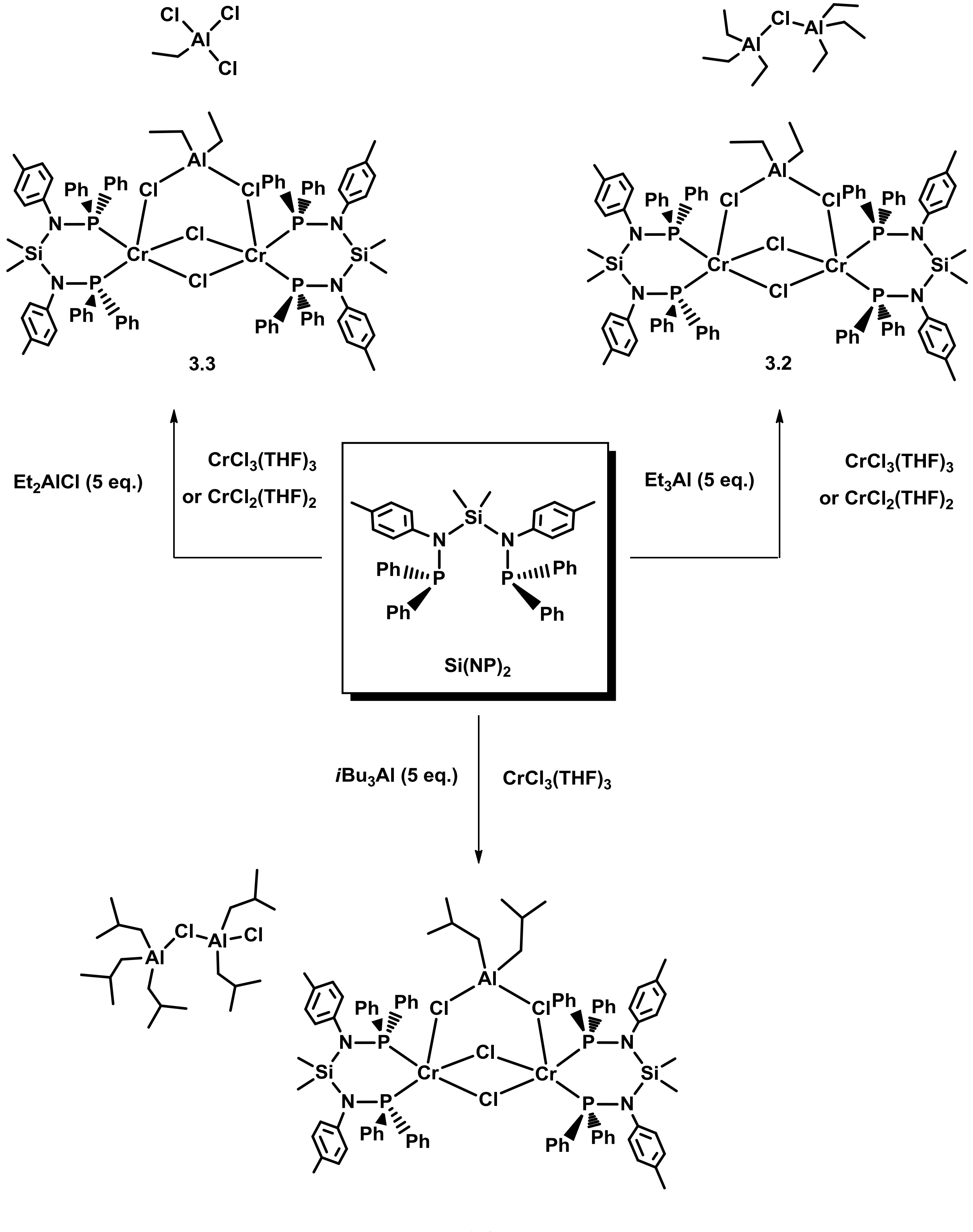
When the ligand was treated with a suspension of $CrCl_2(THF)_2$, there was no reaction as suggested by the lack of color change, even upon heating. Instead when the ligand was treated with $CrCl_3(THF)_3$ in toluene, a greenish suspension formed immediately. Upon heating this suspension, a dark green solution formed which was filtered thus enabling crystallization attempts. However, all our attempts proved unsuccessful as only metal-free ligand could be isolated along with starting $CrCl_3(THF)_3$ (Scheme 3.1). This behavior clearly indicates the presence of association equilibria between the ligand and the chromium salts. Therefore, we have adopted a different strategy to solve this problem such as the treatment of the labile and soluble complexes with Al-alkyl reagents.

Scheme 3.1



The reactions of in situ-generated **3.1** with 5 equivalents of Et_3Al, Et_2AlCl or *i*-Bu_3Al resulted in iso-structural complexes **3.2**, **3.3** and **3.4** (Scheme 3.2). In all cases the metal center undergoes a reduction from Cr(III) to Cr(II), which is quite common in the reactivity of chromium complexes with Al-alkyl reagents.[3a-j,12] Knowing that the resulting complexes have an oxidation state of +2, we successfully managed to isolate **3.2** and **3.3** starting from **Si(NP)$_2$**, $CrCl_2(THF)_2$ and Et_3Al or Et_2AlCl, even though the ligand does not ligate Cr(II) in absence of Al-alkyls. The indentity of the products obtained from the two preparation methods was confirmed by the comparison of the spectroscopic data. This alternative preparation protocol was unsuccessful in the case of *i*-Bu_3Al.

Scheme 3.2


3.3
3.2
Et$_2$AlCl (5 eq.)
CrCl$_3$(THF)$_3$
or CrCl$_2$(THF)$_2$
Si(NP)$_2$
Et$_3$Al (5 eq.)
CrCl$_3$(THF)$_3$
or CrCl$_2$(THF)$_2$
*i*Bu$_3$Al (5 eq.)
CrCl$_3$(THF)$_3$

3.4

The yields of **3.2** and **3.3** were higher when $CrCl_3(THF)_3$ was used as the Cr source instead of $CrCl_2(THF)_2$. This can be attributed to the poor solubility of $CrCl_2(THF)_2$ in both toluene and hexanes. Figures 1-3 show the structures of **3.2**, **3.3** and **3.4** respectively. The three complexes basically possess the same dimetallic and cationic structure with two (ligand)Cr units bridged by two chlorine atoms and one Cl_2AlR_2 residue. The aluminum atom uses the two chlorines to bridge each of the two chromium centers. The coordination geometry around each chromium atom is distorted square-pyramidal with the ligand donor atoms and the two bridging chlorine defining the distorted basal plane. The apical position is occupied by the Cl attached to bridging Al moiety. The bond lengths and bond angles of **3.2**, **3.3** and **3.4** are almost identical and the only difference arises from the unconnected aluminate counter-anion which is completely different as a function of the alkyl groups $[(Et_3AlClAlEt_3)^-$ for **3.2**, $(EtAlCl_3)^-$ for **3.3** and $[(i\text{-}Bu)_3AlCl(i\text{-}Bu)_2AlCl]^-$ for **3.4]**. The Cr..Cr distances are in the non-bonding range (bond length > 3.4 Å)

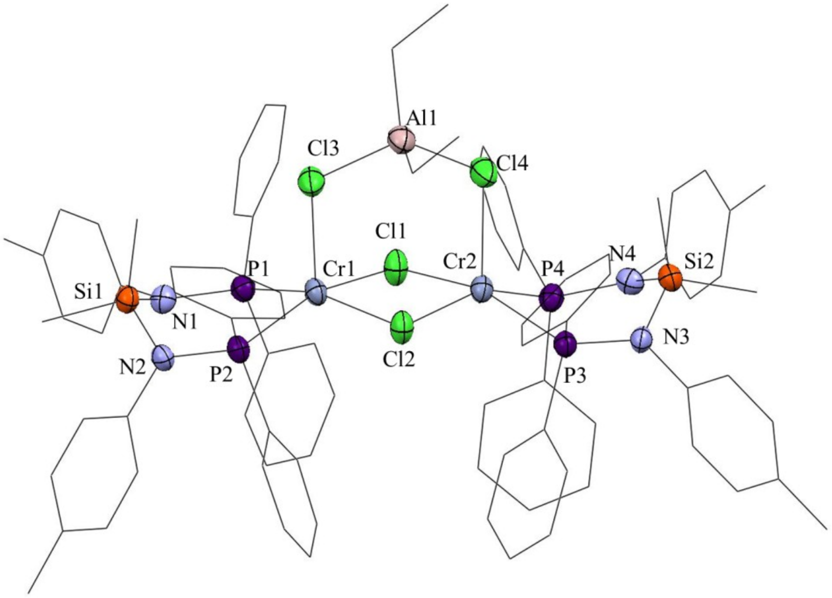


Figure 3.1. Partial thermal ellipsoid drawing of **3.2** at 50% probability. The $[Et_3AlClAlEt_3]^-$ counter-anion has been omitted for clarity. Select bond lengths (Å) and angles (deg) of **3.2**: Cr1-Cl1 2.4051(13), Cr1-Cl2 2.3633(13), Cr1-Cl3 2.5892(14), Cr1-P1 2.4906(13), Cr1-P2 2.5234(14); Cl1-Cr1-Cl2 86.93(4), Cl1-Cr1-P1 88.88(4), Cl3-Cr1-Cl1 91.27(5), P2-Cr1-Cl2 82.77(4), Cr1-Cl2-Cr2 93.39(5).

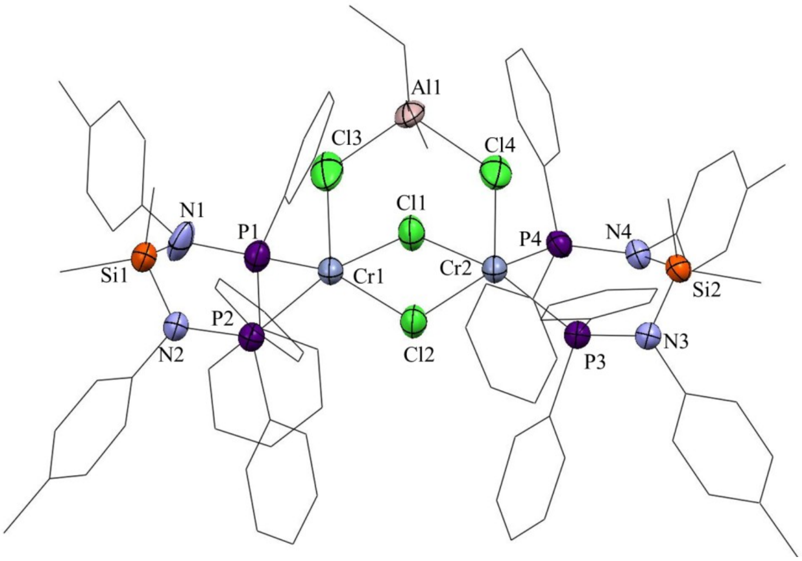


Figure 3.2. Partial thermal ellipsoid drawing of **3.3** at 50% probability. The $[\mathrm{EtAlCl_3}]^-$ counter-anion has been omitted for clarity. Select bond lengths (Å) and angles (deg) of **3.3**: Cr1-Cl1 2.4163(18), Cr1-Cl2 2.3585(18), Cr1-Cl3 2.6188(18), Cr1-P1 2.5256(18), Cr1-P2 2.5003(18); Cl1-Cr1-Cl2 88.86(6), Cl1-Cr1-P1 90.26(6), Cl3-Cr1-Cl1 91.85(6), P2-Cr1-Cl2 82.30(6), Cr1-Cl2-Cr2 94.61(6).

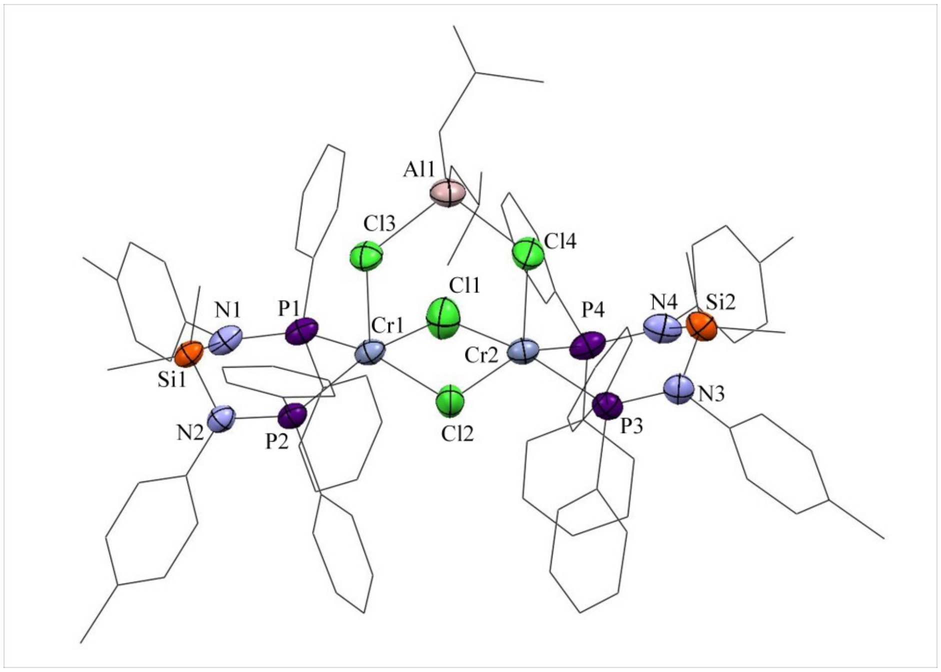
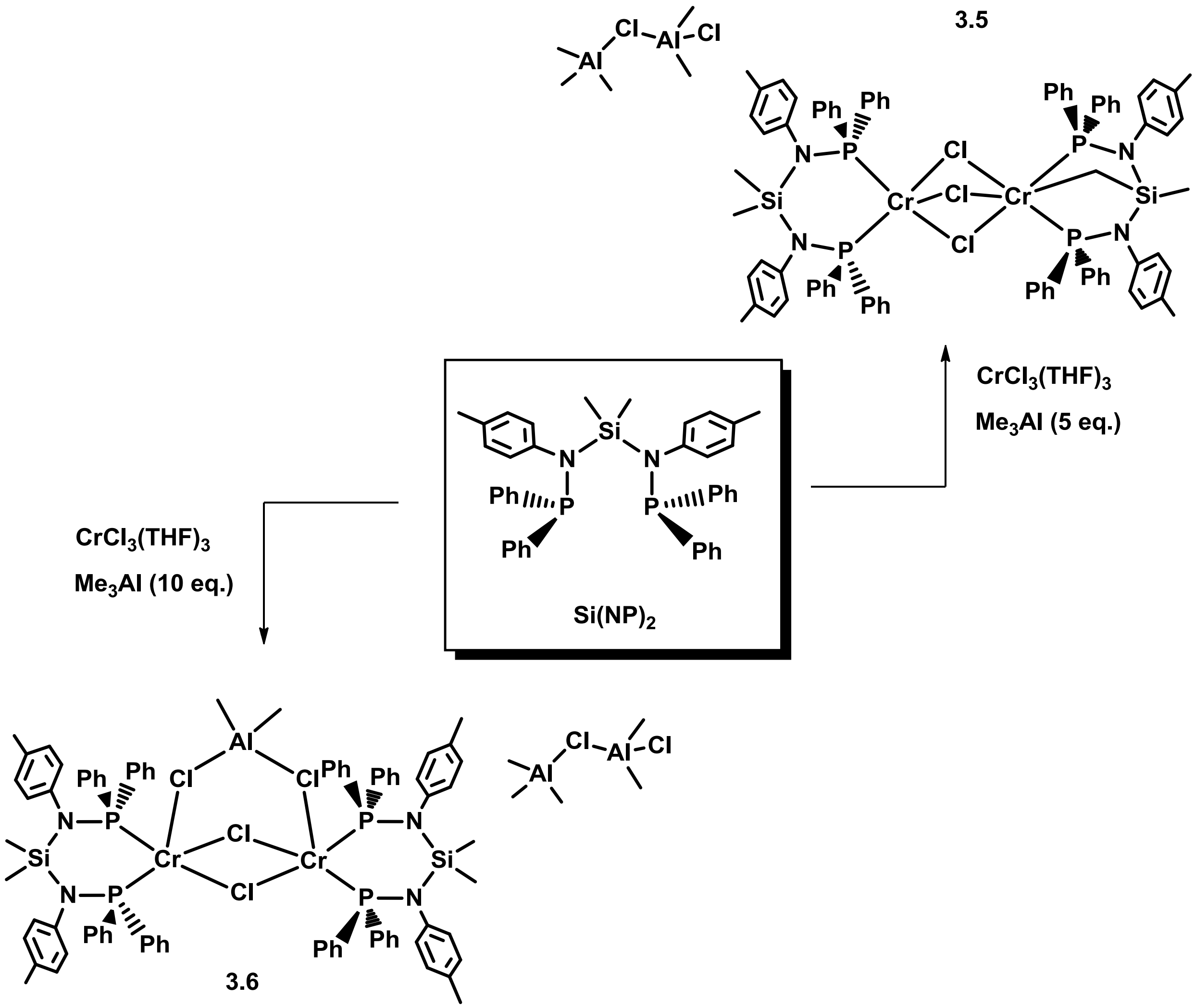


Figure 3.3. Partial thermal ellipsoid drawing of **3.4** at 50% probability. The $[i\mathrm{Bu_3AlCl}i\mathrm{Bu_2AlCl}]^-$counter-anion has been omitted for clarity. Select bond lengths (Å) and angles (deg) of **3.4**: Cr1-Cl1 2.3177(18), Cr1-Cl2 2.3945(16), Cr1-Cl3 2.5837(15), Cr1-P1 2.5122(15), Cr1-P2 2.5190(16); Cl1-Cr1-Cl2 89.39(6), Cl1-Cr1-P2 163.65(7), Cl3-Cr1-Cl1 98.50(7), P1-Cr1-Cl2 156.98(6), Cr1-Cl2-Cr2 91.41(6).

A stoichiometry-dependent behavior was observed in the case of Me_3Al. (Scheme 3.3). Using $CrCl_3(THF)_3$ and 10 eq. of Me_3Al or $CrCl_2(THF)_2$ and 5 eq. Me_3Al, afforded **3.6**. Same result was obtained using the Cr(II) route. The structure is closely related to the previous ones showing the same bridging interactions with –Cl-Al-Cl- residue and two Cl atoms positioned between the two chromium centers. The only difference being the alkyl substituents on bridging Al (dimethyl in this case) and the structure of the aluminate counter-anion $[Me_3AlClAlMe_2Cl]^-$. Instead when **Si(NP)₂** and $CrCl_3(THF)_3$ was treated with 5 eq. of Me_3Al while maintaining a low temperature (-10 ˚C), a mixed-valent Cr(II)-Cr(III) species was isolated (**3.5**).

Scheme 3.3



Apart from the mixed valence state, this new species has three bridging chlorides sited between the two chromium centers (Scheme 3.3). The incomplete reduction during the formation of **3.5** is readily explained with the lower reducing and alkylating power of Me_3Al. When larger stoichiometric ratios of Me_3Al are being used the usual Cr(II)-Cr(II) dimer **3.6** is formed. What was unanticipated in the formation of **3.5** was the direct metallation of one of the silyl methyl groups which has been metathesized to afford an obviously more stabilizing Cr-C bond.

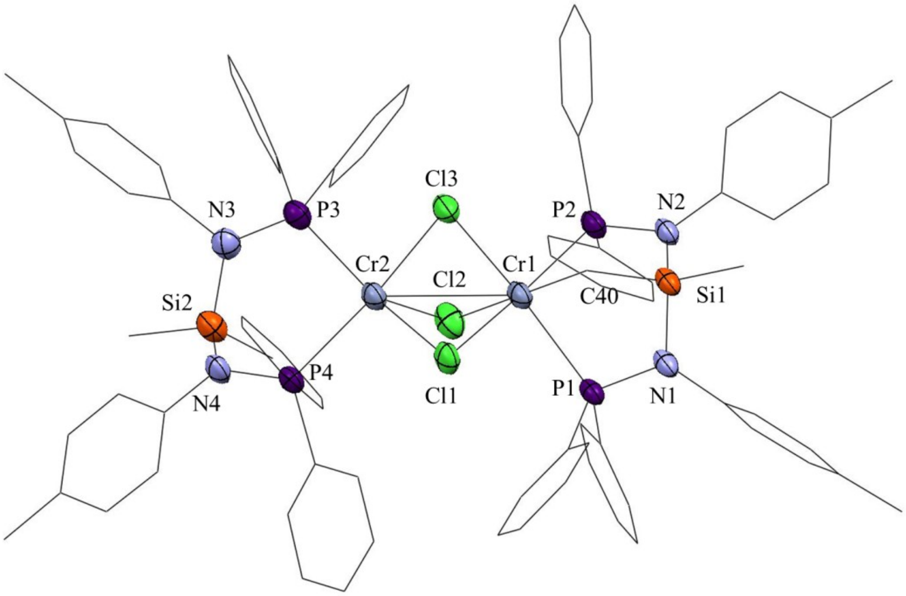


Figure 3.4. Partial thermal ellipsoid drawing of **3.5** at 50% probability. The $[Me_3AlClAlMe_2Cl]^-$counter-anion has been omitted for clarity. Select bond lengths (Å) and angles (deg) of **3.5**: Cr1-P2 2.4933(18), Cr1-P1 2.5082(15), Cr1-C40 2.140(6), Cr1-Cl3 2.4006(15), Cr1-Cl2 2.4296(17), Cr2-P3 2.4765(17), Cr2-P4 2.4808(15), Cr2-Cl3 2.3731(16), Cr2-Cl1 2.3935(16); P2-Cr1-P1 94.72(5), P2-Cr1-C40 80.12(16), P2-Cr1-Cl3 87.67(5), P2-Cr1-Cl1 168.82(6), P3-Cr2-P4 96.13(5), P3-Cr2-Cl1 87.79(5).

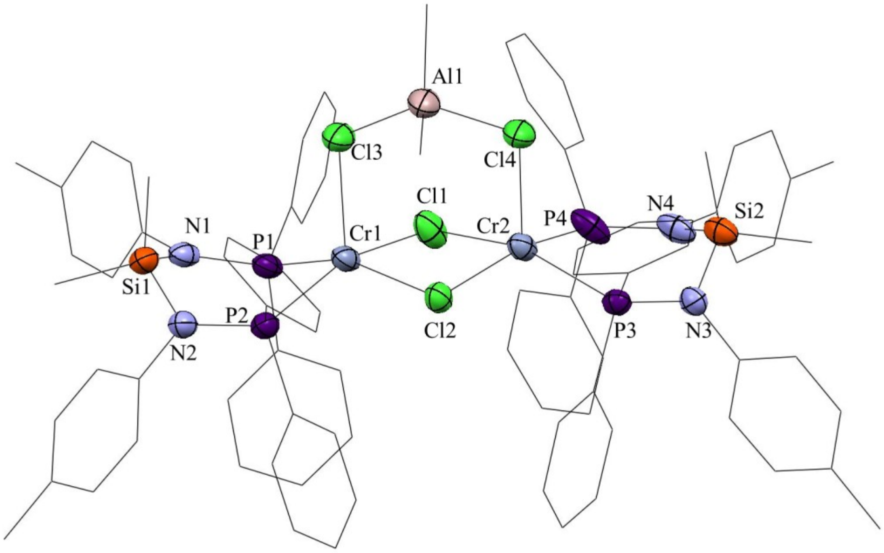
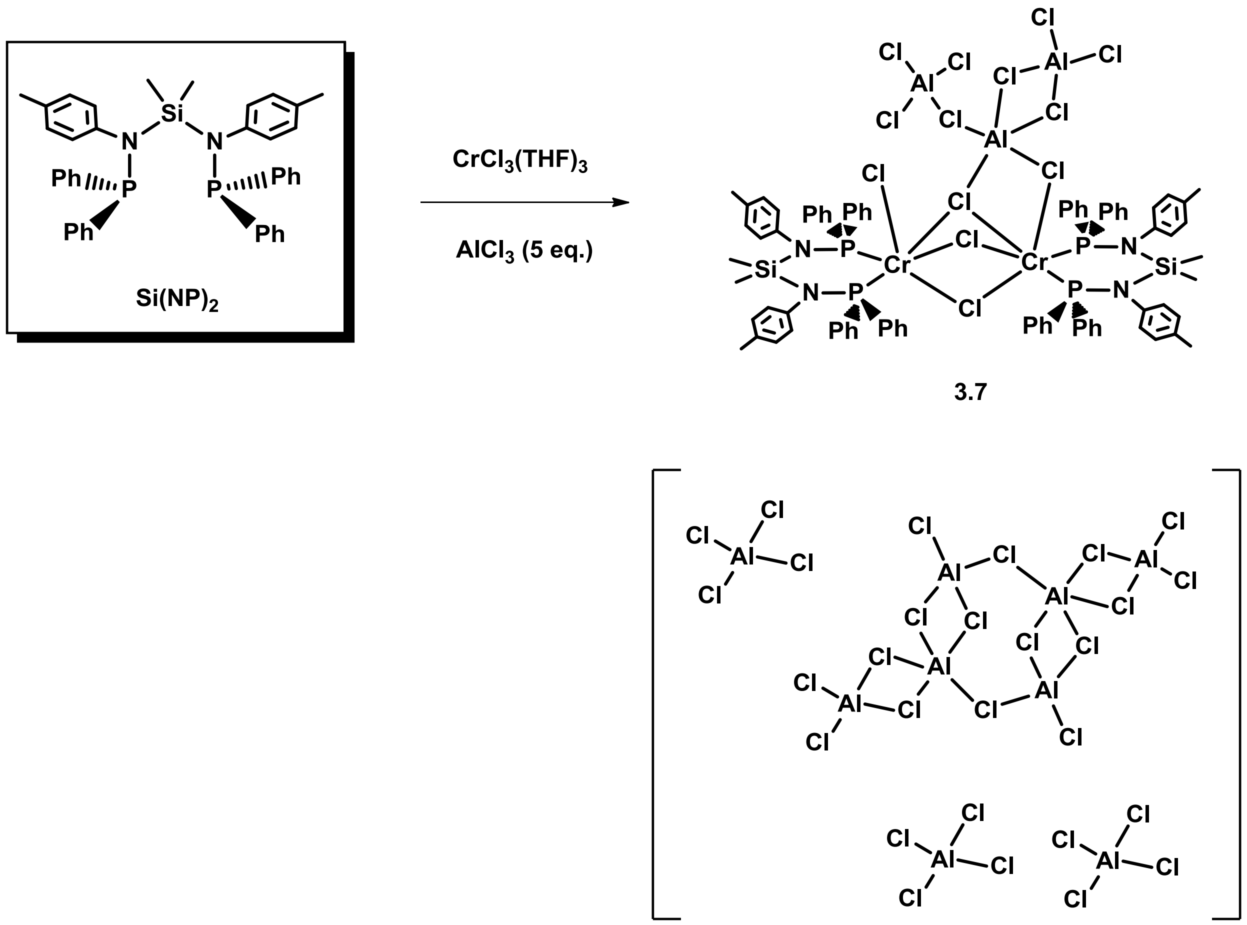


Figure 3.5. Partial thermal ellipsoid drawing of **3.6** at 50% probability. The $[Me_3AlClAlMe_2Cl]^-$counter-anion has been omitted for clarity. Select bond lengths (Å) and angles (deg) of **3.6**: Cr1-Cl1 2.3582(18), Cr1-Cl2 2.4166(18), Cr1-Cl3 2.5815(19), Cr1-P1 2.511(2), Cr1-P2 2.4966(18); Cl1-Cr1-Cl2 85.50(6), Cl1-Cr1-P1 82.22(7), Cl3-Cr1-Cl1 100.15(7), P2-Cr1-Cl2 91.18(6), Cr1-Cl2-Cr2 92.41(16).

Upon treating $CrCl_3(THF)_3$ with a suspension of **Si(NP)$_2$** and 5 eq. of $AlCl_3$ in toluene, an intriguing species **(3.7)** was obtained (Scheme 3.5). Complex **3.7** is cationic and dinuclear with the two metals bridged by three chlorine atoms. As a result of the higher oxidation state, one additional chlorine is terminally bonded to one of the two chromium atoms. The second chromium is instead connected via bridging chlorine to one Al3Cl9 moiety. There are four counter anions associated with two dimeric **3.7** therefore, assigning the trivalent state to each metal center.

Scheme 3.5



3.7

Counter Ions

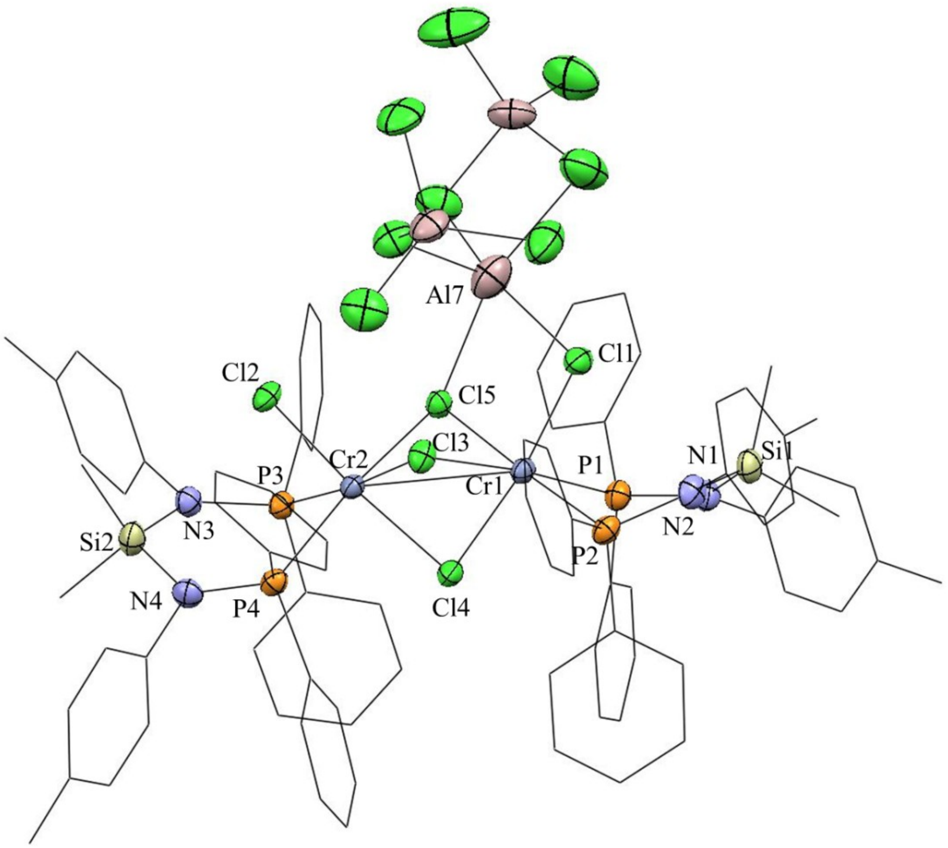


Figure 3.6. Partial thermal ellipsoid drawing of **3.7** at 50% probability. The $3[AlCl_4]^-$ and $[Al_3Cl_6]^{+2}$ counter-ions have been omitted for clarity. Select bond lengths (Å) and angles (deg) of **3.7**: Cr1-P1 2.483(2), Cr1-P2 2.476(2), Cr1-Cl1 2.2685(19), Cr1-Cl5 2.4297(18), Cr1-Cl3 2.4154(19), Cr1-Cl4 2.3559(19), Cr2-P3 2.4775(19), Cr2-P4 2.481(2), Cr2-Cl2 2.2814(18), Cr2-Cl5 2.4066(19), Cr2-Cl3 2.3991(18), Cr2-Cl4 2.3600(18); P1-Cr1-P2 89.36(7), P1-Cr1-Cl1 91.36(7), P1-Cr1-Cl5 94.54(6), P1-Cr1-Cl3 173.76(7), P2-Cl1-Cl4 101.39(7), Cl1-Cr1-Cl5 89.34(7), Cl1-Cr1-Cl3 94.51(7), Cr1-Cl1-Al7 99.7(4), Cr1-Cl5-Al7 87.7(3), P3-Cr2-P4 90.20(7), P3-Cr2-Cl2 86.70(6), P3-Cr2-Cl5 91.55(6), Cr2-Cl5-Al7 124.6(3), Cr2-Cl5-Cr1 79.54(6), Cr2-Cl3-Cr1 79.89(6).

Ethylene oligomerization experiments were carried out on isolated and purified complexes **3.1** – **3.7**, as shown in Table 3.2. Our previous bidentate NP ligand-based systems with ethylenic ($PN(CH_2)_2NP$) and propylenic ($PN(CH_2)_3NP$) bridges displayed a selective oligomerization behavior (1-hexene and 1-octene catalysts respectively).[7c] However with the current ligand system where a one atom -Si- linker is used (PNSiNP), only non-selective oligomerization was observed as possible result of an over-stabilization of the divalent state.

When testing was carried out on the **3.1** in toluene using MAO (methylaluminoxane) as activator, a moderate activity for the formation of a statistical distribution of α-olefin (Schulz-Flory distribution) was observed. Desirably, the oligomeric mixtures were free of unwanted polymers. Instead, when the solvent was switched to methylcyclohexane (MeCy) and DMAO (depleted-MAO) was employed as a activator, the catalyst was essentially inactive. This is attributed to the fact that **3.1** is insoluble in MeCy. The reason for the non-selective behavior becomes apparent when we consider the fact that, in the presence of Al-alkyl activators, (see Scheme 3.2) reduction to Cr(II) was systematically observed.

The testing of the Al-adducts of di-valent chromium **3.2**, **3.3**, **3.4** and **3.6**, gave also the expected non-selective oligomerization activity. Conditions were optimized by doing oligomerization tests on **3.2** which was tested both in toluene (using MAO activator) and MeCy (using DMAO activator) and resulted in Schulz-Flory distributions. Even when a more reducing co-catalyst was added (Et_3Al), selective behavior was not obtained. Therefore it must be concluded that the ligand system under investigation (**Si(NP)$_2$**) does not support the reduction to the lower oxidation state of Cr(I), possibly because of an over-stabilization of the higher states.

Interesting results were obtained when **3.5** was tested in MeCy using DMAO activator. Although the distribution of α-olefins was mainly Schulz-Flory like, there was an enrichment in 1-hexene (38%). Since complex **3.5** is a mixed-valence dimer (containing Cr(II)-Cr(III) core), it can be expected that the two different oxidation states perform different catalysis. In the case of Cr(II) a non-selective oligomerization is to be expected with the typical high activity.[9] Instead, in the case of the Cr(III) center reduction to Cr(I) can be expected with consequent appearance of selective behavior.[8] A similar observation was made when **3.7** was tested under similar conditions. It behaved similarly to **3.5** given the fact that chromium is in the trivalent state.

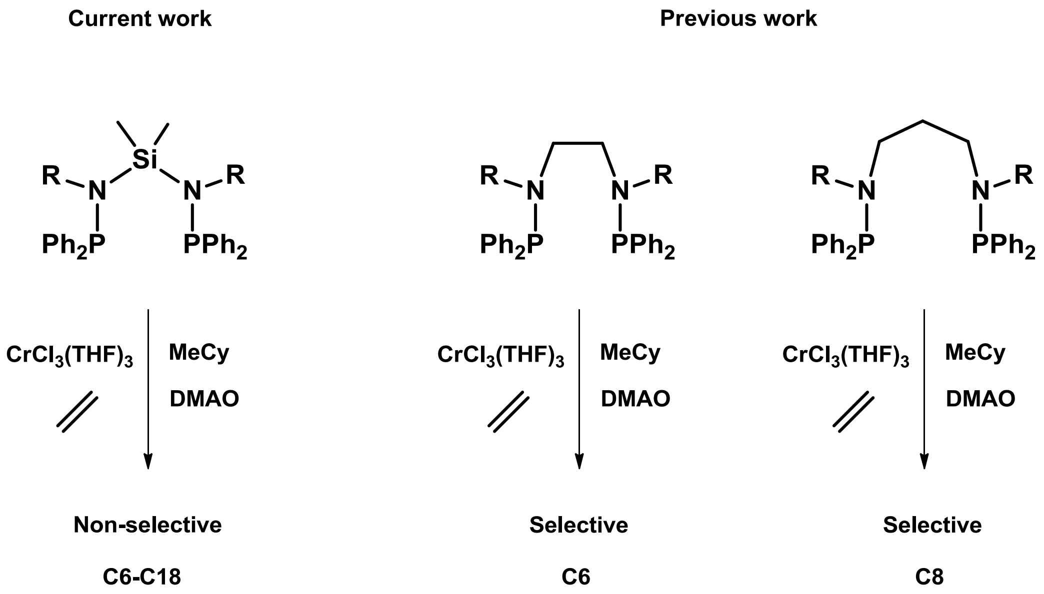
Table 3.2. Ethylene oligomerization results of various complexes.[a]

catalyst	co-catalyst (equiv)	alkenes (mL)	PE (g)	activity (g/g Cr . h)	linear alpha olefins (mol %)						
					C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}
3.1[b]	MAO (400)	38	0	34,833	22	21	17	14	11	9	6
3.1[c]	DMAO (400)	1	0.8	1,942	50	14	7	7	7	8	7
3.2[b]	MAO (400)	19	3.9	22,417	18	18	15	14	13	11	11
3.2[c]	DMAO (400)	23	6.6	29,545	32	12	12	12	11	11	10
3.2[c]	DMAO/Me_3Al (400/80)	6	10.7	19,218	24	11	12	13	13	14	13
3.2[c]	DMAO/Et_3Al (400/80)	6	7.70	15,372	26	11	12	13	13	13	12
3.3[c]	DMAO (400)	25	5.5	30,224	30	11	12	12	12	12	11
3.4[c]	DMAO (400)	26	11.7	38,833	31	11	11	12	12	12	11
3.5[b]	MAO (400)	9	5.9	15,814	17	16	15	14	13	13	12
3.5[c]	DMAO (400)	11	5.0	16,494	38	12	11	11	10	9	9
3.6[c]	DMAO (400)	15	5.7	21,058	28	13	13	13	12	11	10
3.7[c]	DMAO (400)	7	3.7	11,160	37	15	10	10	10	9	9

[a]Conditions: Loading 15 μmol of complex, 80 ˚C temperature, 40 bar (ethylene), 30 min reaction time. [b]100 mL of toluene. [c]100 mL of methylcyclohexane. DMAO = Me_3Al depleted MAO

With the work presented here, we are able to conclude our investigation on bidentate NP based ligands and their catalytic activities with chromium (Scheme 3.6). When tested for ethylene oligomerization, $PN(CH_2)_2NP$ and $PN(CH_2)_3NP$ demonstrated selective behavior,[7c] whereas **Si(NP)$_2$** does not when activated with DMAO in MeCy. Having Si atom in the ligand frame introduces rigidity to the molecule, which imposes some geometric constraints. As a result the ligand demonstrates a favored tendency to support di-valent Cr which does not afford selective ethylene oligomerization.

Scheme 3.6



3.5 Conclusion

We have successfully completed our investigation on bidentate NP ligands towards ethylene oligomerization using chromium metal. While our previous results have shown selective trimerization and tetramerization, the current **Si(NP)$_2$** ligand behaves in a non-selective fashion. This correlates direct to the ability of the different ligands to stabilize different oxidation states of Cr. The work presented here shows that the **Si(NP)$_2$** ligand, upon treatment with Al-alkyls, undergoes a reduction (Cr(III) to Cr(II)) and a dimeric unit is assembled which is bridged by either Cl-Al-Cl or Cl units. These dimers prove to be challenging in two ways; first they do not undergo further reduction to Cr(I) (which would be expected to follow a selective behavior), and secondly they are resilient to dissociation due to the bridging groups. Therefore the observed moderate activities have to be expected.

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Aminophosphine-Based Chromium Catalysts for Selective Ethylene Tetramerization

4.1 Introduction

The growing demand for 1-hexene and 1-octene by polymer manufacturing industry continually stimulates research for finding active and selective catalysts for their preparation from ethylene.[1] The employment of chromium-based catalysts has attained considerable success in developing highly active ethylene trimerization systems of very high selectivity.[2] By contrast, the much sought tetramerization systems remain rare.[3] Even today, the Sasol's PNP,[3a] and diphosphino catalysts of S-K Energy,[3b,5] remain the only two industrially used systems of high-activity. Yet, their selectivity (~70%) remains far from the near to perfect purity obtained for 1-hexene (up to 99%).[2]

As mentioned above, chromium derivatives have provided the most versatile catalysts for the purpose of ethylene selective and non-selective oligomerization.[6,1c,2i,k,3a,7] Yet, it is not infrequent to encounter catalysts producing S-F distribution of oligomers enriched with either 1-hexene or 1-octene and, in addition, forming variable amount of high Mw polymers or waxes. The reason for this multiple behavior has to be searched in the rapid interchange, under *operando* conditions, of the mono-, di- and tri-valent oxidation states.[2f,i-k,t,y,6i,8] In the case of selective oligomerization, the most common protocol is to use trivalent chromium pre-cursors which, upon activation with alkyl-aluminum based co-catalysts, are reduced *in situ* to the monovalent state.[9] The reductive coupling of two ethylene molecules at the expense of the oxidation of the metal affords a five-membered metallacycle. The oligomers are obtained from further ring expansion, via subsequent ethylene insertion events, followed by reductive elimination.[1b,2b,u-v,3d,7b,10] The formation of the seven membered ring and its quantitative reductive elimination is normally regarded as responsible for the formation of 1-hexene with high selectivity. It has been argued that in the case of tetramerization, the same ring-expansion mechanism may operate. In this event, the metallacycle further grows into the nine-membered state and eliminates 1-octene.[2h,11] There have been doubts recently expressed about the possibility for this mechanism to produce 1-octene with very high selectivity.[12] Therefore, an alternative bi-metallic mechanism[12] has been proposed as a possibility to guide the search for highly selective tetramerization systems. The challenge clearly remains about how to drive a reaction towards such a mechanism and to conclusively prove such hypothesis. [13-19]

In principle, acting on the ligand system is one of the possibilities to influence the mechanism and to drive the reaction towards either tri- or tetramerization. Given the success of amino phosphine based ligands for selective oligomerization[2i,3a-c,4,5,6d,14] we have been studying chelating NP based ligands, which have proven able to selectively support both tri- and tetramerization catalysts. In particular, the $Ph_2P(R)N(CH_2)_nN(R)PPh_2$ ligand framework has produced particularly encouraging results. In search for further confirmations, we have now explored modified ligands where one of the NP arms has been replaced by a different coordinating group. This is an attempt to further stabilize the monovalent state and generate better performing catalysts. Herein we describe the behavior of $Ph_2PN(Me)(CH_2)_2X$ [X = NMe_2 **(PNN)**; PPh_2 (**PNP**); Py **(PNPy)**].

4.2 Experimental

All manipulations were done under inert nitrogen atmosphere using Schlenk glassware or in a dry-box. Solvents were dried using aluminum oxide purification system. Chemicals were used from commercial sources and used as received. Et_3Al was purchased from Strem and used as received. Methylaluminoxane (MAO, 20% in toluene) was purchased from Albemarle Corporation. Me_3Al depleted MAO (DMAO) was prepared by removing (*in vacuo* 2 mmHg) all volatiles under moderate heating (40 ˚C) for 6 hours. Elemental analysis were carried out by using Perkin-Elmer 2400 CHN analyzer. Magnetic susceptibilities were measured using Johnson Matthey magnetic susceptibility balance at room temperature; sample preparation was performed inside a dry-box using calibrated, sealed tubes. X-ray crystal data were determined using a Bruker diffractometer equipped with a Smart CCD area detector and with Bruker Kappa APEXII CCD diffractometer. NMR spectra were recorded on Bruker Avance 300 MHz spectrometer at 300 .

4.2.1 Synthesis of Ligands

Preparation of $Ph_2PN(Me)(CH_2)_2NMe_2$ (PNN)

A solution of N,N,N'-trimethylenediamine (10.4 mL, 80.0 mmol) in THF (180 mL) was cooled to 0°C followed by the addition of Et_3N (12.8 mL, 92.0 mmol). To this solution chlorodiphenylphosphine (14.3 mL, 80.0 mmol) was added drop-wise and the resulting mixture stirred overnight at room temperature. After filtration and solvent removal *in vacuo*, the product (**PNN**) was obtained as a pale yellow liquid (18.9 g, 66.1 mmol, 83%). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.42 (m, 10H), 3.21 (m, 2H), 2.56 (d, J = 5.8 Hz, 3H), 2.40 (t, J = 7.58, 2H), 2.20 (s, 6H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 139.5, 132.1, 128.3, 128.1, 58.6, 54.8, 45.8, 37.4. ^{31}P NMR (300 MHz, $CDCl_3$) δ: 64.55 (s).

Preparation of $Ph_2PN(Me)(CH_2)_2Py$ (PNPy)

A solution of 2-(2-methylaminoethyl)pyridine (10.0 mL, 72.3 mmol) in THF (180 mL) was cooled to 0°C and added with Et_3N (11.6 mL, 83.1 mmol). Chlorodiphenylphosphine (12.9 mL, 72.3 mmol) was slowly added and the resulting mixture stirred overnight at room temperature. After work up as above, a yellow liquid of **PNPy** was isolated (20.1 g, 62.7 mmol, 87%). ^1H NMR (300 MHz, $CDCl_3$) δ: 8.43-6.53 (m, 14H (Ph and Py H's)), 3.52 (m, 2H), 2.90 (t, J = 7.0 Hz, 2H), 2.40 (d, J = 5.6, 3H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 160.0, 149.3, 139.2, 136.2, 131.8, 128.3, 128.0, 123.3, 121.1, 56.9, 38.2, 37.0. ^{31}P NMR (300 MHz, $CDCl_3$) δ: 61.65 (s).

Preparation of $Ph_2PN(Me)(CH_2)_2PPh_2$ (PNP)

2-(Methylamino)ethanol (15.0 mL, 186.7 mmol) was dissolved in $CHCl_3$ (180 mL) and the solution cooled to 0°C. Thionyl chloride (14.2 mL, 196.1 mmol) was added and the resulting suspension stirred at room temperature overnight. The volume of $CHCl_3$ was reduced and EtOH was added (~50 mL) to quench the excess of thionyl chloride. The solvent was removed *in vacuo*, and the resulting off-white solid recrystallized twice with Et_2O and EtOH mixture (20:80). The shiny colorless crystals of $HN(Me)(CH_2)_2Cl.HCl$ so obtained were washed with cold EtOH and dried (10.5 g, 80.8 mmol, 44%). ^1H NMR (300 MHz, $CDCl_3$) δ: 9.82 (s, br, 2H), 3.97 (t, J = 6.2 Hz, 2H), 3.31 (p, J = 6.2 Hz, 2H), 2.78 (t, J = 5.6 Hz, 3H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 52.7, 41.9, 33.8.

A THF solution of (100 mL) *t*-BuOK (5.6 g, 50.3 mmol) was added with Ph_2PH (3.5 mL, 20.1 mmol) and stirred for 30 min at room temp. $HN(Me)(CH_2)_2Cl.HCl$ (2.6 g, 20.1 mmol) was added to the solution and refluxed overnight, whereby the dark red color turned milky white. The solvent was removed under reduced pressure and the residue stirred with 10% $HCl_{(aq)}$, and washed with Et_2O. The aqueous solution was washed with 10% $NaOH_{(aq)}$ and extracted with Et_2O. The organic solution was washed with brine, dried over anhydrous $MgSO_4$ and evaporated. The residue was passed through a short alumina column to give $HN(Me)(CH_2)_2PPh_2$ as a colorless oil (2.2 g, 9.1 mmol, 74%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.42 (m, 10H), 2.69 (q, J = 8.5 Hz, 2H), 2.38 (s, 3H), 2.25 (t, J = 7.3 Hz, 2H), 1.09 (s, br, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 138.4, 132.6, 128.6, 128.4, 48.8, 36.3, 28.9. ^{31}P NMR (300 MHz, $CDCl_3$) δ: -23.66 (s).

A solution of $HN(Me)(CH_2)_2PPh_2$ (2.2 g, 9.1 mmol) in THF (50 mL) was treated with Et_3N (1.9 mL, 10.4 mmol). This solution was cooled to 0°C and Ph_2PCl (1.6 mL, 9.1 mmol) was added dropwise. The resulting suspension was stirred overnight at room temperature. The mixture was filtered and the supernatant evaporated to dryness affording a viscous white wax of **PNP** (2.2 g, 5 mmol, 58%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.39 (m, 20H), 3.22 (m, 2H), 2.54 (d, J = 5.9 Hz, 3H), 2.29 (m, 2H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 139.0, 138.3, 132.6, 132.1, 128.5, 128.4, 128.2, 53.4, 37.0, 28.2. ^{31}P NMR (300 MHz, $CDCl_3$) δ: 63.34 (s), -20.95 (s).

4.2.2 Synthesis of Complexes

Preparation of (PNN)$CrCl_3$(THF) (4.1)

A suspension of $CrCl_3(THF)_3$ (0.37 g, 1.0 mmol) in toluene (7 mL) was treated with **PNN** (0.29 g, 1.0 mmol). The color turned green within a few minutes and the suspension was stirred for 4 hours. A small amount of insoluble material was removed by centrifugation. The resulting green solution was dried *in vacuo* and the resulting solid washed with hexanes (3 x 3 mL), to give a green microcrystalline solid **4.1** (0.41 g, 0.8 mmol, 78%). $\mu_{eff} = 3.89\ \mu_B$. Elemental Analysis % calculated for $C_{21}H_{31}Cl_3CrN_2OP$ (found): C 48.80 (48.62), H 6.05 (5.99), N 5.42 (5.29).

Preparation of (PNN)$CrCl_3$(CH_3CN) (4.2)

$CrCl_3(THF)_3$ (0.37 g, 1.0 mmol) and **PNN** (0.29 g, 1.0 mmol) were suspended in a 1:2 mixture of acetonitrile and toluene (7 mL) and stirred for 4 hours. The resultant dark-green solution was centrifuged. The supernatant was layered with hexanes (2 mL) and stored at -30 ˚C for 3 days. Dark green/blue crystals of **4.2** were isolated, washed with cold hexanes (3 mL) and dried *in vacuo* (0.24 g, 0.5 mmol, 48%). μ_{eff} = 3.80 μ_B. Elemental Analysis % calculated for $C_{19}H_{26}Cl_3CrN_3P$ (found): C 46.98 (47.08), H 5.39 (5.47), N 8.65 (8.72).

Preparation of (PNPy)CrCl$_3$(THF) (4.3)

Identical procedures as **4.1** afforded a dark green solid of **4.3** (0.51 g, 0.9 mmol, 92%). μ_{eff} = 3.93 μ_B. Elemental Analysis % calculated for $C_{24}H_{29}Cl_3CrN_2OP$ (found): C 52.33 (52.38), H 5.31 (5.22), N 5.09 (5.18).

Preparation of (PNPy)CrCl$_3$(CH$_3$CN) (4.4)

A suspension of $CrCl_3(THF)_3$ (0.37 g, 1.0 mmol) in a 1:2 mixture of acetonitrile and toluene (7 mL) was treated with **PNPy** (0.32 g, 1.0 mmol) and stirred for 4 hours. The dark green solution was centrifuged and the supernatant solution was layered with hexanes (2 mL) and stored at -30 ˚C for 3 days. After that time, dark green crystals of **4.4** were collected and washed with cold hexanes (3 mL) and dried (*in vacuo*) (0.27 g, 0.5 mmol, 52%). μ_{eff} = 3.80 μ_B. Elemental Analysis % calculated for $C_{22}H_{24}Cl_3CrN_3P$ (found): C 50.84 (50.92), H 4.65 (4.72), N 8.08 (8.17).

Preparation of (PNP)CrCl$_3$(THF) (4.5)

Identical procedures as **4.1** afforded an olive green solid of **4.5** (0.46 g, 0.7 mmol, 67%). μ_{eff} = 3.87 μ_B. Elemental Analysis % calculated for $C_{31}H_{35}Cl_3CrNOP_2$ (found): C 56.59 (56.48), H 5.36 (5.27), N 2.13 (2.07).

Preparation of $[(HN(Me)(CH_2)_2Py)CrCl_2Et]_2$ (4.6)

A suspension of **PNPy** (0.32 g, 1.0 mmol) and $CrCl_3(THF)_3$ (0.37 g, 1.0 mmol) in toluene (7 mL) was treated with Et_3Al (0.34 g, 3 mmol) in a drop-wise manner and the resultant dark green solution was stirred for 10 min. After centrifugation and separation of the insoluble precipitate by centrifugation, the solution was layered with hexanes (2 mL) and allowed to stand undisturbed at -30 °C for 3 days. X-ray quality crystals were isolated, washed with cold hexanes (2 x 2 mL) and dried in *vacuo* (0.28 g, 0.4 mmol, 49%). $\mu_{eff} = 4.00\ \mu_B$. Elemental Analysis % calculated for $C_{20}H_{34}Cl_4Cr_2N_4$ (found): C 41.68 (41.44), H 5.95 (5.87), N 9.72 (9.66).

4.3 X-Ray data

Table 4.1. Table of crystal data and refinements for **4.2, 4.4** and **4.6**.

	4.2	**4.4**	**4.6**
Formula	$C_{19}H_{26}Cl_3CrN_3P$	$C_{48}H_{54}Cl_6Cr_2N_8P_2$	$C_{48}H_{64}Cl_4Cr_2N_4$
Mw	485.75	1121.63	942.83
Space group	Monoclinic, P 2(1)/c	Triclinic, P-1	Triclinic, P-1
***a* (Å)**	7.9622(5)	8.3782(8)	8.9902(9)
***b* (Å)**	19.5652(11)	8.8107(8)	10.9172(12)
***c* (Å)**	14.3538(9)	19.7975(17)	13.7957(14)
α, (deg)	90	94.270(5)	86.118(7)
β, (deg)	103.072	101.713(5)	84.501(6)
γ, (deg)	90	109.324(5)	66.904(6)
V (Å^3)	2178.1(2)	1334.4(2)	1239.1(2)
Z	4	1	1
Radiation	0.71073	0.71073	0.71073
T (K)	200(2)	200(2)	200(2)
D_{calcd} (g cm^{-3})	1.481	1.396	1.264
μ_{calcd} (mm^{-1})	0.977	0.809	0.689
F_{000}	10004.0	578	496.0
R, Rw^{2a}	0.0400, 0.0994	0.0625, 0.1510	0.0449, 0.1330
GoF	1.017	1.026	1.025

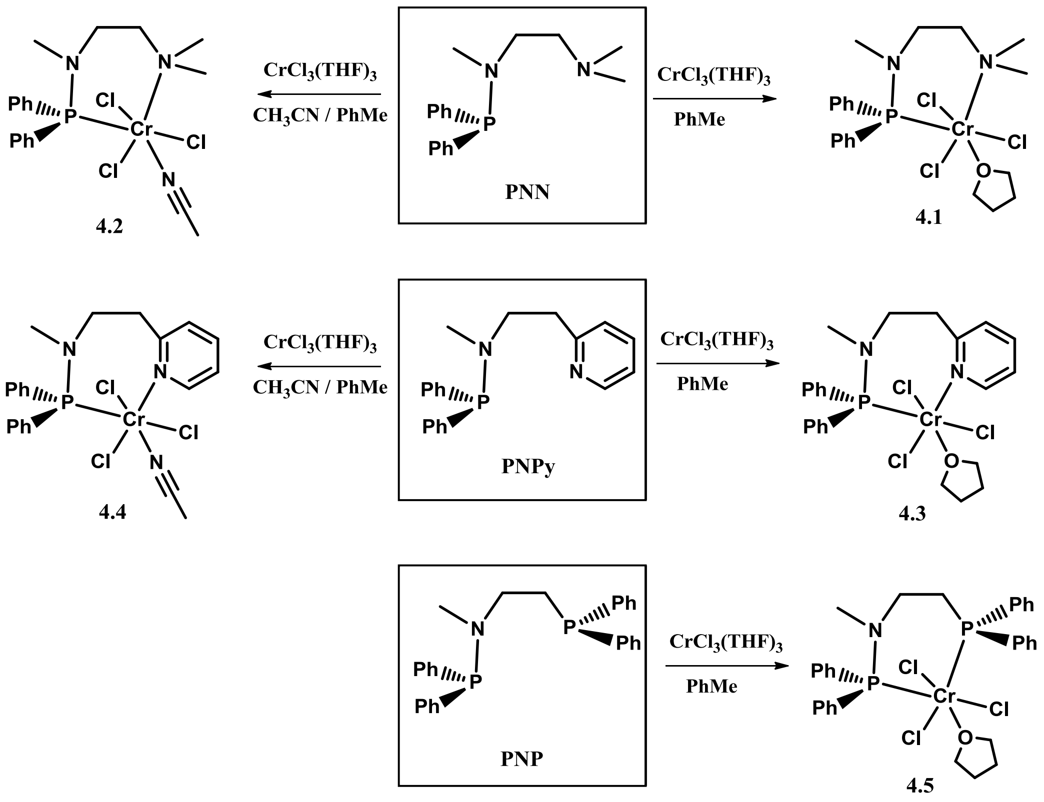
[a] $R = \Sigma jFoj - jFcj/\Sigma jFj$. $Rw = [\Sigma(jFoj - jFcj)2/\Sigma wFo2]^{1/2}$

4.4 Results and Discussion

The ligands $Ph_2PN(Me)(CH_2)_2NMe_2$ (**PNN**) and $Ph_2PN(Me)(CH_2)_2Py$ (**PNPy**) were synthesized in high yields by the condensation reaction between the appropriate diamine or aminopyridine and chlorodiphenylphosphine. The synthesis of **PNP** was a non-straightforward, multi-step process where the chloro-amine was synthesized first, followed by the addition of one phosphine (Ph_2PH) and finally of the second phosphine residue (Ph_2PCl). The NMR spectra indicated that the ligands were acceptably pure. Complexations with $CrCl_3(THF)_3$ were carried out in toluene, obtaining instant color change from purple to green upon mixing. The complexes were prepared by direct reaction with $CrCl_3(THF)_3$ isolated in crystalline form or as analytically pure microcrystalline materials from toluene. The magnetic moment measurements gave the values as expected for the d^3 electronic configuration of trivalent chromium in octahedral fields. Attempts to crystallize the complexes from toluene solutions were unsuccessful. However, $(PNN)CrCl_3(CH_3CN)$ (**4.2**) and $(PNPy)CrCl_3(CH_3CN)$ (**4.4**) were obtained in suitable crystalline form from acetonitrile/toluene mixtures.

The crystal structure of **4.2 (**Figure 4.1) features the typical octahedral geometry of Cr(III). The bi-dentate ligand **PNN** occupies two coordination sites and forms a 6-membered chelate through the P and terminal N atoms. The chlorides occupy three sites while one molecule of CH_3CN completes the coordination sphere. All the bond lengths and bond angles are in the

Scheme 4.1



expected range. In the case of **4.4** (Figure 4.2), a very similar octahedral geometry was observed. The only unexpected feature is the bending of the coordinated CH_3CN molecule (169.9°). Complexes **4.1**, **4.3** and **4.5** are presumed to have a similar connectivity due to the fact that the only difference arises from the presence of a coordinated THF molecule.

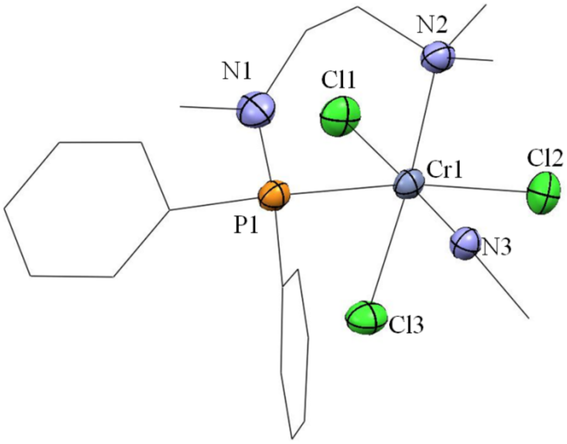


Figure 4.1. Partial thermal ellipsoid drawing of **4.2** at 50% probability. Select bond lengths (Å) and angles (deg): Cr1-P1 2.5272(7), Cr1-N2 2.1827(19), Cr-Cl1 2.2982(6), Cr1-Cl3 2.3122(7), Cr1-N3 2.0663(18); P1-Cr1-N2 90.96(5), P1-Cr1-Cl3 83.65(2), N2-Cr1-Cl2 92.58(6), N2-Cr1-Cl3 174.59(6), P1-Cr1-Cl2 169.31(2), Cl1-Cr1-N3 177.16(6).

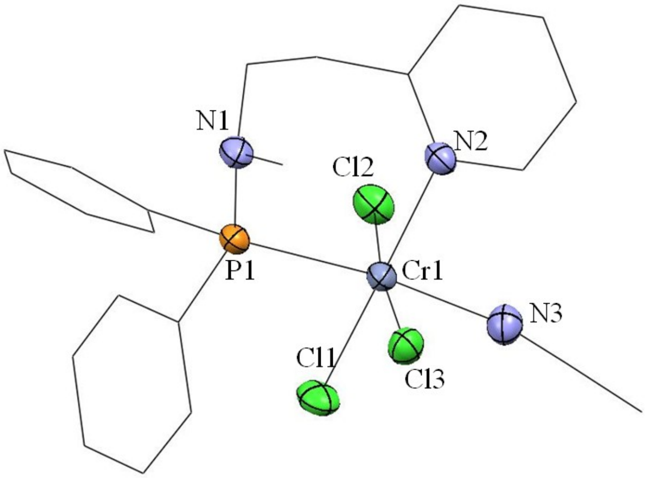
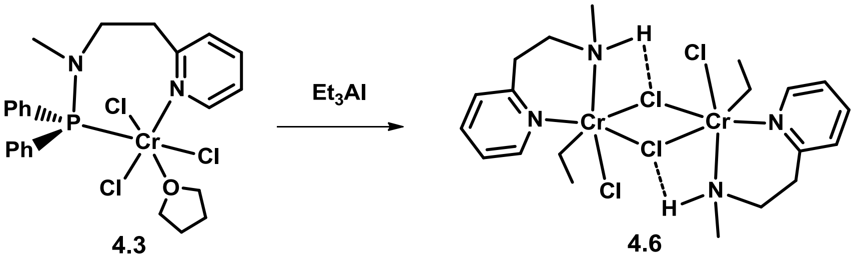


Figure 4.2. Partial thermal ellipsoid drawing of **4.4** at 50% probability. Select bond lengths (Å) and angles (deg): Cr1-P1 2.4933(14), Cr1-N2 2.149(3), Cr-Cl1 2.2964(13), Cr1-Cl3 2.3244(15), Cr1-N3 2.108(4); P1-Cr1-N2 92.72(10), P1-Cr1-Cl3 85.05(5), N2-Cr1-Cl2 87.28(11), N2-Cr1-Cl3 89.50(11), P1-Cr1-Cl2 100.33(5), Cl1-Cr1-N3 88.31(12).

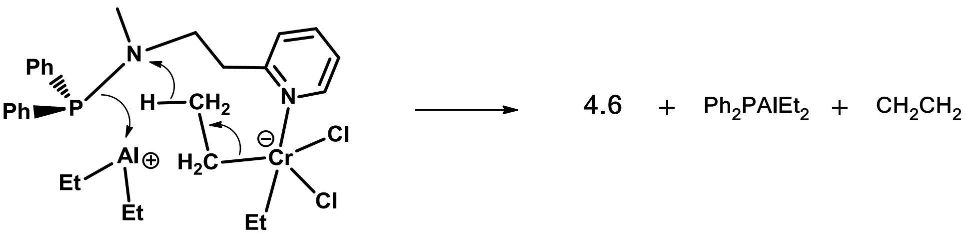
When (PNPy)CrCl$_3$(THF) (**4.3**) was treated with 3 equivalents of Et$_3$Al in toluene, a rare example of ethyl organochromium derivative[17d] (**4.6**) was obtained (Scheme 2). Even further, the phosphino unit has been removed while the residual amino moiety has been protonated. This can be inferred from both structural as well as FT-IR data (intense and sharp band at 3450 cm^{-1}).

Scheme 4.2



The metal, surprisingly, preserved the trivalent state throughout this non-obvious transformation. While the cleavage of the P-N bond can be easily ascribed to a nucleophilic attack by the alkyl group of Et$_3$Al, the protonation of the nitrogen atom cannot be explained unless speculating on possible intervention of the chromium center (Scheme 4.3). In other words,

Scheme 4.3



after the preliminary alkylation of the metal center, if one assumes formation of an anionic chromium/aluminum metallate, hydrogen transfer and elimination of ethylene may lead to the formation of **4.6**.

The connectivity of the dimeric **4.6** was yielded by an X-ray crystal structure (Figure 4.3). The edge-sharing bi-octahedral structure is composed by the two octahedral Cr(III) atoms bridged by two chlorines. Each chromium bears one terminally bonded ethyl group coplanar with the flat Cr_2Cl_2 unit and one terminally bonded chlorine in the axial position. The amino pyridine moiety has the pyridine nitrogen atom in the equatorial position and the amino group on the axial one. The positions of the amino protons were yielded by difference Fourier maps and be found in the proximity of the bridging chlorides (2.84 Å). Their presence is further corroborated by the pyramidalization of the N atom.

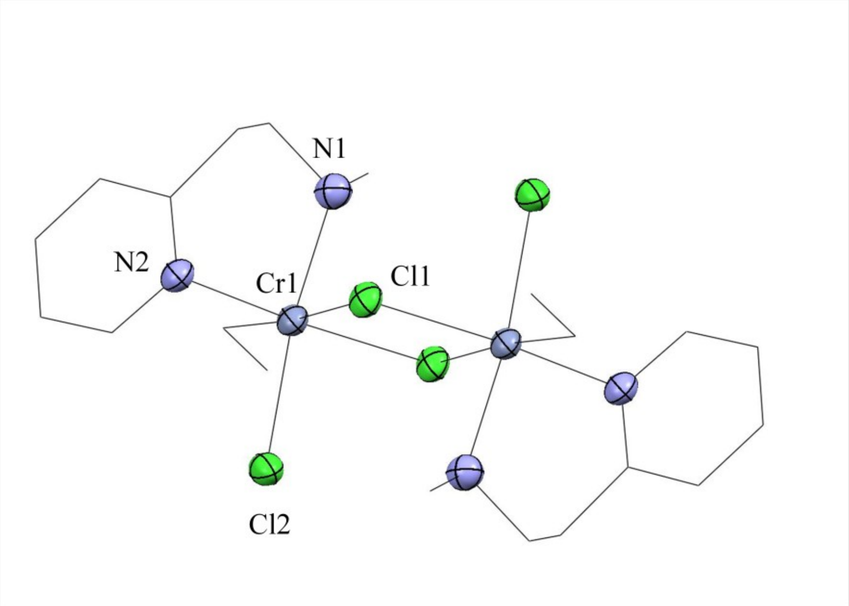


Figure 4.3. Partial thermal ellipsoid drawing of **4.6** at 50% probability. Select bond lengths (Å) and angles (deg): Cr1-N1 2.1255(18), Cr1-N2 2.1264(16), Cr-Cl1 2.3863(6), Cr1-Cl2 2.3778(6); N1-Cr1-N2 92.04(7), N1-Cr1-Cl1 86.01(5), N1-Cr1-Cl2 172.62(5), N2-Cr1-Cl1 171.05(5), Cl1-Cr1-Cl2 87.23(2), C1-N1-C3 108.05(18); C1-N1-Cr1 114.83(13), C3-N1-Cr1 118.24(14).

Ethylene oligomerization experiments were performed on the analytically pure complexes. When **4.1** – **4.6** were activated with MAO (methylaluminoxane) in toluene, a non-selective distribution of *α*-olefins (Schulz-Flory type) was obtained with high activity and free of unwanted polymeric by-products (Table 4.1). This behavior suggests that the catalytically active species obtained upon activation contains chromium in its divalent state.[6h,7b,16i,c,17a,d] Even in case of further reduction to the monovalent state, the presence of toluene may form species such as Cr(I)-η^6-toluene,[15] effectively quenching the activity of the catalytic sites. Therefore, to avoid the poisoning effect of toluene,[10c] catalytic runs were performed in methylcyclohexane (MeCy). In this case, the aluminum based activator DMAO (toluene and Me_3Al depleted MAO) was necessarily used for solubility reasons. Adopting these new conditions switched the catalytic behavior from non-selective oligomerization to selective tri- and tetramerization (in the case of **4.1**-**4.3**). The activity was only moderate and unwanted

Table 4.1. Ethylene oligomerization results.[a]

catalyst	**co-catalyst (equiv)**	**alkenes (mL)**	**PE (g)**	**activity (g/g Cr . h)**	**linear *α*-olefins (mol %)**						
					C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}
4.1[b]	MAO (500)	48	0	44,000	29	27	17	11	8	5	3
4.1[c]	DMAO (500)	10	2.6	12,513	11	89	0	0	0	0	0
4.1[c]	DMAO/Et_3Al (500/50)	10	0.8	10,179	46	54	0	0	0	0	0
4.2[c]	DMAO (500)	10	1.6	11,244	30	70	0	0	0	0	0
4.3[b]	DMAO (500)	3	1.3	4,506	25	75	0	0	0	0	0
4.5[b]	MAO (500)	54	0	49,500	16	22	20	14	13	9	6
4.5[c]	DMAO (500)	6	1.0	6,731	39	32	9	8	5	4	3
4.5[c]	DMAO/Et_3Al (500/50)	28	6.8	33,937	26	27	16	14	9	5	3
4.6[b]	-	-	-	-	-	-	-	-	-	-	-
4.6[b]	MAO (500)	33	1.4	32,045	21	23	21	19	16	13	11
4.6[c]	-	-	-	-	-	-	-	-	-	-	-
4.6[c]	DMAO (500)	13	2.3	14,929	43	26	8	7	6	5	5

[a] Conditions: Loading 30 µmol of complex, 80 ˚C temperature, 40 bar (ethylene), 30 min reaction time. [b] 100 mL of toluene. [c] 100 mL of methylcyclohexane. DMAO = Me_3Al depleted MAO

polyethylene material was also formed. Yet the high selectivity for 1-octene is puzzling and along with the presence of polymer, suggests simultaneous formation of more than one catalytically active species in different oxidation states. We tentatively suggest that the trivalent state is responsible for the formation of polymeric material. Such catalytically active species may be formed by either lack of reduction or through series of disproportionations, triggered by the chromium redox dynamism. [3d,11e,17]

When **4.1** was activated with DMAO in MeCy, a moderate activity and very high selectivity towards 1-octene (C_6:C_8 = 11:89) was obtained. Even though this level of activity has been recently observed in other NP systems,[19] such a high selectivity remains both rare and intriguing.[1b,c,3d] In an attempt to favor reduction to Cr(I), more reducing conditions were employed by adding Et_3Al to DMAO. A marked drop in selectivity was instead observed (C_6:C_8 = 46:54%). Similar activation of **4.2** with DMAO still decreased the selectivity for 1-octene (C_6:C_8 = 30:70%). The presence of CH_3CN in the metal coordination sphere (**4.2**) instead of THF (**4.1**) influences the behavior of the active species by reducing the selectivity and overall activity. Therefore, further testing with complexes containing CH_3CN was not further pursued.

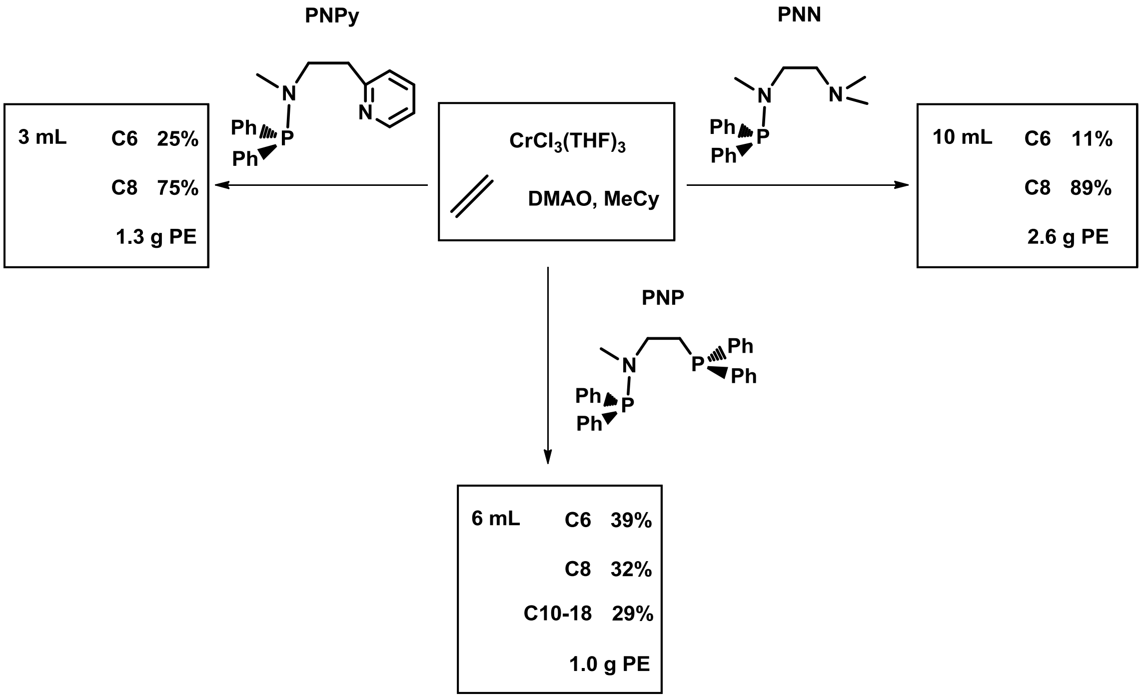
When the pyridine-containing derivative **4.3** was activated with DMAO in MeCy, a good/average selectivity for 1-octene was obtained (C_6:C_8 = 25:75%). The activity was significantly reduced with respect to **4.1**. This could be the result of an over-stabilizing power of the pyridine moiety possibly slowing the reduction of the chromium center.

Testing of complex **4.6** (obtained from alkylation of **4.3**) was carried out in the absence of activators searching for possible self-activating behavior. While the presence of activator proved to be necessary, only non-selective oligomerization was obtained for this species. This suggests that the amino-phosphine moiety is indeed essential for selective behavior.

The catalytic behavior of **5** was probed in MeCy using DMAO as a cocatalyst. This species is non-selective, showing only a minor enrichment towards 1-hexene and 1-octene fractions (C_6:C_8 = 39:32%). The minor enrichment in C_6 and C_8, along with the formation of polymer, is again an indication of the presence of redox dynamism generating the other two catalytically active states.

The catalytic behavior is sumarized in Scheme 4.4. When comparing the different base donor groups, the ligand with the amino residue displays the best selectivity towards 1-octene (89%) as well as producing the highest activity. The ligand with the pyridine moiety maintains a still high selectivity towards 1-octene (75%) but with a noticeable decrease of activity. In the case of phosphine residue containing ligand (**PNP**), the activity switches towards non-selective Schulz-Flory with enrichment in 1-hexene (C6) and 1-octene (C8) fractions. This behavior was quite unanticipated since the phosphorous donors are in principle expected to provide the best functions to stabilize the lower valence states.

Scheme 4.4



4.5 Conclusion

In our previous work we developed a highly selective 1-octene catalyst based on bidentate NP ligand, following a possible bimetallic mechanism.[19] With the work presented here based on **PNP**, **PNPy** and **PNP** ligand framework, we have observed a delicate balance exists between 1-hexene *vs.* 1-octene formation possibly due to the fact that metallacyclic mechanism is followed in the present case. This balance is dictated by the ligand supporting monovalent chromium. The highest selectivity towards 1-octene was achieved in the case of **PNN** ligand (complex **4.1**) (89% C_8). Unfortunately, our attempts of isolating active intermediates by reacting the complexes with alkyl-Al species were unsuccessful, and in the case of **PNPy** treatment with Et_3Al resulted in ligand fragmentation and isolation of **4.6** which proved to be a non-selective oligomerization catalyst. Nonetheless, a highly selective ethylene tetramerization chromium catalyst has been discovered therefore encouraging further research.

4.6 References

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Highly Active Chromium (II) Ethylene Oligomerization Catalytic System

5.1 Introduction

Ethylene oligomerization is a relevant industrial process which continues to attract considerable attention from researchers in the field of polyolefins.[1] The mixture of linear α-olefins that result from oligomerization, usually C_4-C_{20} in chain length, have specific applications depending on their molecular weight. These encompass plasticizers, manufacture of linear low-density polyethylene, surfactants, detergents, adhesives, fragrances, corrosion protective coatings, lubricants and other household and industrial uses.[2]

Conceptually, non-selective ethylene oligomerization is not different from a polymerization process truncated at the early stage (Cossee-Arlman mechanism), thus resulting in a statistical distribution of α-olefins.[3] For the purpose of ethylene oligomerization, either selective[4] or non-selective[5] catalysts based on tri-valent chromium have been widely used. Such catalysts have also been used for ethylene polymerization.[6] The reason for this versatile behavior can be attributed to the underlying redox dynamism exhibited by chromium in the presence of alkylating agents.[7] Catalytic ethylene oligomerization is usually carried out in the presence of Al-based alkylating agents. The very preliminary step is the formation of tri-valent organo chromium pre-catalysts. These species are know to readily reduce, depending on the nature of the supporting ligand, to the di- or mono-valent state, each with its own distinct catalytic behavior.[7] Rapid interconversion (*via* disproportionation) of the mono- di- and trivalent oxidation states often occurs thus resulting in polymeric by-products fouling Schulz-Flory distributions of oligomers, occasionally enriched in 1-hexene or 1-octene.[8,4o-s,5-7] Hence in addition to the traditional roles, the ligand dictates the various oxidation states, thus controlling the outcome of the catalytic cycle. Unsurprisingly, obtaining polymer-free, selective oligomerization catalysts is a primary task in industrial research.

For this work we have targeted divalent chromium. The rationale was twofold: on one side Cr(II) has been shown to be responsible for non-selective Schulz-Flory distribution of oligomers and therefore we wish to confirm the possibility of preparing polymer-free non-selective oligomerization catalysts;[9] on the other, should reduction occur, the divalent state in principle provides easier accessibility to the selective monovalent state. The bidentate NP based ligands, $Ph_2PN(R)(CH_2)_nN(R)PPh_2$, $Ph_2PN(R)Si(Me)_2N(R)PPh_2$ and $Ph_2PN(R)(CH_2)_2X$ (X = $N(Me)_2$ or PPh_2), were designed with the aim of supporting the reduction of Cr(III) to Cr(I) to enable selective ethylene tri- or tetramerization. These systems are conceptually different from the divalent Schulz-Flory catalysts in that they follow a ring expansion metallacycle redox mechanism.[10,4i] For the purpose of stabilizing Cr(II) we extended our ligand library by exploring the novel bidentate $Ph_2P(CH_2)_2N(Me)H$ ligand.

5.2 Experimental

All manipulations were carried out under an inert nitrogen atmosphere using Schlenk glassware or a dry-box. Solvents were dried using aluminum oxide purification system. Chemicals were obtained from commercial sources and used as received. Me_3Al was purchased from Strem and used as received. Methylaluminoxane (MAO, 20% in toluene) was purchased from Albemarle Corporation. Me_3Al depleted MAO (DMAO) was prepared by removing (*in vacuo* 2 mmHg) all volatiles *in vacuo* and under moderate heating (40 ˚C) for 6 hours. Elemental analyses were performed using Perkin-Elmer 2400 CHN analyzer. Magnetic susceptibilities were recorded using a Johnson Matthey magnetic susceptibility balance at room temperature. Samples were prepared inside a dry-box using calibrated, sealed tubes. X-ray crystal data were determined using a Bruker diffractometer equipped with a Smart CCD area detector and with Bruker Kappa APEXII CCD diffractometer. NMR spectra were recorded on Bruker Avance 300 MHz spectrometer at 300 K. Oligomerization reactions were carried out under pressure in a 300 mL Parr reactor equipped with stirrer and temperature control.

5.2.1 Synthesis of Ligands

Preparation of $Ph_2P(CH_2)_2N(Me)H$ (PN)

2-(Methylamino)ethanol (15.0 mL, 186.7 mmol) in $CHCl_3$ (180 mL) was cooled to 0°C. Thionyl chloride (14.2 mL, 196.1 mmol) was added drop-wise and the resultant suspension was stirred at room temperature overnight. The volume of $CHCl_3$ was reduced (to ~70 mL) and EtOH was added (~50 mL), to quench the excess of thionyl chloride. Solvent was completely removed *in vacuo* and the resultant off-white solid was recrystallized twice with Et_2O and EtOH mixture (20:80). The shiny white crystals of $HN(Me)(CH_2)_2Cl.HCl$ which separated were washed with cold EtOH and dried under vacuum (10.5 g, 80.8 mmol, 44%). ^1H NMR (300 MHz, $CDCl_3$) δ: 9.82 (s, br, 2H), 3.97 (t, J = 6.2 Hz, 2H), 3.31 (p, J = 6.2 Hz, 2H), 2.78 (t, J = 5.6 Hz, 3H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 52.7, 41.9, 33.8.

A solution of t-BuOK (5.6 g, 50.3 mmol) in THF (100 mL) was added with Ph_2PH (3.5 mL, 20.1 mmol) and stirred for 30 min at room temp. $HN(Me)(CH_2)_2Cl.HCl$ (2.6 g, 20.1 mmol) was added to the solution and refluxed overnight, whereby the dark red color turned to milky white. Solvent was removed under reduced pressure and the residue suspended in 10% $HCl_{(aq)}$, and washed with Et_2O. The aqueous solution was washed with 10% $NaOH_{(aq)}$ and extracted with Et_2O. The organic solution was washed with brine, dried over anhydrous $MgSO_4$ and evaporated. The residue was passed through a short alumina column to give $HN(Me)(CH_2)_2PPh_2$ as a colorless oil (2.2 g, 9.1 mmol, 74%). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.42 (m, 10H), 2.69 (q, J = 8.5 Hz, 2H), 2.38 (s, 3H), 2.25 (t, J = 7.3 Hz, 2H), 1.09 (s, br, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 138.5, 132.6, 128.6, 128.4, 48.8, 36.3, 28.9. ^{31}P NMR (300 MHz, $CDCl_3$) δ: -23.66 (s).

5.2.2 Synthesis of Complexes

Preparation of Complex 5.1

A solution of **PN** (1.22 g, 5.0 mmol) in THF (20 mL), was treated with *n*-BuLi (2.79 mL, 5.5 mmol, 2.0 M in hexanes) at 25 ˚C and stirred for 24 hrs. Solid $CrCl_2(THF)_2$ (1.34 g, 5.0 mmol) was added to the mixture affording a dark green solution after 4 hrs of stiring. The solvent was removed *in vacuo* and the residue was redissolved in THF (15 mL). The insoluble residues were removed *via* centrifugation and the solution was left to stand at -30 ˚C for 2 days, upon which dark green crystals of **5.1** were isolated and washed with cold hexanes (3 x 2 mL) and dried under vacuum (3.62 g, 3.5 mmol, 72%). $\mu_{eff} = 5.53\ \mu_B$. Elemental Analysis % calculated for $C_{46}H_{66}Cl_4Cr_2Li_2N_2O_4P_2$ (found): C 53.50 (52.98), H 6.44 (6.03), N 2.71 (2.32).

Preparation of Complex 5.2

A solution of **5.1** (0.16 g, 0.15 mmol) in toluene (5 mL) was cooled to -30 ˚C for about 5 min, and treated with Me_3Al drop-wise (0.05 g, 0.75 mmol). The resulting dark blue solution was stirred at room temperature for 20 min. The insoluble solid material was discarded by centrifugation, the supernatant layered with hexanes (2 mL) and stored at -30 ˚C for 4 days. Blue block-shaped crystals of **5.2** were isolated and washed with cold hexanes (3 x 2 mL) and dried (0.05 g, 0.05 mmol, 31%). $\mu_{eff} = 5.76\ \mu_B$. Elemental Analysis % calculated for $C_{34}H_{46}Al_2Cl_4Cr_2N_2P_2$ (found): C 48.36 (48.12), H 5.49 (5.28), N 3.32 (3.19).

5.3 X-Ray data

Table 5.1. Table of crystal data and refinements for **5.1** and **5.2**.

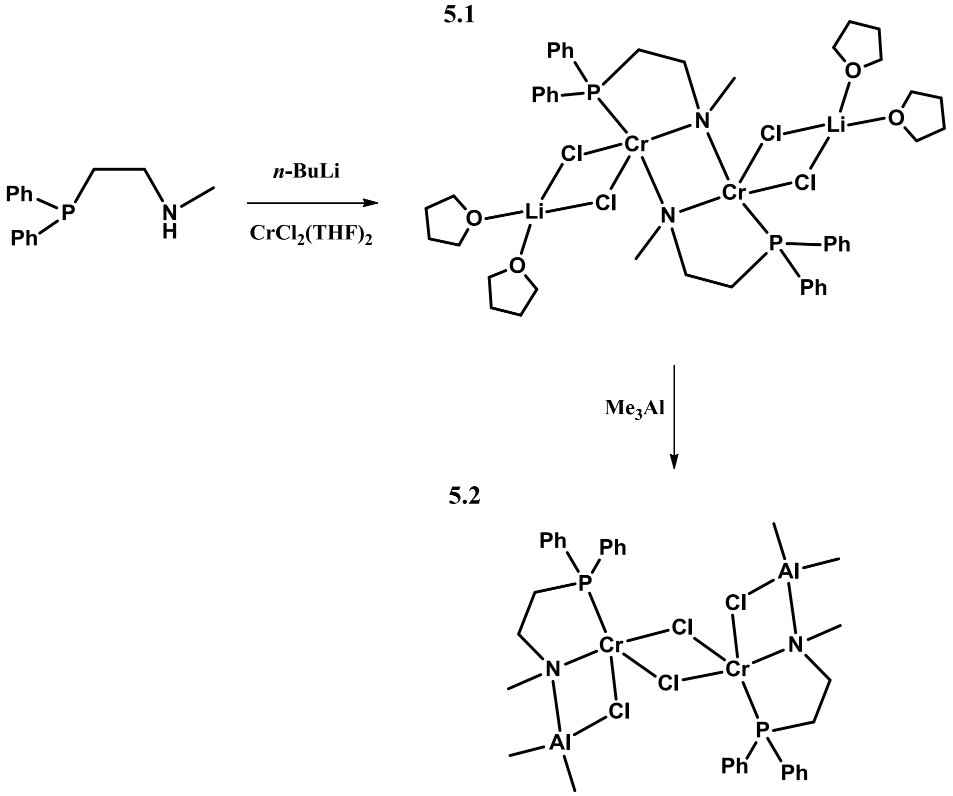
	5.1	**5.2**
Formula	$C_{46}H_{78}Cl_4Cr_2Li_2N_2O_4P_2$	$C_{20.5}H_{27}AlCl_2CrNP$
Mw	1044.72	468.28
Space group	Monoclinic, C 2/c	Monoclinic, C 2/c
a **(Å)**	27.6775(16)	26.5680(3)
b **(Å)**	11.6847(8)	12.1697(2)
c **(Å)**	16.2092(10)	16.0878(2)
α, (deg)	90	90
β, (deg)	90.189	116.546(1)
γ, (deg)	90	90
V **(Å^3)**	5242.1(6)	1.337
Z	4	8
Radiation	0.71073	0.71073
T (K)	200(2)	200(2)
D_{calcd} (g cm^{-3})	1.324	1.337
μ_{calcd} (mm^{-1})	0.721	0.833
F_{000}	2208.0	1944.0
R, Rw^{2a}	0.0614, 0.1977	0.0303, 0.0788
GoF	1.011	1.011

[a] $R = \Sigma jFoj - jFcj/\Sigma jFj$. $Rw = [\Sigma(jFoj - jFcj)2/\Sigma wFo2]^{1/2}$

5.4 Results and Discussion

The ligand $Ph_2P(CH_2)_2N(Me)H$ (**PN**) was prepared by first synthesizing $Cl(CH_2)_2N(Me)H$, which, upon treatment with Ph_2PK, gives **PN** in moderate yield. The purity was assessed by NMR spectroscopy. Complex **5.1** was prepared by treatment of $[Ph_2PCH_2CH_2N(Me)]Li$ (deprotonated using *n*-BuLi) with a $CrCl_2(THF)_2$ suspension in THF. Immediate color change from teal blue to dark green indicated complex formation (Scheme 5.1).

Scheme 5.1



The crystal structure **5.1** show a dimeric arrangement with two very distorted square pyramidal divalent chromium atoms, bridged by the N atom of two NP ligands. The pentacoordinated coordination geometry around each metal center is defined by the two bridging nitrogen atoms of the two bridging ligands and two chlorine, in turn attached to one Li(THF)$_2$ unit. The phosphine pendant is located on the axial position The Cr-Cr non-bonding distance (2.7625(13) Å) is as expected for a dinitrogen bridged dimeric structure (~1.90 Å).[11]

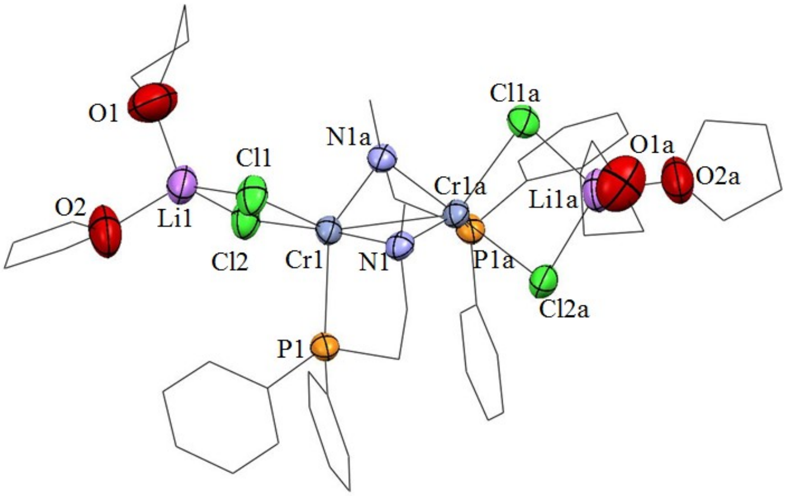


Figure 5.1. Partial thermal ellipsoid drawing of **5.1** at 50% probability. Select bond lengths (Å) and angles (deg) of **1**: Cr1-Cl1 2.4408(13), Cr1-Cl2 2.5318(13), Cr1-P1 2.5042(13), Cr1-N1 2.087(3), Cr1-Cr1a 2.7625(13); Cl1-Cr1-Cl2 88.22(5), Cl2-Cr1-P1 105.72(5), P1-Cr1-N1 82.40(10), N1-Cr1-N1a 88.39(15), Cr1-N1-Cr1a 82.87(13).

In an attempt to isolate a catalytically active intermediate, **5.1** was treated with Me_3Al (in toluene) (Scheme 5.1). An immediate color change from green to dark-blue was observed and X-ray quality crystals were isolated from layering a toluene solution with hexanes. The structure of **5.2** shows again a dimeric structure with two Cr(II) metal centers bridged by two chlorine atoms (Figure 5.2). The ligand appears to have rearranged its bonding mode in the sense that it switched from the bridging-chelating to chelating. The coordination geometry around each divalent chromium is distorted square pyramidal with the equatorial plane defined by the two bridging chlorine and the two ligand P and N donor atoms. A third chlorine is located on the axial position in turn bridging, together with the ligand N atom, one $AlMe_2$ residue.

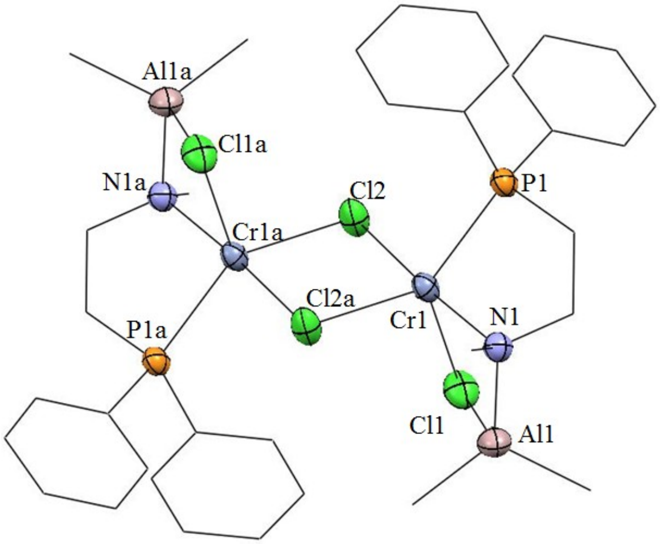


Figure 5.2. Partial thermal ellipsoid drawing of **5.2** at 50% probability. Select bond lengths (Å) and angles (deg) of **5.2**: Cr1-P1 2.4563(5), Cr1-N1 2.1080(14), Cr1-Cl1 2.5277(5), Cr1-Cl2 2.3825(5), Cr1-Cl2a 2.4835(5); P1-Cr1-N1 82.68(4), N1-Cr1-Cl1 81.65(4), Cl1-Cr1-Cl2 96.129(18), Cr1-Cl2-Cr1a 93.215(16).

Ethylene oligomerization experiments were performed on analytically pure **5.1** and **5.2**. When **5.1** was activated with MAO (methylaluminoxane) in toluene, a very large amount (92 mL) of a Schulz-Flory distribution of oligomers was obtained. The highest activity was observed with low loading of MAO and at a relatively low temperature (150 eq, 40 ˚C). The catalytic cycle produced α-olefins free of any unwanted polyethylene (74 mL of α-olefins in 30 mins). By extending the 30 minute run time to 2 hours, it was found that the catalyst remained active, as evidenced from the increase in the total amount of oligomers produced (from 74 mL to 92 mL, polymer-free). Although the observed catalytic activity is not record high, the polymer-free products make **5.1** an industrially relevant Schulz-Flory catalyst.[12] When **5.1** was tested using methylcyclohexane as the solvent and DMAO (Me_3Al depleted MAO) as activator, the catalytic behavior was essentially switched to polymer only. This striking difference in selectivity between the two solvents had been observed with our previous NP based catalysts as well.[13] It may be ascribed to a combination of factors including the ability of toluene to coordinate monovalent chromium and to poison its catalytic activity,[14] as well as its ability to favor or disfavor the disproportionation of chromium thus stabilizing certain oxidation state at the expenses of others.

The alkyl-Al adduct **5.2** was expected to be closer to the active species as generated *in situ* upon activation with MAO (which contains about 20% free Me_3Al). However, no self-activating behavior was observed and further testing was carried out with MAO in toluene. Surprisingly, **5.2** required much harsher conditions to achieve moderate activity, 150 eq. MAO, 70 ˚C. The lower activity compared to **5.1** can be attributed to the nature of the pre-catalyst. In the case of **5.1** (Figure 5.1), it can be seen that the dimeric species is bridged *via* amido N atoms. Upon treatment of **5.1** with Me_3Al, this bridge is broken and the structure undergoes a rearrangement (**5.2**, Figure 5.2). In the absence of coordinating ethylene molecules, **5.2** forms a relatively stable dimer with bridging Cl atoms. It can therefore be reasoned that such a dimer would need to be dissociated in order to make room for catalysis thus explaining the necessity for higher temperatures.

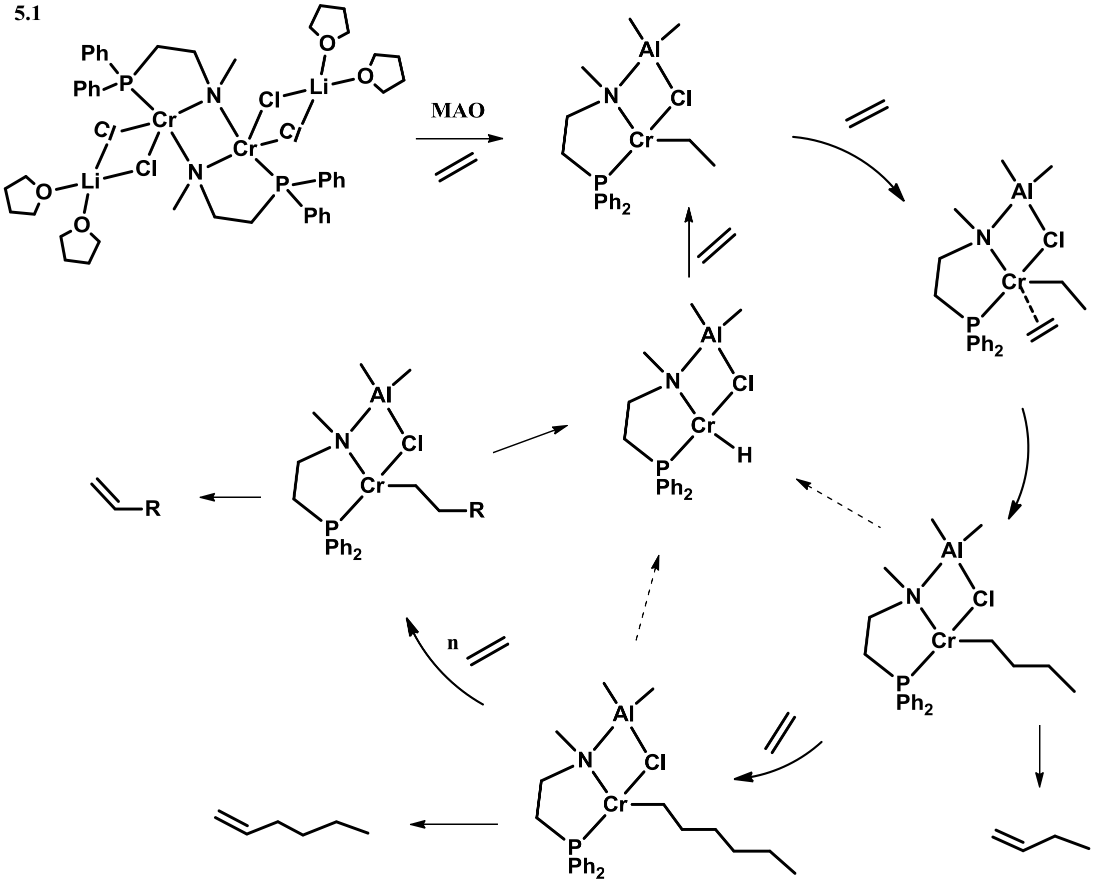
Table 5.2. Ethylene oligomerization results of **5.1** and **5.2**.[a]

catalyst	co-catalyst (equiv)	alkenes (mL)	PE (g)	activity (g/g Cr . h)	linear alpha olefins (mol %)						
					C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}
5.1[b]	MAO (150)	34	0	46,750	24	23	18	13	10	7	5
5.1	MAO (150)	74	0	101,750	35	26	16	10	6	4	3
5.1[c]	MAO (150)	52	0	71,500	37	26	16	10	6	4	1
5.1	MAO (75)	10	0	13,750	34	26	16	10	7	4	3
5.1	MAO (300)	61	0	83,875	34	26	16	10	6	5	3
5.1[e]	MAO (150)	92	0	31,625	31	26	17	11	7	5	3
5.1	DMAO (150)	34	0.9	48,462	35	27	17	10	6	4	1
5.1[f]	Me_3Al (20)	0	0	0	0	0	0	0	0	0	0
5.1[d]	DMAO (150)	1	0.9	3,125	37	23	8	8	8	8	8
5.2[b,f]	-	0	0	0	0	0	0	0	0	0	0
5.2[b]	MAO (150)	22	0	30,250	22	21	17	14	11	8	7

[a] Conditions: Loading 10 µmol of catalyst, 40 ˚C temperature, 40 bar (ethylene), 30 min reaction time, 100 mL of toluene. [b] 70 ˚C temperature. [c] 25 ˚C temperature. [d] 100 mL of methylcyclohexane. [e] 2 hours reaction time. [f] 25 µmol of catalyst. DMAO = Me_3Al depleted MAO

Given that complex **5.1** upon treatment with Me_3Al generates **5.2** (MAO has 20% Me_3Al), and that they both behave similarly by producing a Schulz-Flory distribution of oligomers, a possible rationalization of the catalytic behavior is shown in Scheme 5.2. Upon activation with MAO and in the presence of ethylene, an alkylated Cr(II) species similar to **5.2** is formed. Oligomerization occurs via the classical non-redox Cosse-Arlman mechanism.

Scheme 5.2



5.5 Conclusion

We have previously done extensive work on amino-phosphine (N-P) ligands where we discovered highly selective ethylene tetramerization catalysts.[13] With the work reported herein we have extended our ligand library based on NP donor atoms by reporting the chromium catalysis of $Ph_2P(CH_2)_2N(Me)H$ (**PN**) towards ethylene oligomerization. The isolated Cr(II) complexes **5.1** and **5.2** showed high activity towards oligomerization forming polymer-free Schulz-Flory distribution. The isolated Al-adduct **5.2** sheds light into the shape of the active species generated upon activation with MAO in the presence of ethylene. The **PN** ligand in its deprotonated form proves to be highly stabilizing towards divalent chromium. As a result of this stabilization, there is an increase in activity as well as an extended catalyst lifetime. Further work along these lines should explore the stabilizing potential of aliphatic phosphines in conjunction with amido N atoms.

5.6 References

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Conclusion

With the work presented in this thesis, we can say with confidence that the quest for truly selective ethylene tetramerization catalysts based on chromium has been significantly advanced. Our work indicates that in order to rationalize a highly selective 1-octene catalyst, a different synthetic strategy needs to be followed; one that involves the possibility of a bi-metallic mechanism. The intellectual challenge that needs to be addressed is the designing of a ligand system capable of bringing two Cr(I) metal centers in non-bonding distance, which are then capable of forming metallacycles that eventually fuse together and eliminate 1-octene. Although we were not successful in isolating an active intermediate that would conclusively support our bi-metallic hypothesis, the fact that a highly selective tetramerization catalyst has been discovered is an encouraging finding.

Our work was conclusive and illuminating due to the fact that a number of ligand modifications were done to paint the complete picture. We explored the catalytic performance of bidentate NP ligands with a one, two or three atom bridge. These subtle modifications proved to have a significant effect on the selectivity, resulting in either selective tetramerization, trimerization or non-selective Schulz-Flory distribution of α-olefins.

Other ligands were also explored while keeping the ligand design theme aminophosphine-based. By replacing one of the NP chelates to having a base donor, we were successful in developing yet another highly selective tetramerization catalyst. In this case however, we argue that the mechanism for selectivity is the traditional ring-expansion one, instead of a bi-metallic one. And finally the anionic N-P ligand we developed proved to be a highly active Schulz-Flory catalyst that did not produce any polymeric by-products.

Appendix A

Generalized Oligomerization Procedure

A Parr reactor was dried at 115 °C in an oven overnight and then placed under vacuum at 120 °C for 1h prior to each run. After cooling to the appropriate temperature, the required solvent and co-catalyst were added with stirring. After 10 min from mixing, the catalyst was injected under a stream of ethylene and immediately pressurized. The reaction was allowed to run for the required time after which the temperature was reduced to 5 °C with an ice bath. After venting the reactor, a mixture of MeOH/HCl conc. (40 mL/ 10 mL) was used to quench the reaction mixture. The organic phase was separated and analysed by GC-MS and ^{1}H-NMR. Precautions were taken to maintain the temperature as low as possible during the workup to minimize loss of volatiles.

Appendix B

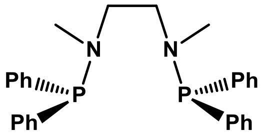
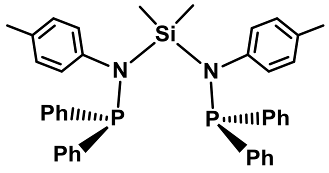
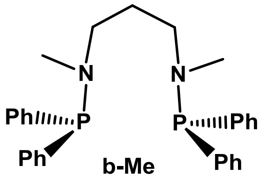
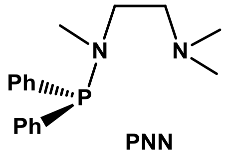
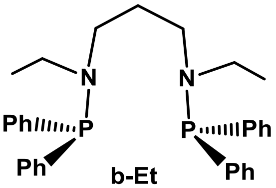
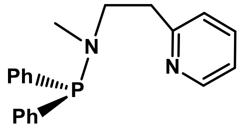
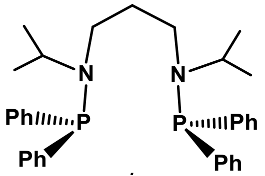
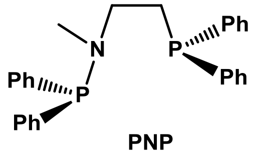
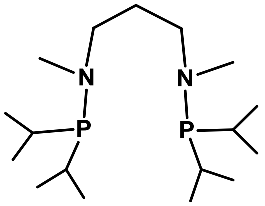
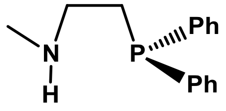
X-ray Crystallography Procedure

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.

Appendix C

NMR Spectra of Synthesized Ligands

The following series of NMR spectra were recorded on Bruker Avance 300 MHz spectrometer at 300 K, using $CDCl_3$ as the solvent.

Ligand	Figure	Ligand	Figure
 **a-Me**	1	 **Si(NP)$_2$**	6
 **b-Me**	2	 **PNN**	7
 **b-Et**	3	 **PNPy**	8
 **b-^{i}Pr**	4	 **PNP**	9
 **b-P^{i}Pr**	5	 **PN**	10

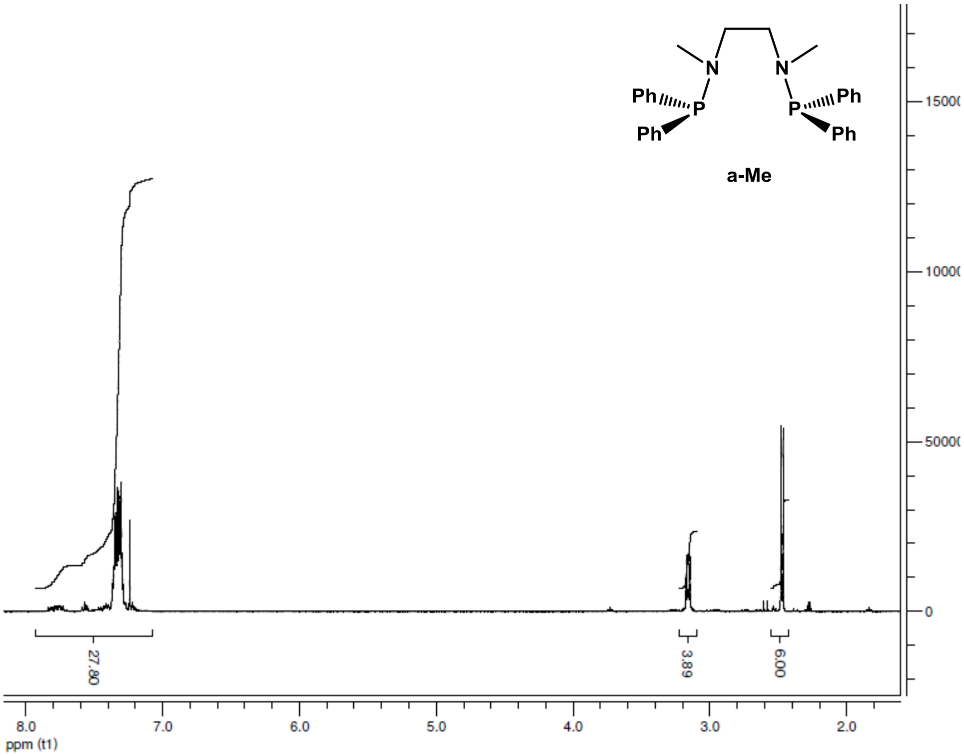


Figure 1a. ^{1}H NMR of **a-Me.**

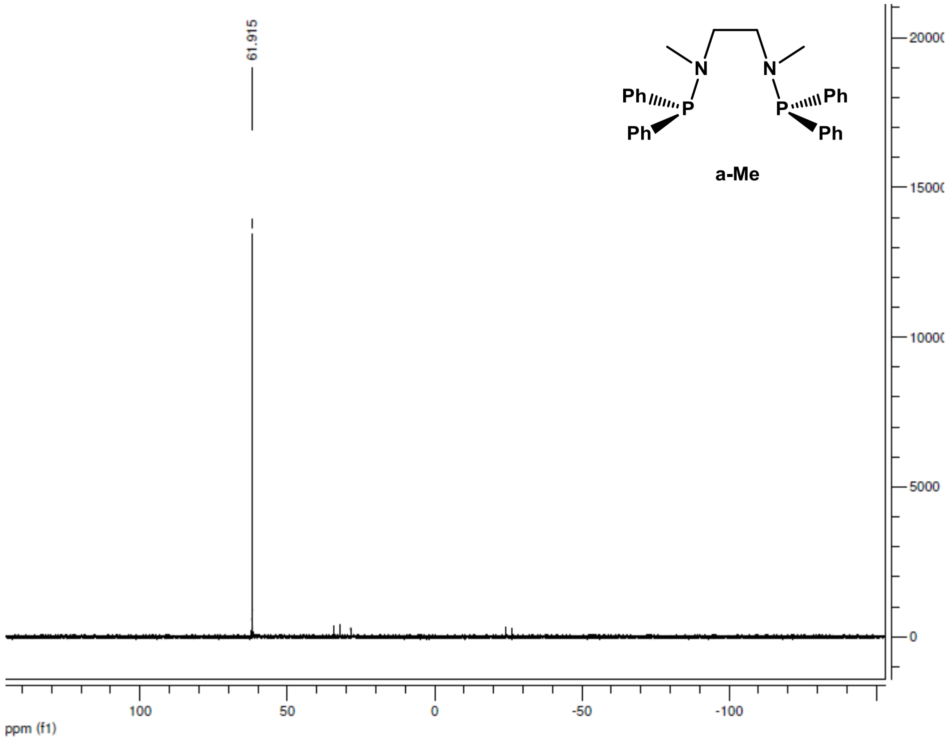


Figure 1b. ^{31}P NMR of **a-Me.**

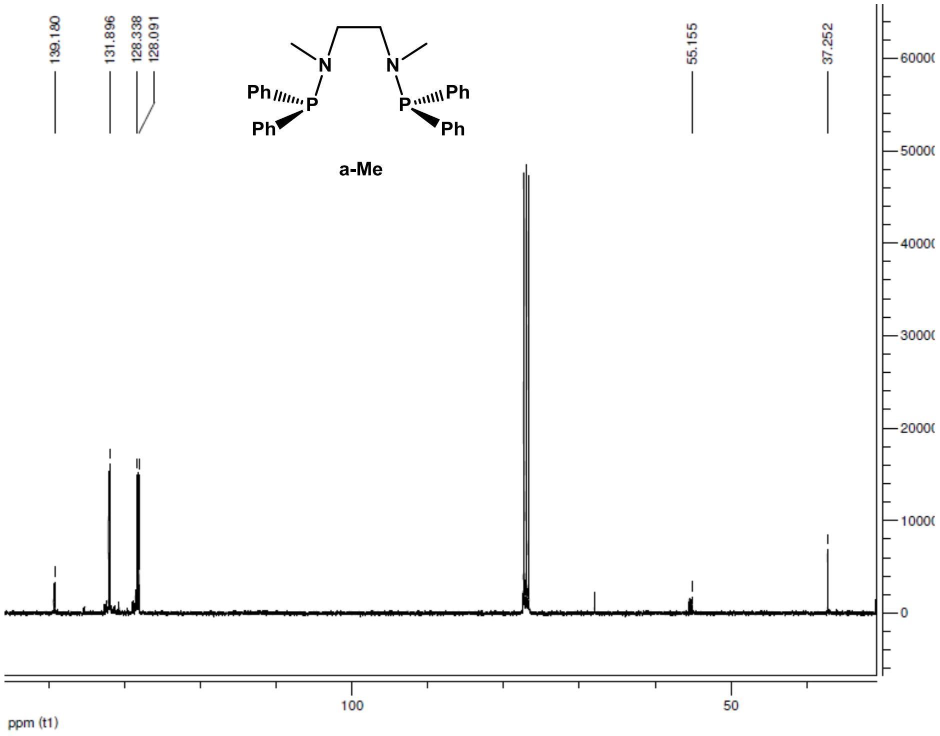


Figure 1c. ^{13}C NMR of **a-Me.**

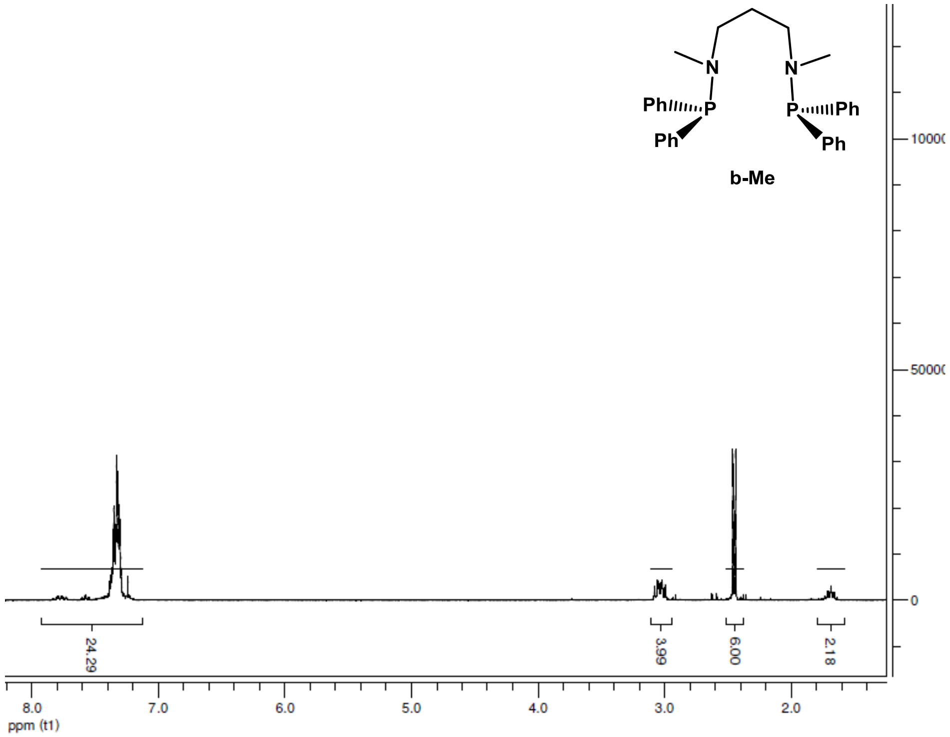


Figure 2a. ^{1}H NMR of **b-Me.**

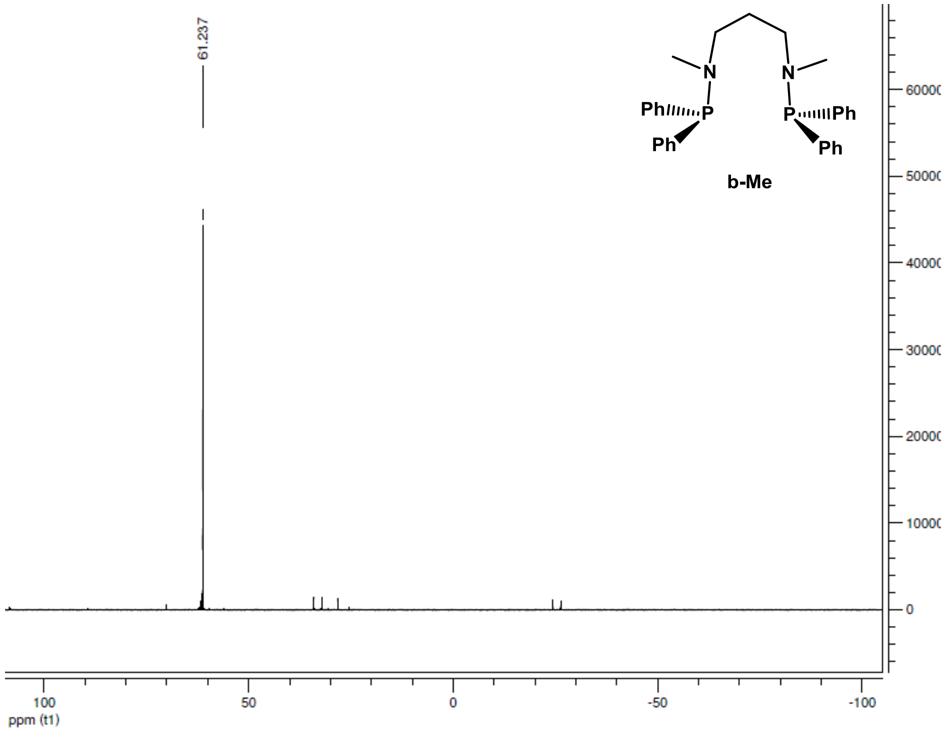


Figure 2b. ^{31}P NMR of **b-Me.**

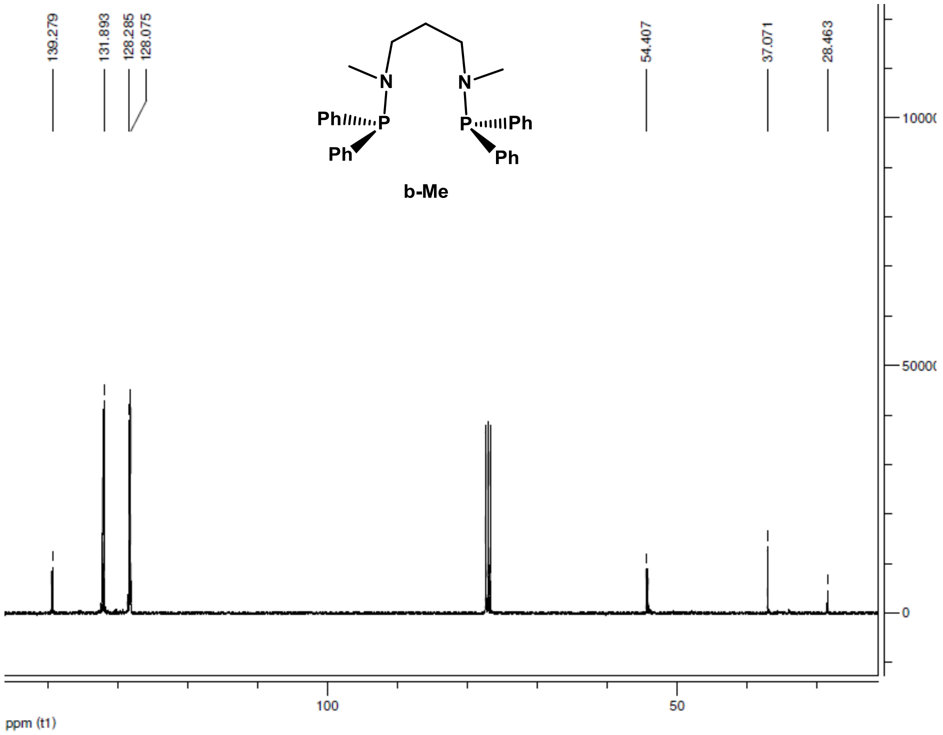


Figure 2c. ^{13}C NMR of **b-Me.**

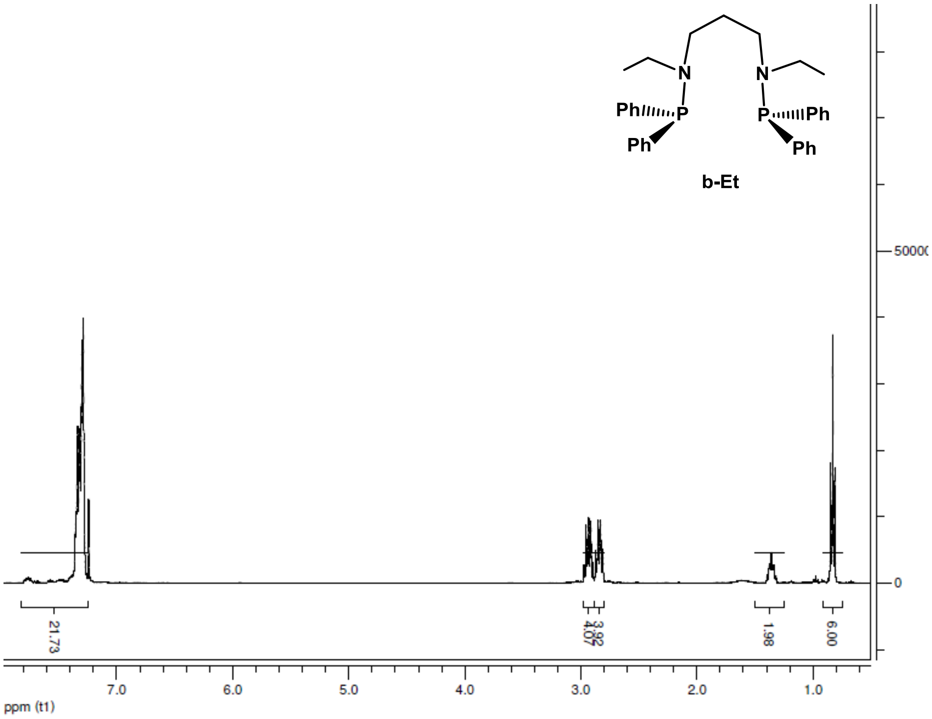


Figure 3a. ^{1}H NMR of **b-Et.**

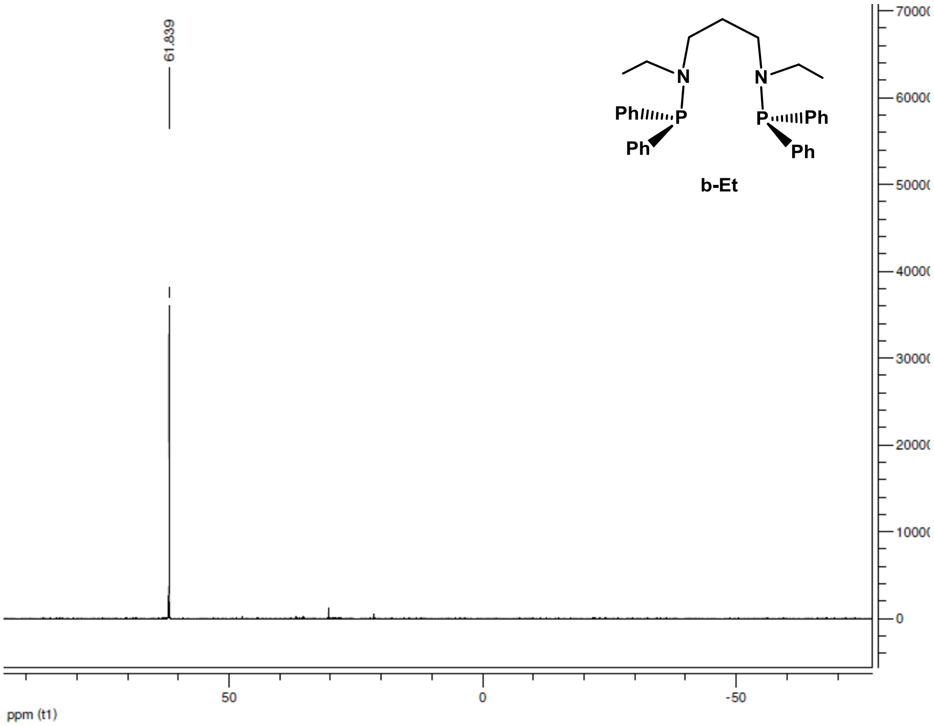


Figure 3b. ^{31}P NMR of **b-Et.**

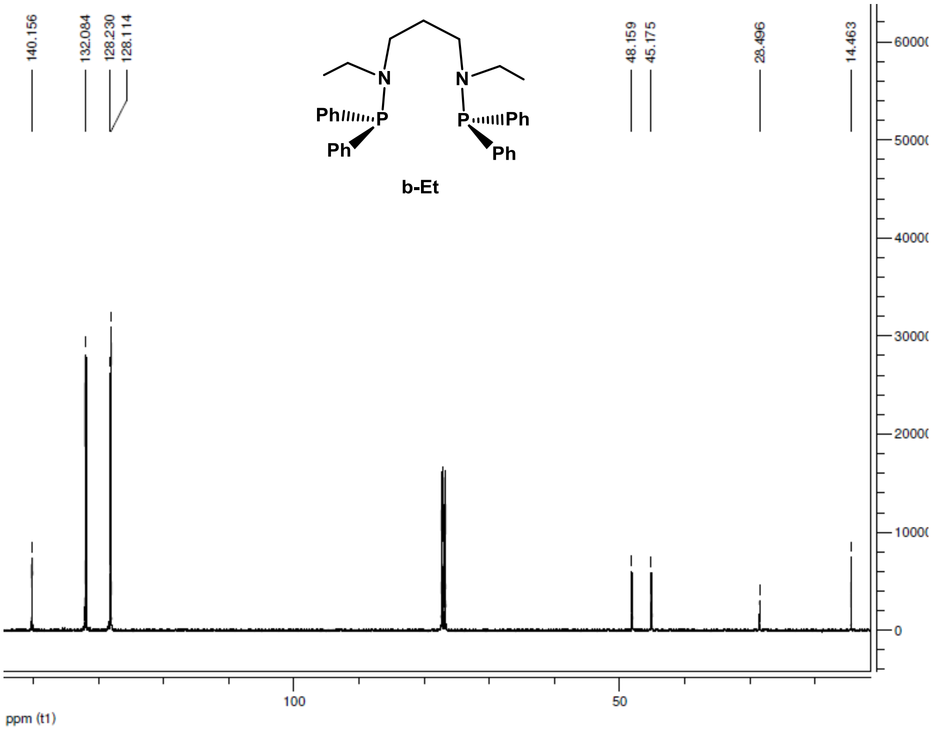


Figure 3c. ^{13}C NMR of **b-Et.**

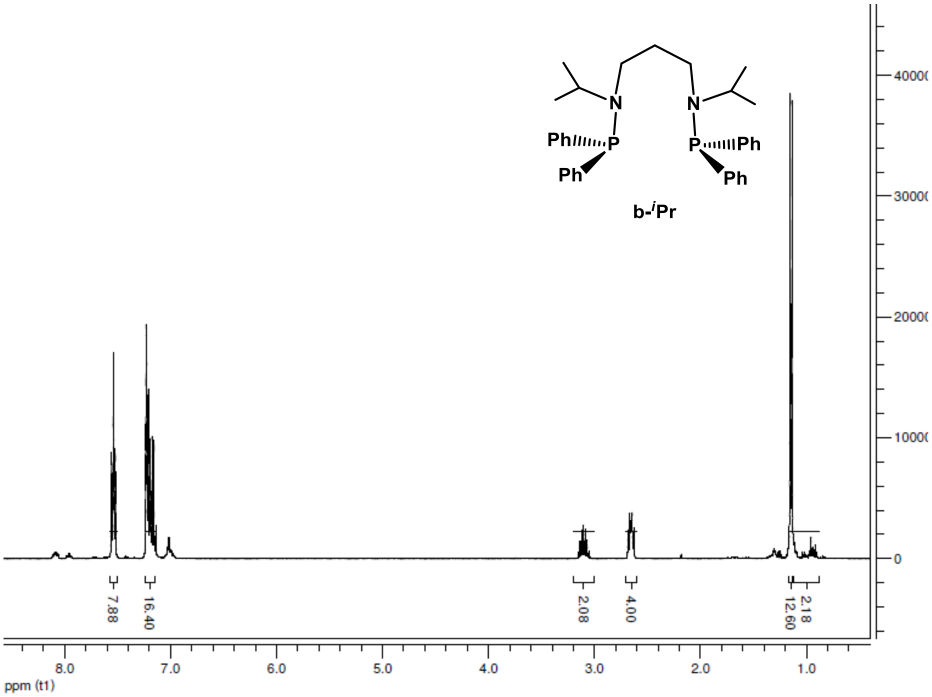


Figure 4a. ^{1}H NMR of **b-^{i}Pr.**

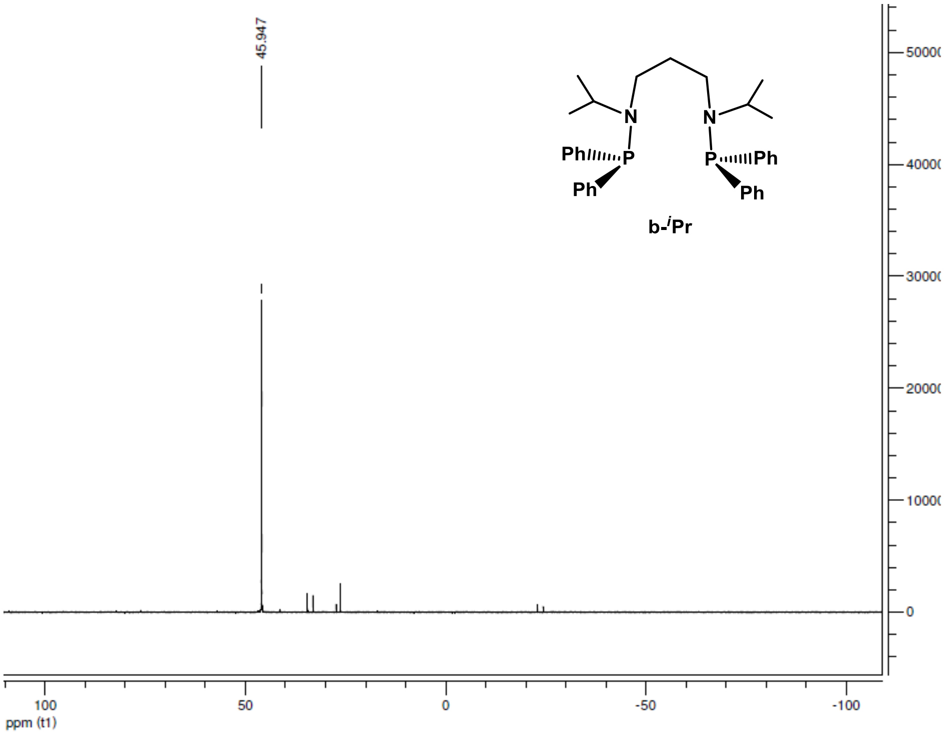


Figure 4b. ^{31}P NMR of **b-^{i}Pr.**

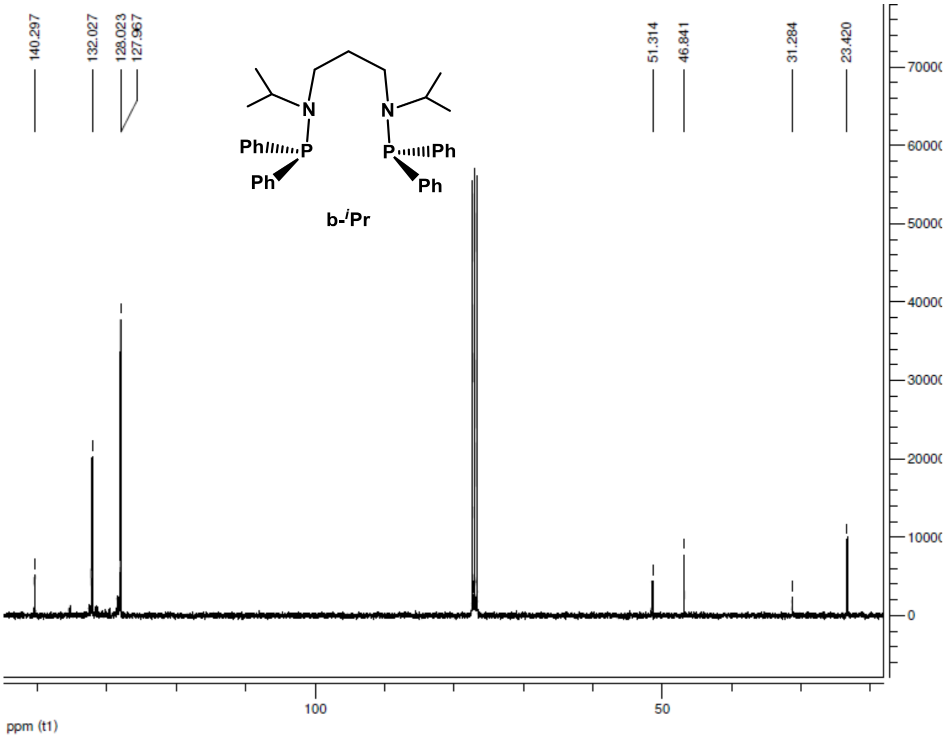


Figure 4c. ^{13}C NMR of **b-^{i}Pr.**

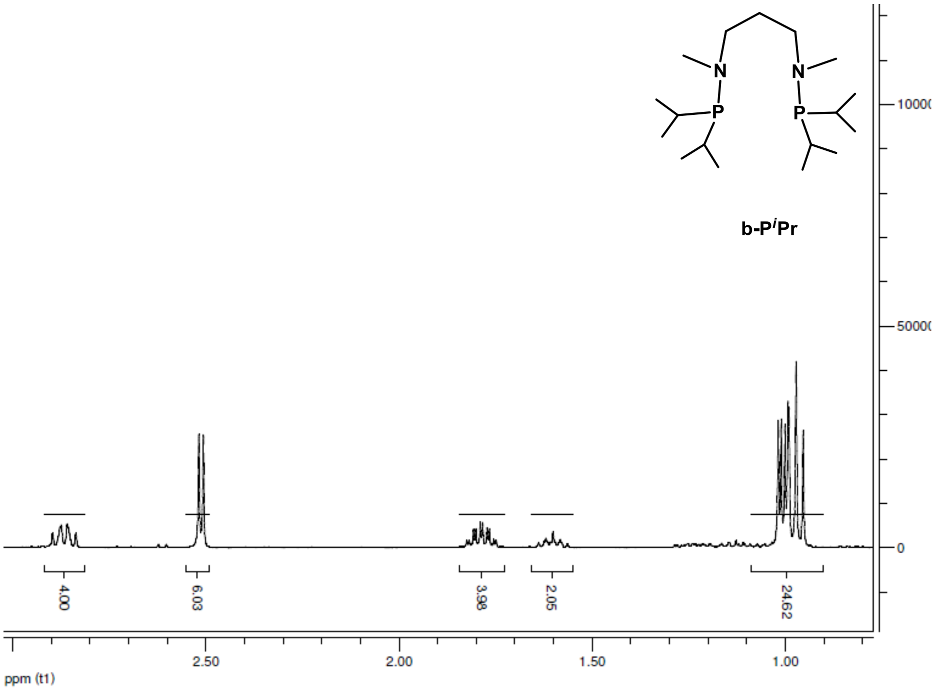


Figure 5a. ^{1}H NMR of **b-P^{i}Pr.**

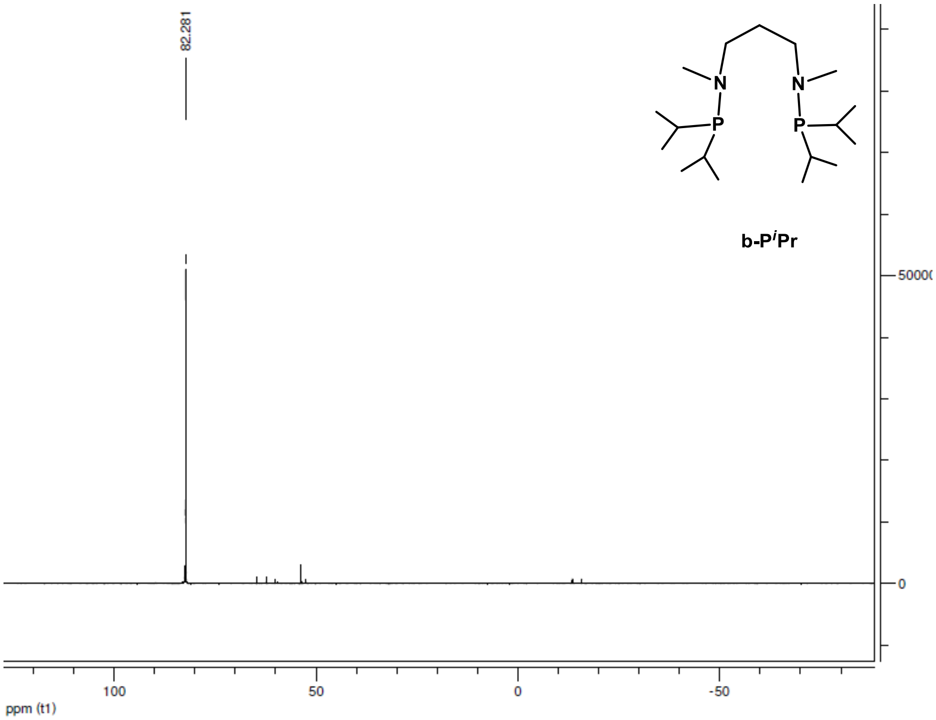


Figure 5b. ^{31}P NMR of **b-P^{i}Pr.**

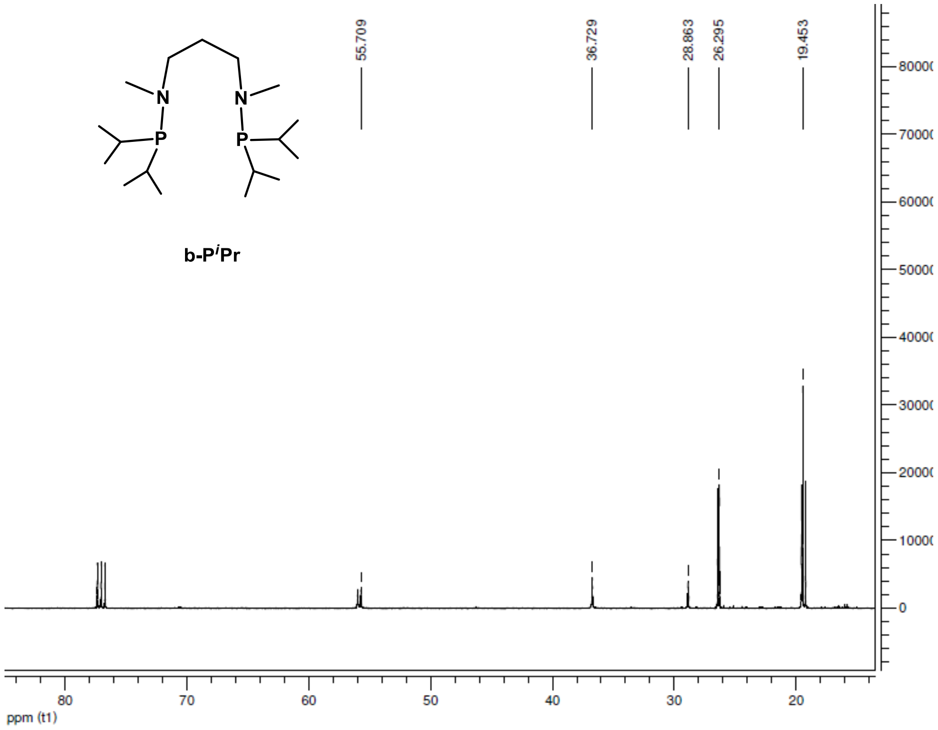


Figure 5c. ^{13}C NMR of **b-P^{i}Pr.**

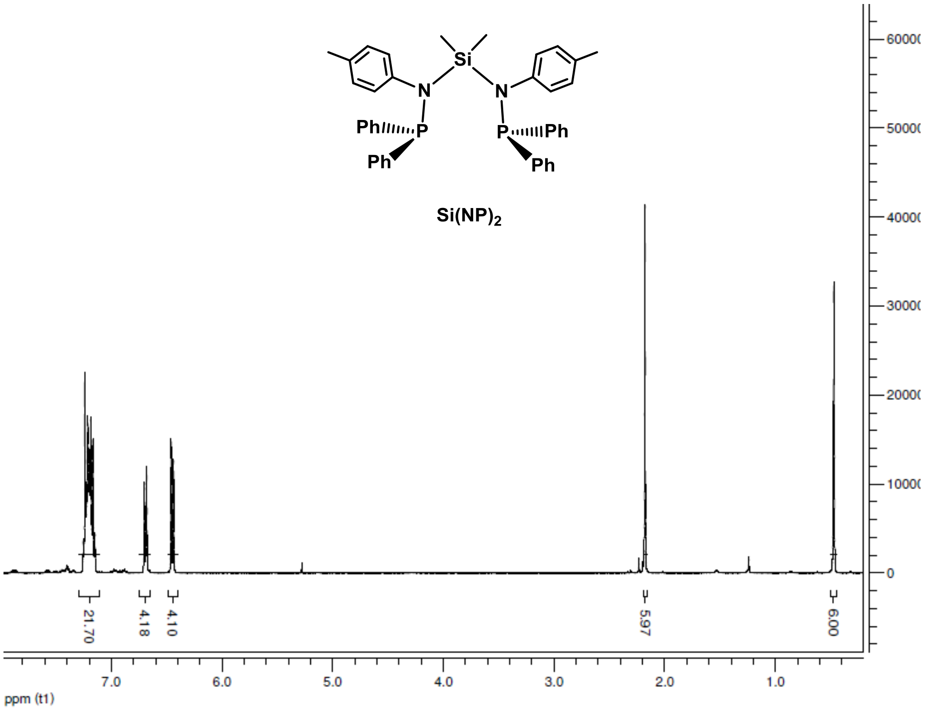


Figure 6a. ^{1}H NMR of **Si(NP)$_2$.**

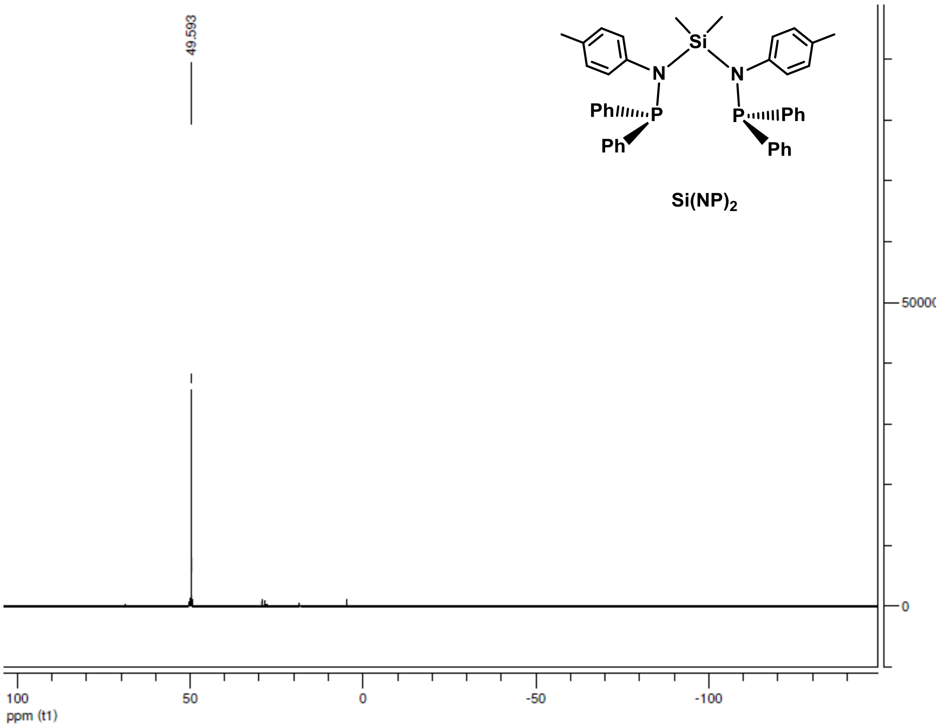


Figure 6b. ^{31}P NMR of **Si(NP)$_2$.**

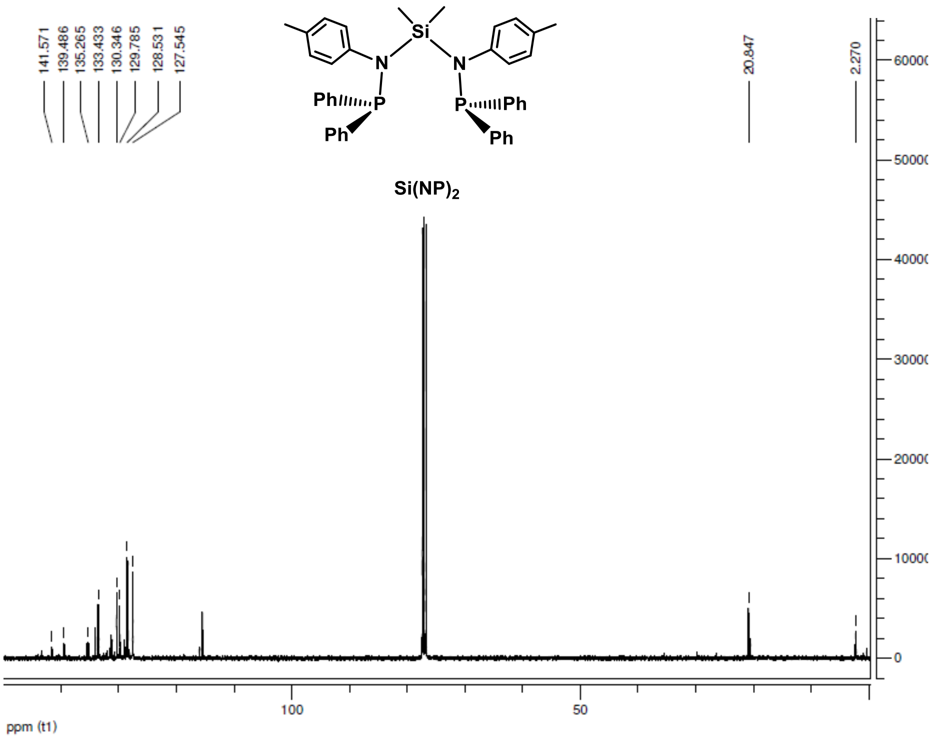


Figure 6c. ^{13}C NMR of **Si(NP)$_2$.**

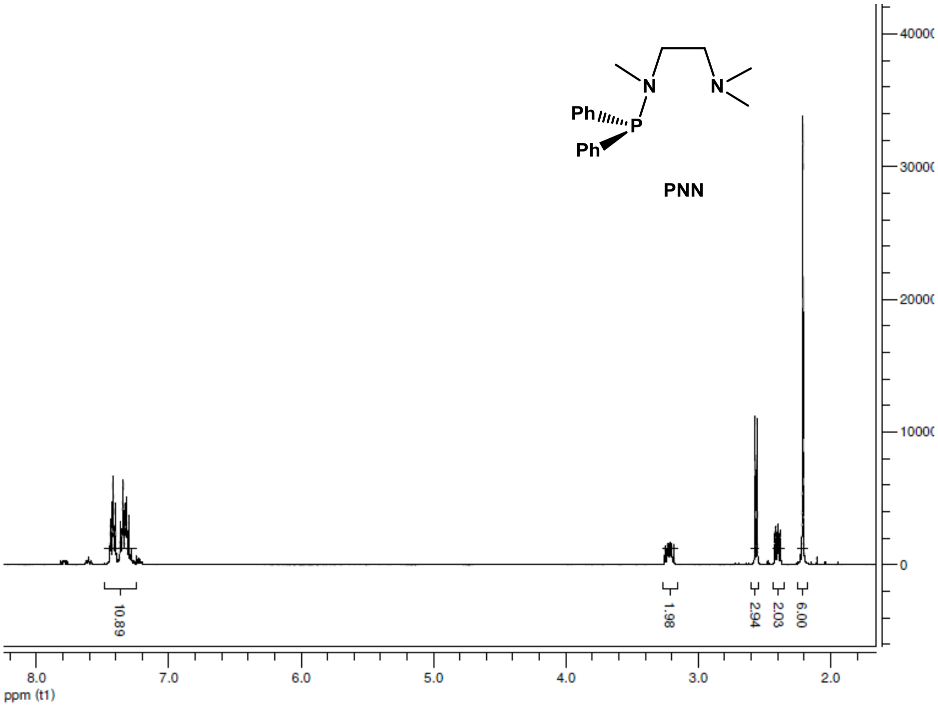


Figure 7a. ^{1}H NMR of **PNN.**

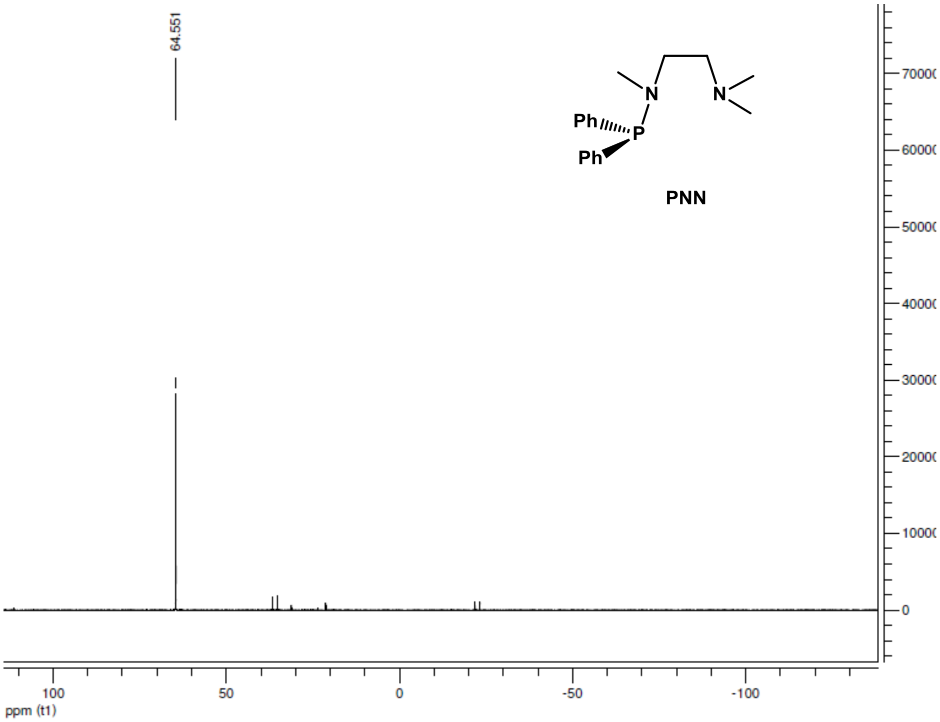


Figure 7b. ^{31}P NMR of **PNN.**

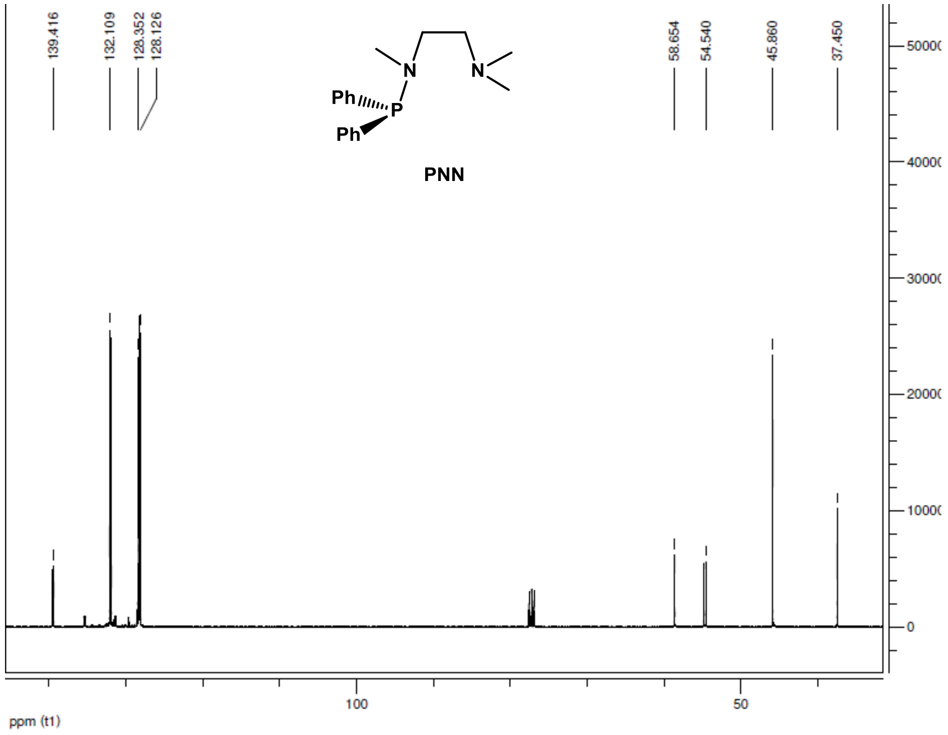


Figure 7c. ^{13}C NMR of **PNN.**

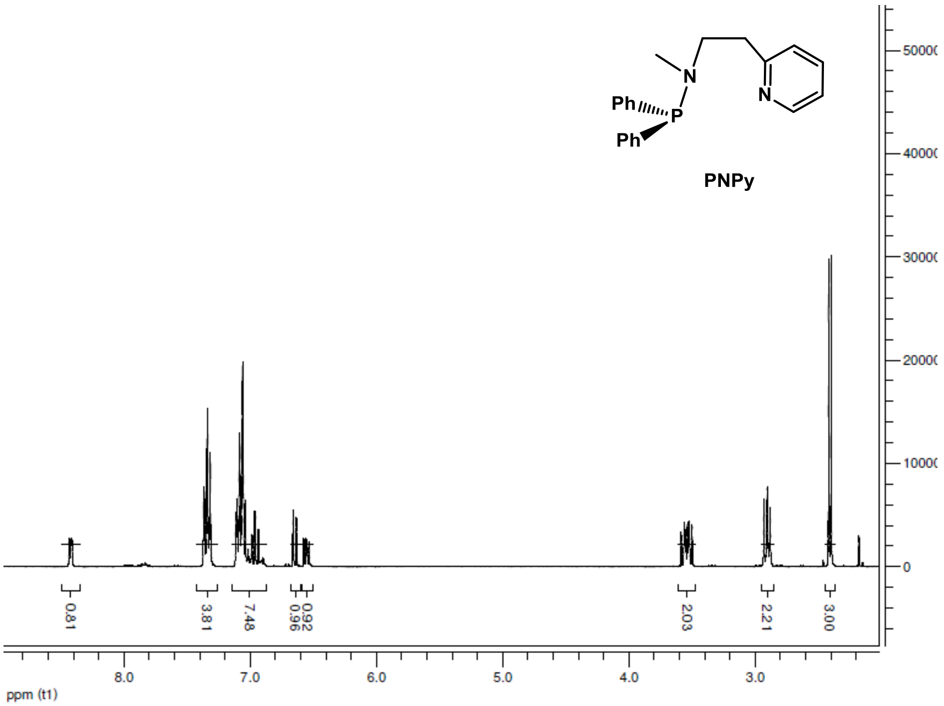


Figure 8a. ^{1}H NMR of **PNPy.**

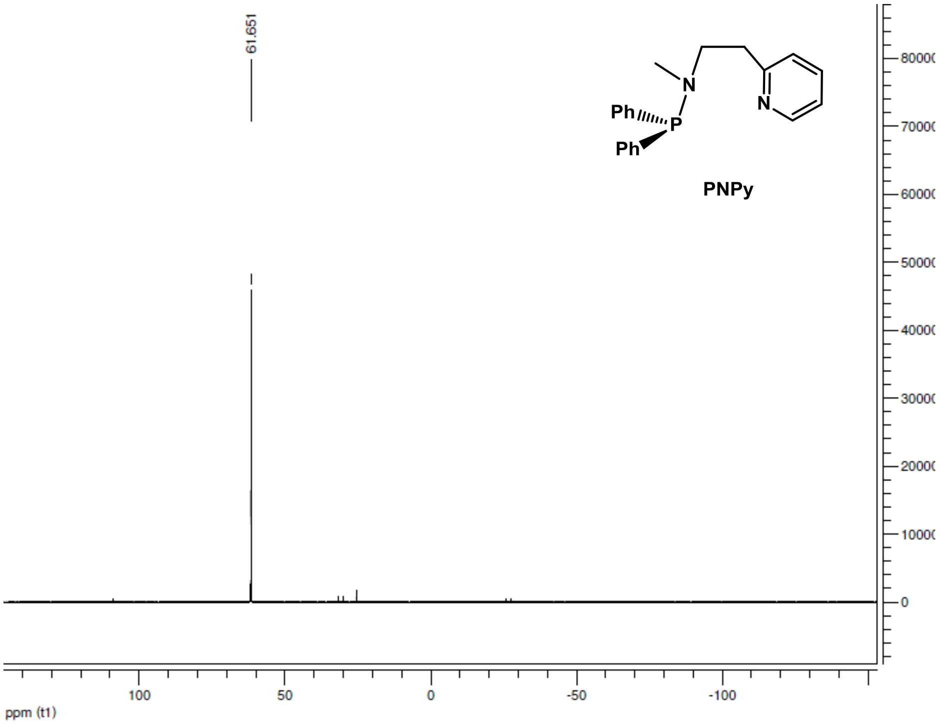


Figure 8b. ^{31}P NMR of **PNPy.**

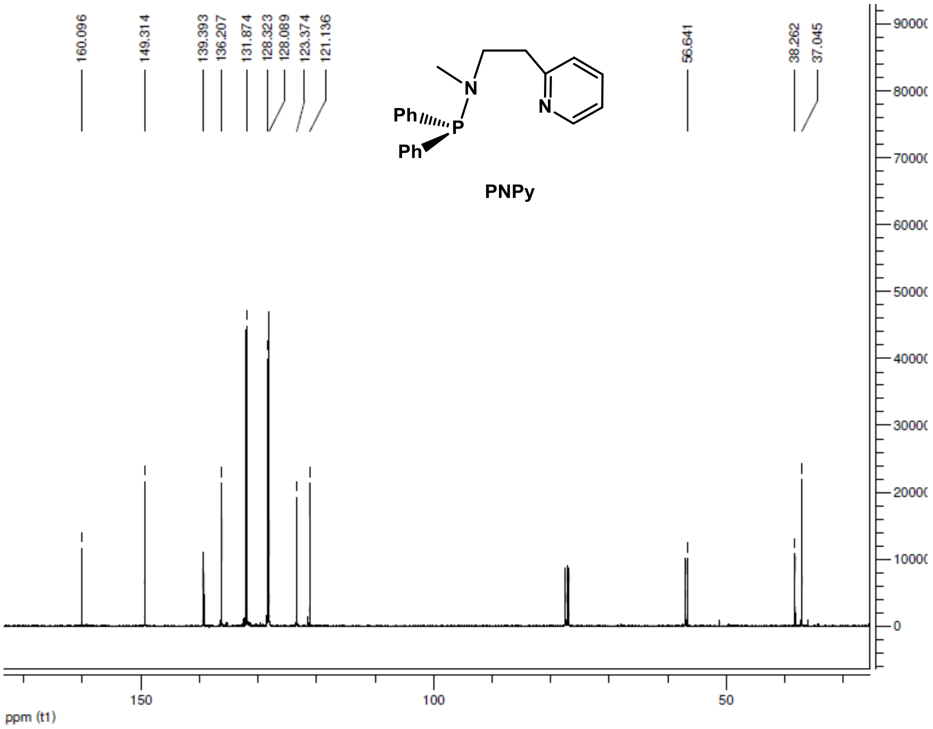


Figure 8c. ^{13}C NMR of **PNPy.**

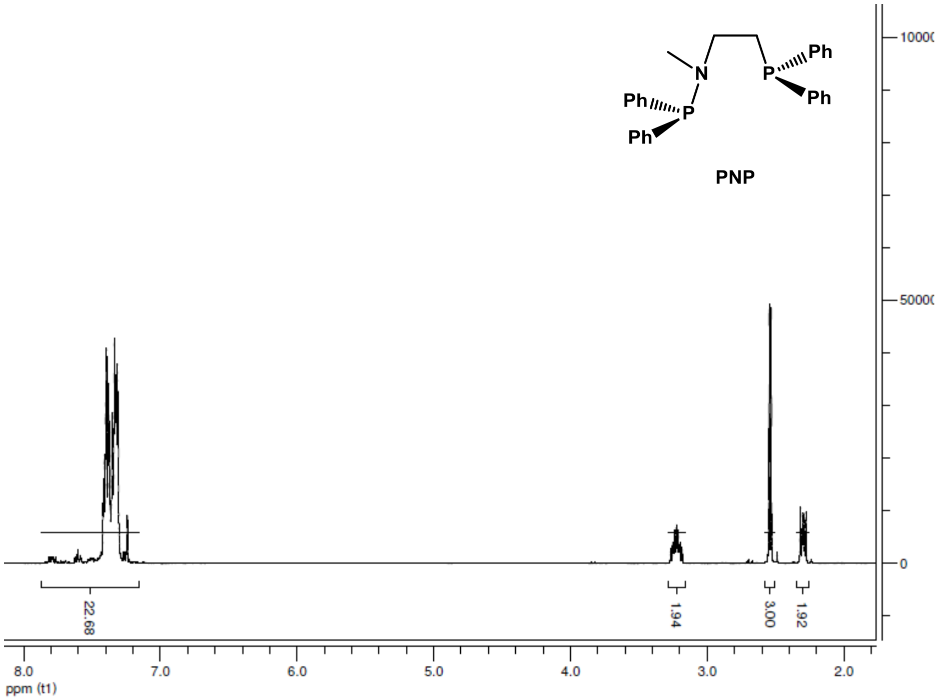


Figure 9a. ^{1}H NMR of **PNP.**

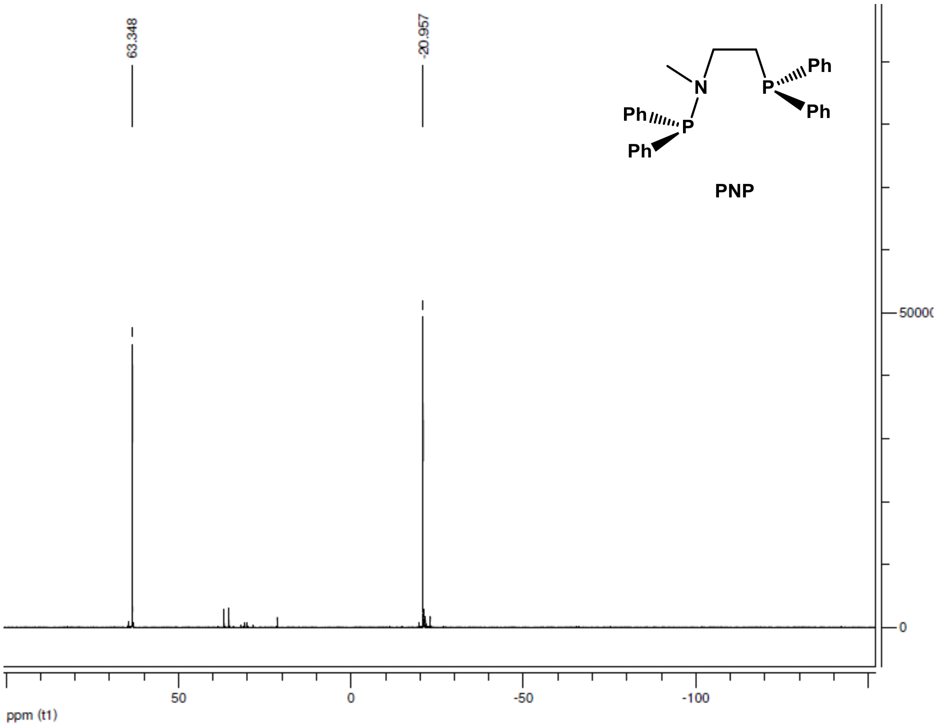


Figure 9b. ^{31}P NMR of **PNP.**

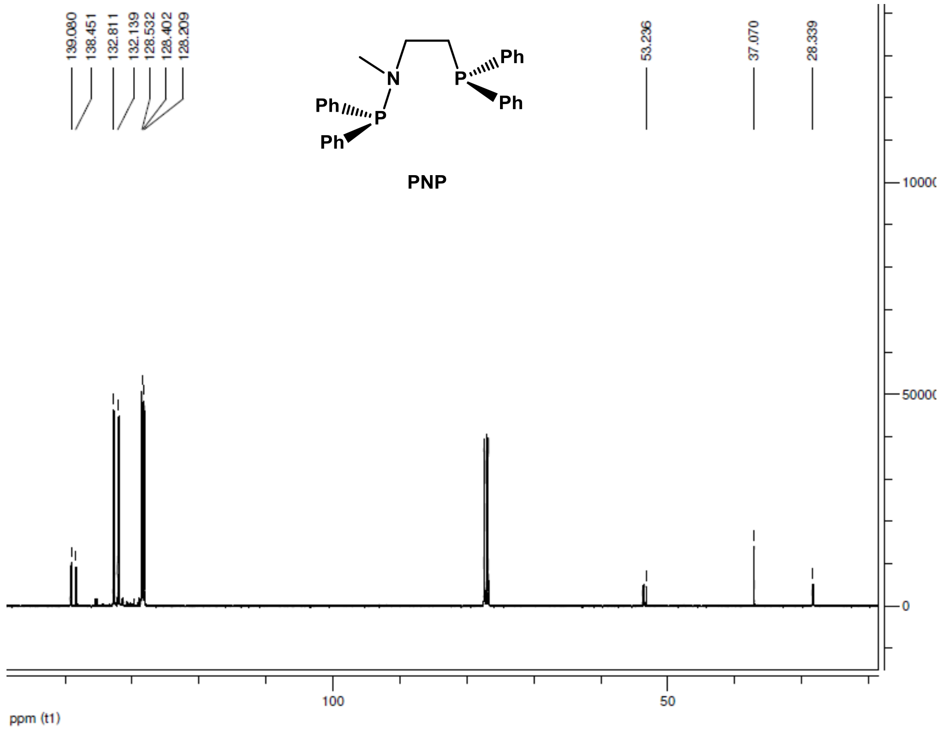


Figure 9c. ^{13}C NMR of **PNP.**

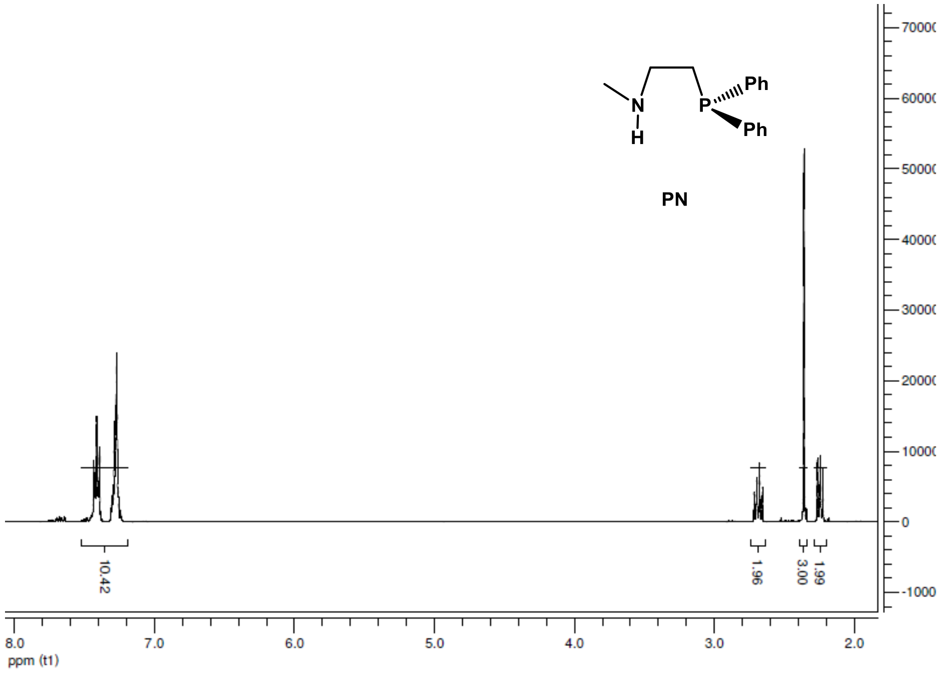


Figure 10a. ^{1}H NMR of **PN.**

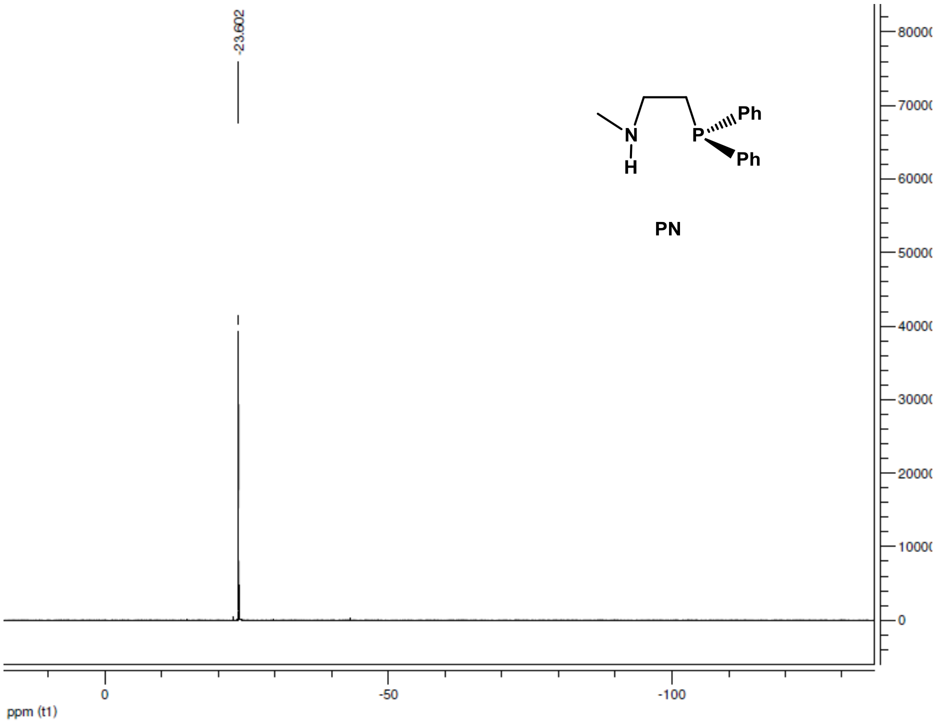


Figure 10b. ^{31}P NMR of **PN.**

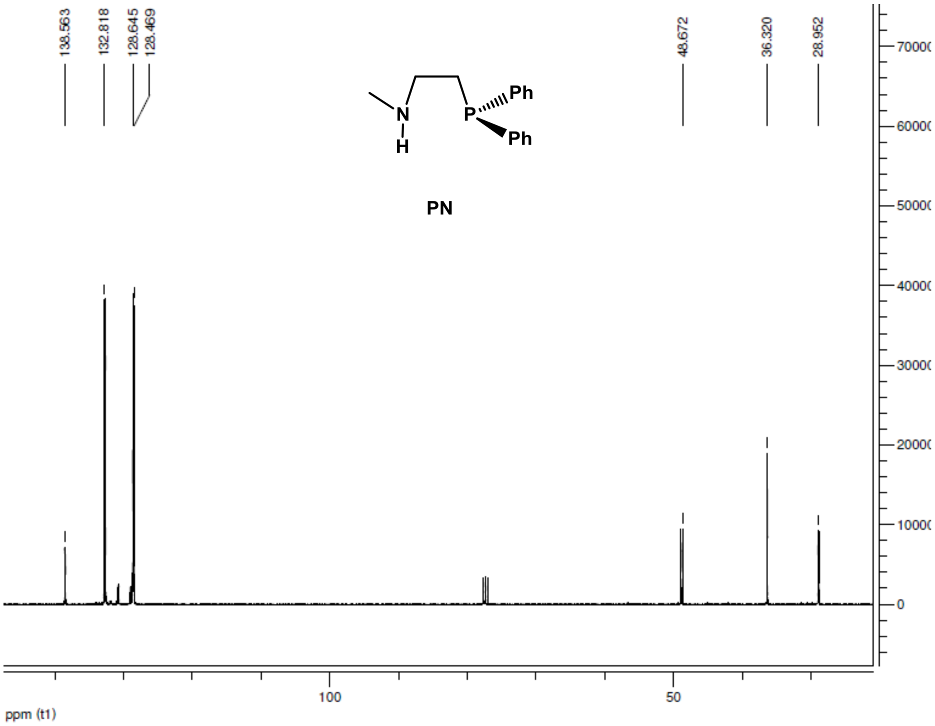


Figure 10c. ^{13}C NMR of **PN.**