Chapter 1

The Selective Oligomerization of Ethylene Using Chromium Diphosphine Catalysts

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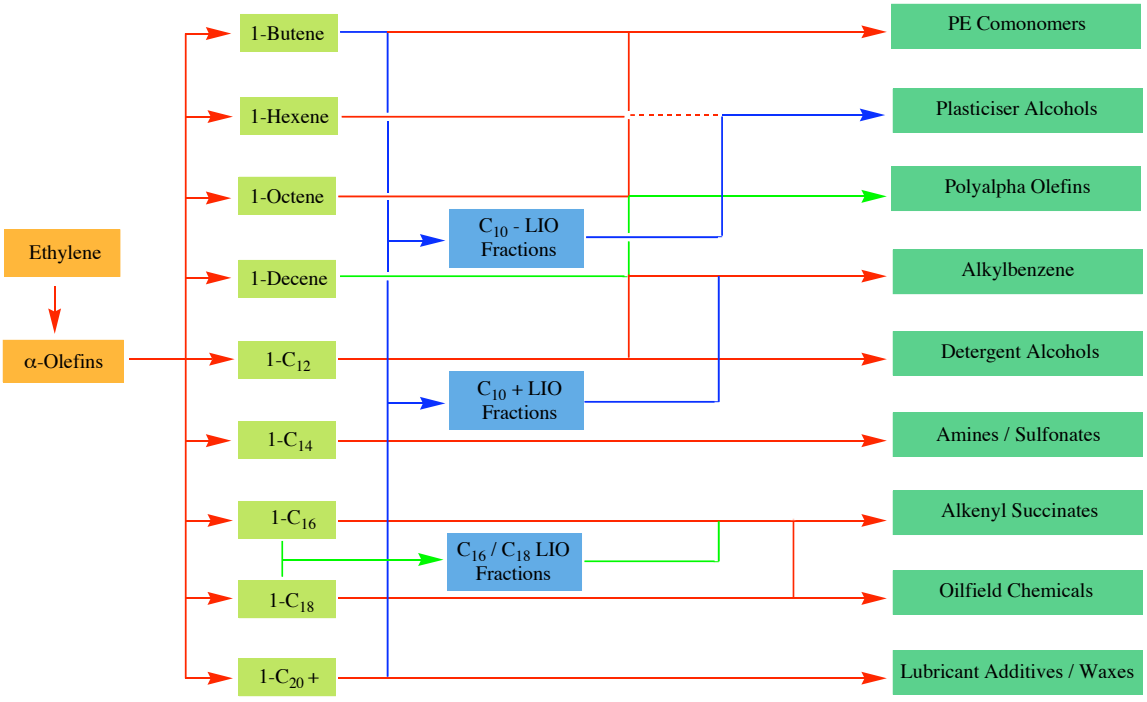
Abstract

A series of *bis*(diphenylphosphino)amine ligands with a donor group attached to the nitrogen linker have been prepared. Metalation of these ligands with chromium trichloride provides precursors to highly active, relatively stable, and selective catalysts for trimerization and tetramerization of ethylene. It has been demonstrated in oligomerization reactions performed at 1 and 4 atm of ethylene that these new systems increase total productivity by enhancing catalyst stability, as compared with those lacking a donor group on the diphosphine ligand. The product distributions and minor byproducts provide information relevant to mechanistic issues surrounding these types of reactions. Catalyst decomposition follows second-order kinetics, and does not involve diphosphine dissociation. Furthermore, the solvent effects in the trimerization and tetramerization of ethylene to 1-hexene and 1-octene with an aluminoxane-activated chromium catalyst bearing a *bis*(diphenylphosphino)amine ligand are also investigated. While reactions in non-polar solvents exhibit poor activity at lower ethylene pressures, those in more polar solvents, such as chlorobenzenes and fluorobenzenes, are highly active and generate very little undesired polymer. Varying the solvent has a significant impact on 1-hexene/1-octene selectivity. Experiments with potentially coordinating additives result in a higher tendency for 1-octene formation. Changes in the aluminoxane co-catalyst have a notable effect on catalyst productivity, however selectivity remains unaffected. The results presented in this work reflect the high tunability of this system by simple modifications of the reaction medium.

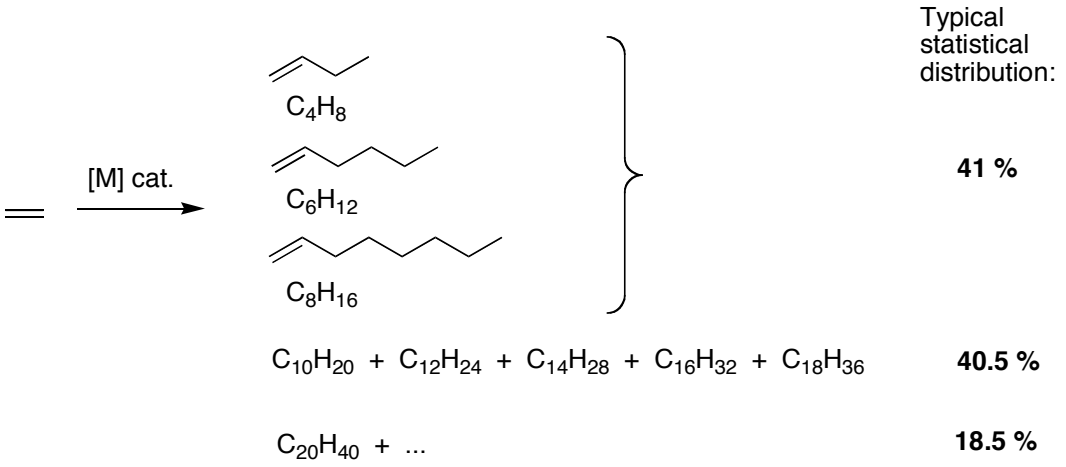
Introduction

Linear α-olefins (LAOs) are valuable commodity chemicals used as precursors in many areas of industry, such as detergents, synthetic lubricants, plasticizer alcohols, as well as co-monomers in the production of linear low-density polyethylene (LLDPE), as is depicted in Scheme 1.[1] In the year 2004, 35 million tons of LDPE/LLDPE and 25 million tons of high-density polyethylene (HDPE) were consumed worldwide, and consumption is predicted to grow by 5% *per annum* at least until 2010,[2] emphasizing the need for large supplies of olefins. Among the LAOs, 1-hexene and 1-octene are particularly attractive as they allow the formation of co-polymers with good tear resistance and other desirable properties.[3]



Scheme 1. Chart depicting the various uses of LAOs in the chemical and petrochemical industries (from ref. 1).

Most industrial processes however produce these α-olefins in a non-selective manner by the oligomerization of ethylene. Such processes typically generate a mathematical distribution (Schulz-Flory or Poisson) of α-olefins, which very often does not match market demand. Examples of non-selective ethylene oligomerization reactions include the Shell Higher Olefin Process with a nickel-based catalyst, Albermarle and Chevron Processes with aluminum, and the Idemitsu Process, which employs an aluminum / zirconium catalyst.[4] The typical statistical distribution of a mixture of LAOs, shown in Scheme 2, implies that separation by distillation is required when isolating LAOs for specific applications. With the high cost involved with separating mixtures of olefins comes the inevitable limitation in yield of a particular olefin, hallmark of a statistical distribution.



Scheme 2. Typical distribution of LAOs in industrial non-selective oligomerization processes.

Interest in the development of selective ethylene oligomerization processes has increased tremendously over the last decade. It is noteworthy to point out that while it is desirable to increase selectivity towards an olefin with a specific carbon number, it is even more crucial to maximize the purity of the α-olefin within its fraction. Indeed,

separation of terminal olefins from their internal isomers is more challenging and expensive than the separation of α-olefin homologs. After the key discovery 40 years ago by Manyik et *al*. of Union Carbide Corporation that, during the polymerization of ethylene using a catalyst composed of Cr(III) 2-ethylhexanoate activated by partially hydrolyzed tri-isobutylaluminum (PIBAO), 1-hexene could be formed through the trimerization of ethylene leading to copolymers,[5] several selective ethylene trimerization systems have been reported.[6-28] While some are based on titanium[17-19] and tantalum,[22] the most abundant and successful systems are based on chromium. The ligands supporting chromium have been quite diverse, ranging from aromatic fragments, such as pyrrolyl, maleimidyl and cyclopentadienyl ligands, to multidentate heteroatomic ligands. In fact, a system comprised of a mixture of chromium salts, aluminum alkyls and pyrrole bases has been used commercially by the Chevron-Phillips Chemical Company to produce 1-hexene *via* ethylene trimerization. This plant was brought on line in 2003 as part of the Q-Chem I project in Qatar.

Among the heteroatomic multidentate ligands reported are found triazacycloalkane ligands,[29,30] tris(pyrazolyl)methane ligands,[31] and a number based on phosphorous, nitrogen, oxygen and sulfur donors (examples are shown in Figure 1). The catalysts are most commonly formed *in situ* by pre-mixing the chromium precursors with the ligand and reacting the mixture with a large excess of aluminum-based activators. In some cases however, an isolated ligated chromium complex is reacted with the aluminum activator,[9,10,25,26] while in other rare cases, well-defined catalyst precursors can be activated by stoichiometric reagents, such as borate salts.[9,10,25]

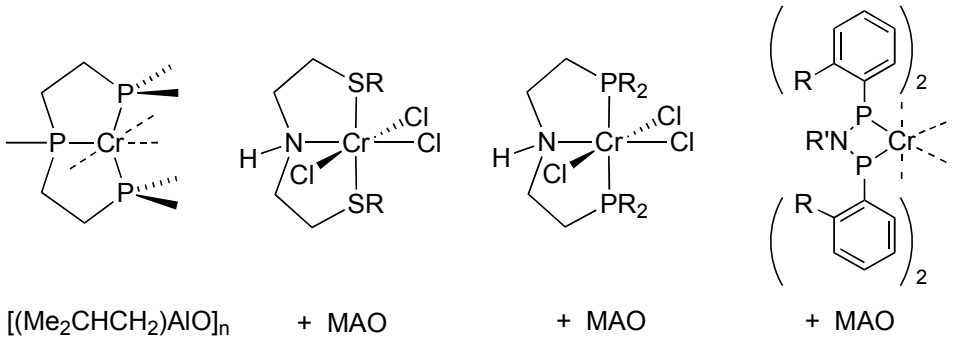
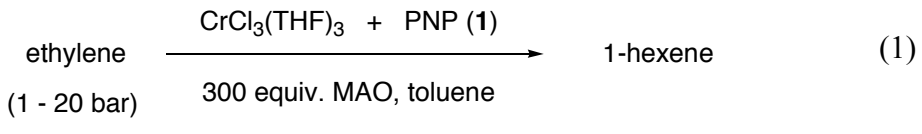
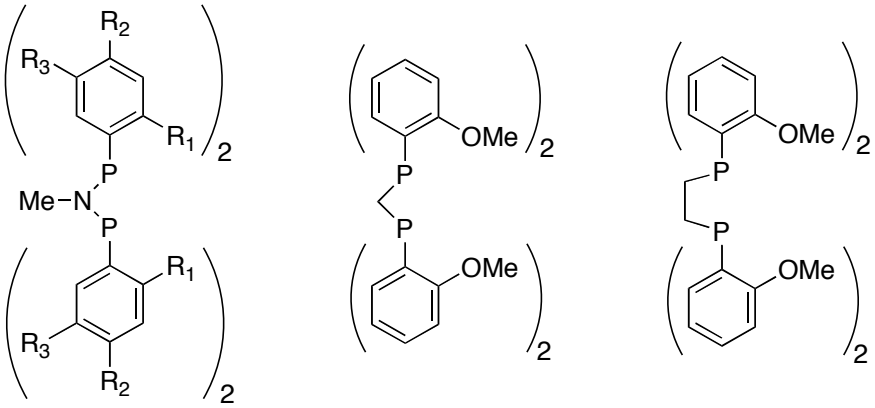


Figure 1. Examples of ethylene trimerization systems based on heteratomic multidentate ligands.

A few years ago, Wass and co-workers at BP Chemicals reported a system comprised of a chromium(III) chloride complex, a diphosphazane ligand and a large excess of methylaluminoxane (MAO) in toluene, which could trimerize ethylene to 1-hexene with unprecedented activity and, more remarkably, with 1-hexene purity within the C_6 fraction of over 99.9% (eq. 1).[21] During initial ligand screening, it was claimed that two key features were required on the diphosphazane ligand, called PNP, in order to obtain an active species for this reaction (Figure 2). The first feature involves the presence of a nitrogen atom in the ligand backbone. It was claimed that systems containing ligands **6** and **7** did not generate active species. Furthermore, it was reported that ether functionalities were required at the *ortho* positions on the aryl groups on phosphorous. Indeed, it was shown that when methoxy groups lacked at the *ortho* position but were instead placed at the *meta* or *para* positions no trimerization could be observed. These findings were later shown not to be accurate as Overett et *al*. reported that ligands without *o*-ether substitution could generate systems capable of performing the trimerization reaction at high pressures of ethylene (30 – 45 bar).[11,32] Furthermore, a chromium(III) complex bearing ligand **6** was shown to trimerize ethylene upon activation, albeit with low activity (Appendix 1).





* **1**: R^1 = OMe, R^2 = R^3 = H
2: R^1 = Et, R^2 = R^3 = H
3: R^1 = R^3 = H, R^2 = OMe
* **4**: R^1 = R^3 = OMe, R^2 = H
* **5**: R^1 = OMe, R^2 = H, R^3 = F

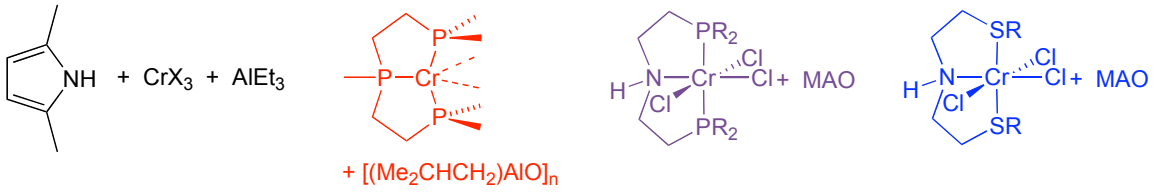
* = active for trimerization

Figure 2. Ligands tested for the chromium-supported trimerization of ethylene.

When this system is compared to other high-performing ethylene trimerization catalysts based on chromium, such as the Phillips catalyst or Albemarle's Triphos system or even Sasol's mixed-donor ligand systems, it is notable that activity is significantly improved. Moreover, lower pressures of ethylene (20 bar) are needed to achieve these results; this becomes significant because it is believed that the trimerization reaction is second-order in ethylene. As mentioned earlier, in addition to high activity, this catalyst system provides extremely high purity of 1-hexene within the C_6 fraction. This remarkable selectivity renders this the best performing ethylene trimerization system to date.

Table 1. Comparison of ethylene trimerization catalyst systems based on chromium.

	Cr/pyrrole (Phillips)	Cr/Triphos (Albemarle)	Cr/P_2NH (Sasol/IC)	Cr/S_2NH (Sasol/IC)	Cr/PNP (bp)
Productivity (g/gCr.h)	100,000 (at 54 bar)	17,000 (at 50 bar)	37,400 (at 40 bar)	160,840 (at 30 bar)	1,033,000 (at 20 bar)
Selectivity to C_6 (%)	94.5 @ 68% conversion		94	98.4	90.0
Purity of 1-hexene (%)	99.6	99.0	99.1	99.7	> 99.9



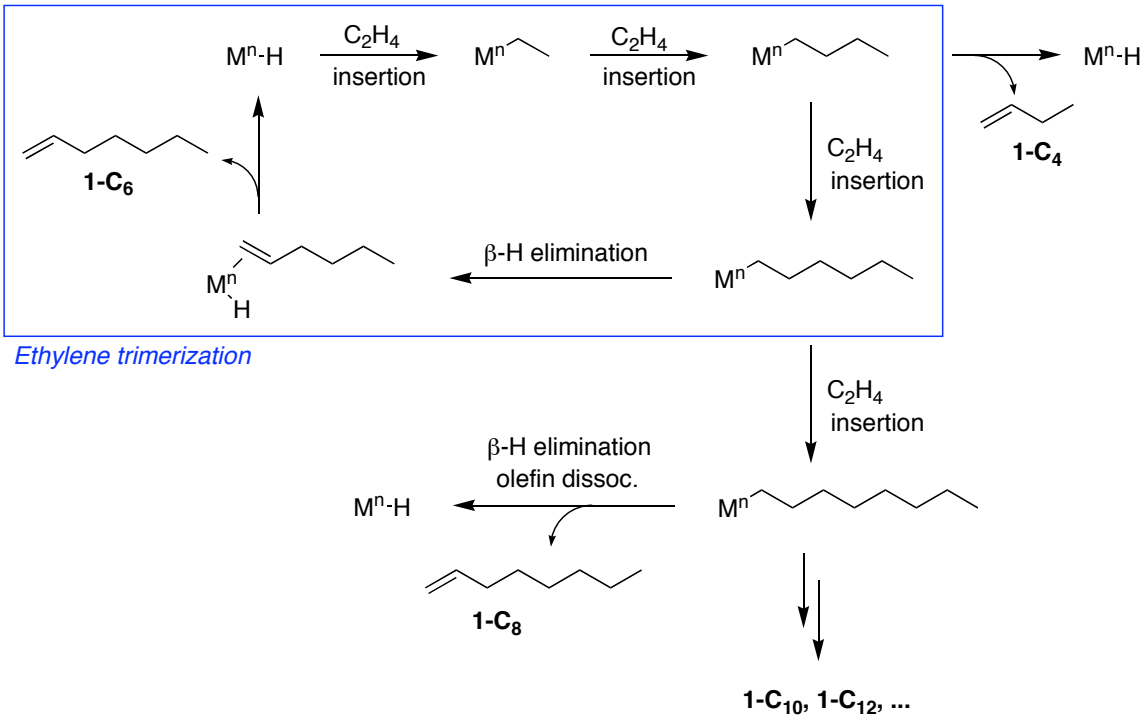
The generally accepted mechanism in a typical non-selective ethylene oligomerization process is a Cossee-Arlman-type mechanism featuring successive olefin insertion steps followed by β-H elimination to generate the observed distribution of α-olefins (Scheme 3). This mechanism could not reasonably explain the selectivity towards C_6 products in the selective ethylene trimerization reactions mentioned above. Instead, a mechanism involving metallacyclic intermediates is believed to be in place during selective oligomerizations (Scheme 4). Briggs first proposed this mechanism during a study of a three-component chromium catalyst for selective ethylene trimerization.[33] In contrast to the Cossee-Arlman-type mechanism, in which the metal maintains its oxidation state throughout the reaction, the metallacycle mechanism features an n/n+2 redox couple. Two molecules of ethylene coordinate to chromium, which then undergoes oxidative coupling, generating a chromacyclopentane. It is believed that the transition state for β-H elimination from the chromacyclopentane leading to 1-butene is geometrically too strained to allow facile β-H elimination, which is depicted by the

minimal yield of 1-butene observed. A third molecule of ethylene coordinates and subsequently inserts into the Cr-C bond to generate a chromacycloheptane. From the chromacycloheptane, release of 1-hexene is fast preventing further ring growth and thus formation of higher α-olefins. Jolly and coworkers demonstrated the thermal stability of the chromacyclopentane relative to the seven-membered ring, further supporting the results obtained during catalytic runs.[34] The major byproducts of the reaction are C_{10} olefins that reflect cotrimerization, where 1-hexene is inserted into the ring. Strong evidence supporting a mechanism involving chromacyclic intermediates has been revealed by Bercaw and coworkers in a deuterium labeling study.[9] Using a 1:1 mixture of C_2H_4 and C_2D_4, they were able to determine the isotopic distribution of the 1-hexene isotopologs during a catalytic run by GC-MS. The isotopic distribution was consistent with that expected of a mechanism involving cyclic intermediates. Furthermore, this result also effectively ruled out the possibility of a Cossee-Arlman-type mechanism.

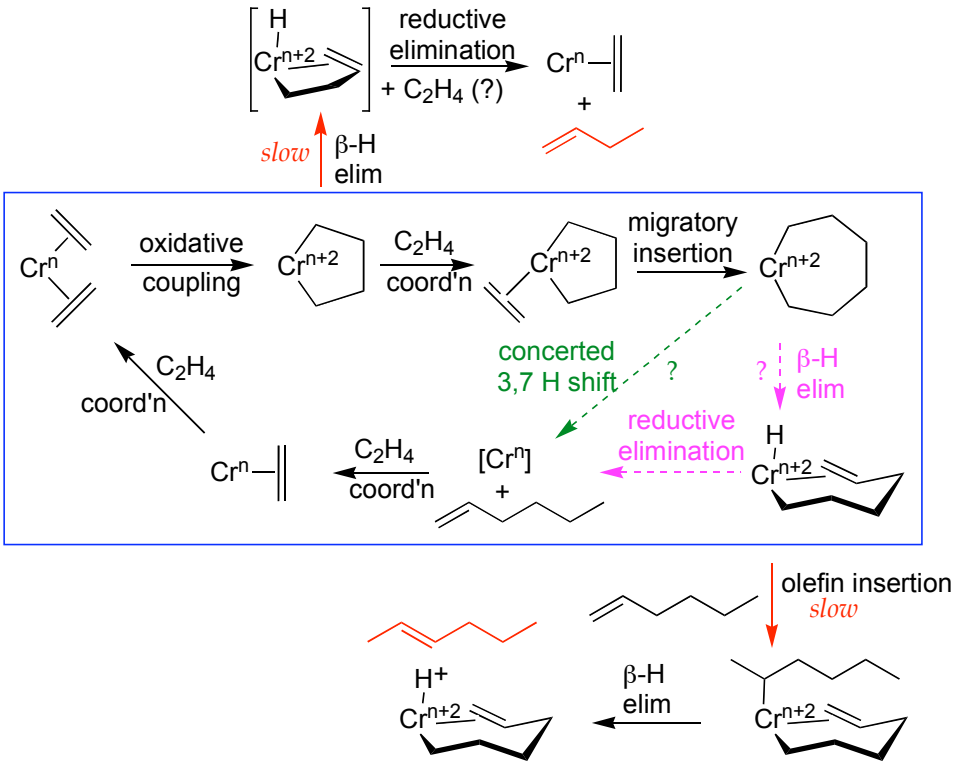
Two pathways are currently proposed for the formation of 1-hexene during the catalytic cycle. The first involves β-H elimination from the chromacycloheptane, generating a chromium hexenyl hydride intermediate, which then undergoes reductive elimination to release the olefin (Scheme 4, pink arrows). However, theoretical studies performed on titanium,[35-37] tantalum,[38] and chromium-based[39] systems have suggested that the release of 1-hexene happens through one concerted step involving a 3,7- hydride shift (Scheme 4, green arrow; eq. 2). No experimental studies could elucidate this problem.

The nature of certain intermediates involved in the process and more importantly the catalytically active species remain undetermined. Furthermore, the nature of the metal

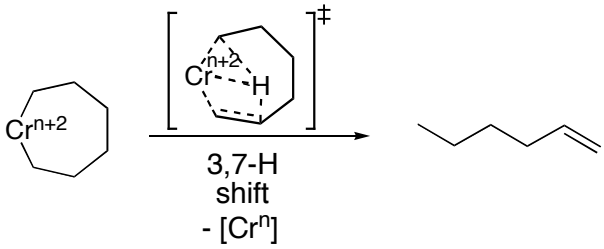
oxidation state is also highly debated. A metallacyclic mechanism would require a two-electron redox cycle; however, while a chromium(I)-chromium(III) redox cycle is currently favored, certain studies seem to suggest that a chromium(II)-chromium(IV) cycle might also be operational. Indeed, it was shown that alkyl aluminum species are capable of inducing oxidation state changes with the chromium complexes.[40-43] Furthermore, systems involving chromium(II) starting materials have also exhibited activity.[41,42]



Scheme 3. Cossee-Arlman-type mechanism during a generic ethylene oligomerization.



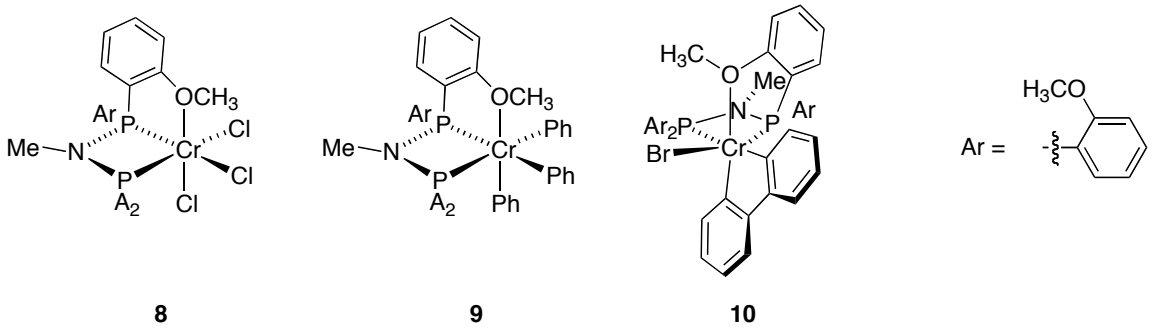
Scheme 4. Metallacycle mechanism in chromium-catalyzed selective ethylene trimerization.



(2)

Extensive investigation of the original BP ethylene trimerization system performed by Bercaw and coworkers led to the synthesis and study of various chromium complexes, which modeled the parent catalyst. Valuable insight was obtained by isolating various PNP-ligated chromium(III) complexes, which upon activation catalyze the trimerization of ethylene to 1-hexene (Figure 3).[9] Spectroscopic evidence as well as crystallographic analysis reveal that the *ortho*-methoxy groups on the aryl functionalities are involved in coordination to the metal center. Indeed, all three complexes **8-10** are hexacoordinate and display a (P,P,O)-κ^3 coordination of the diphosphine to the chromium

center as established by single crystal X-ray diffraction as well as ^{2}H NMR. Deuterating the methoxy positions allowed the use of ^{2}H NMR as a convenient method to study the solution behavior of the paramagnetic complexes.[10,25] The experiments established a dynamic exchange process of the ether groups, which can be frozen out at low temperature. At these lower temperatures, the ^{2}H NMR spectra display two peaks in a 1 to 3 ratio of integrals corresponding to one coordinated methoxy group, which is significantly paramagnetically downfield-shifted, and three uncoordinated groups. Upon warming above two coalescence temperatures, one peak remains, providing evidence supporting a dynamic process involving ether exchange.



8 **9** **10**

Figure 3. Chromium complexes as models of the original BP ethylene trimerization catalyst.

These findings suggest that the methoxy groups might act as hemilabile donors capable of stabilizing key intermediates or transition states during catalysis. Complexes **8**-**10** constitute the first well-characterized precursors to this type of ethylene trimerization catalysts. Complex **8** can be activated with excess MAO, while **9** and **10** are activated with stoichiometric amounts of $H(Et_2O)_2B[C_6H_3(CF_3)_2]_4$ and $NaB[C_6H_3(CF_3)_2]_4$, respectively, all generating an active species capable of giving turnovers and selectivity comparable to the original BP system.

The role of the donor functionality was further investigated by synthesizing other complex analogs with ligands containing various heteroatoms. A few examples are shown in Figure 4.[10,44] Substituting the methoxy groups with dimethylamino or thioether groups leads to the formation of chromium complexes with significantly altered coordination modes. Complex **11** features a (N,P,N)-κ^3 coordination mode arranged in a *meridional* fashion, while **12** similarly favors a (S,P,S)-κ^3 coordination however in a *facial* manner leaving the second phosphine group uncoordinated. These arrangements strongly contrast that of complexes **8**-**10** and demonstrate the preference of the chromium center in coordinating nitrogen and sulfur heteroatoms rather than phosphorous and oxygen. The drastic changes also affect catalysis, as the precursors do not generate active species upon activation. This further emphasizes the need for hemilabile donors. Mixed-ligand species **13** and **14** are further examples depicting the preferred affinity towards nitrogen and sulfur functionalities.

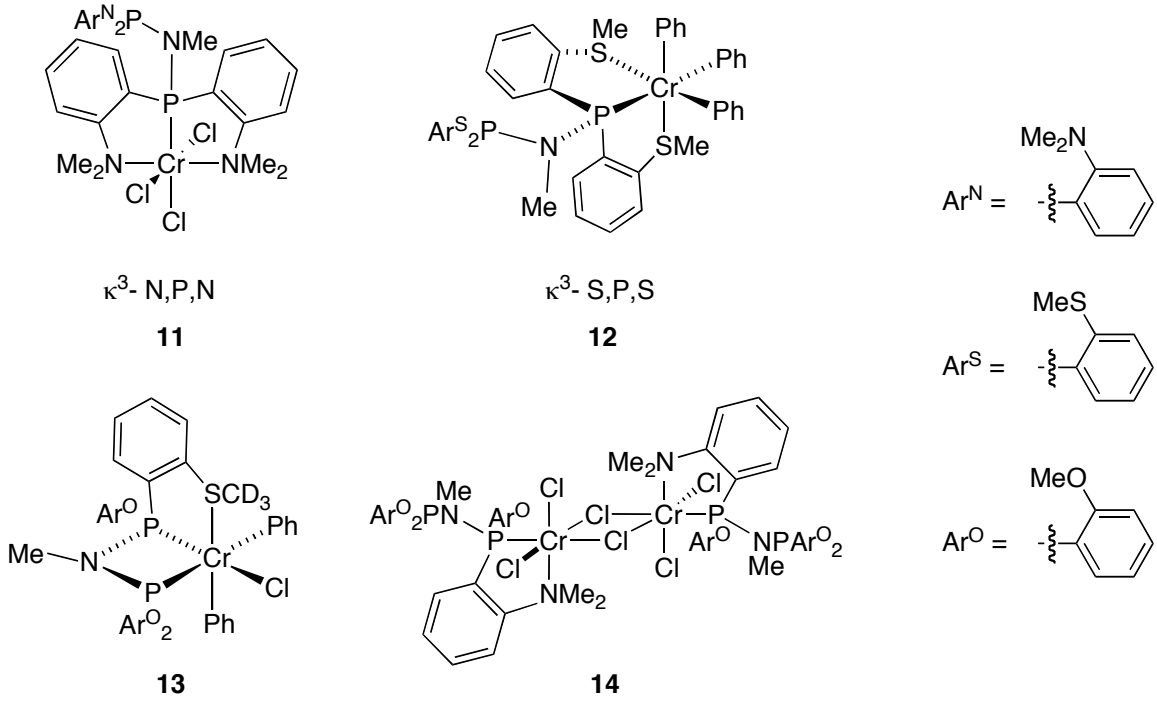


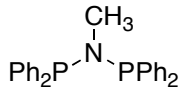
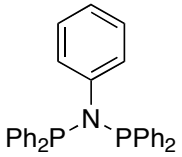
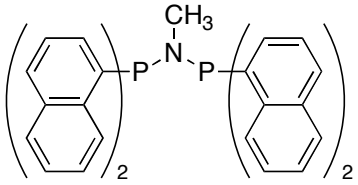
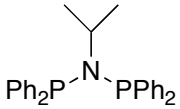
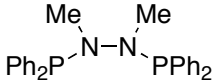
Figure 4. Models containing various heteroatomic donor functionalities.

The Selective Tetramerization of Ethylene to 1-Octene

It had been postulated that selective 1-octene formation *via* the same mechanism as in ethylene trimerization was not feasible due to the instability of the chromacycloheptane, which would generate 1-hexene rather than coordinate and insert a fourth molecule of ethylene. However, it has been shown recently by researchers at Sasol as well as Bercaw and coworkers in separate efforts that 1-octene can be selectively generated using chromium-based systems similar to that of the BP trimerization catalyst.[45,26] Bollmann and coworkers at Sasol first reported a catalyst consisting of a mixture of a chromium(III) precursor and a PNP ligand in toluene with an excess of an aluminoxane activator.[45] It is worth noting that the ligands tested all lack a donor functionality, such as an ether group on the aryl groups on the phosphines. They observed unprecedented selectivity towards C_8 products, which almost exclusively contain 1-

octene. In fact, the best result obtained was with a PNP ligand containing phenyl substituents on the phosphines and an *iso*-propyl group on the nitrogen backbone (Table 2).

Table 2. Examples of Sasol's ethylene tetramerization systems (conditions: 0.033 mmol $Cr(THF)_3Cl_3$ or $Cr(acac)_3$, 2 equiv. ligand, 300 equiv. MAO, 100 mL toluene, 30 min.).[45]

Ligand	P (bar), T (°C)	Productivity (g/gCr h)	C8 (%)	1-C8 Purity (%)
	30, 65	26,500	59.0	94.1
	30, 65	8,570	61.6	97.8
	30, 65	52,600	54.2	93.4
	45, 45	272,400	68.3	98.8
	45, 45	26,200	58.8	98.4

Following the initial reports, numerous studies investigated the various aspects of the reaction, as well as the development of other catalyst systems capable of tetramerizing ethylene selectively to 1-octene. Using a similar approach employed previously in the Bercaw laboratories, Overett *et al.* performed labeling studies on their tetramerization systems, which demonstrated that the reaction mechanism mirrors that of

the more established ethylene trimerization process.[46] Indeed GC-MS data showed that the reaction occurred *via* chromacyclic intermediates and ruled out the possibility of a Cossee-Arlman-type mechanism. This finding is significant as it refutes the initial belief that higher olefins could not be produced *via* the metallacyclic mechanism due to the inherent instability of higher ring sizes. By varying reaction conditions and more specifically ethylene concentrations (pressures), it is possible to access larger rings by favoring insertion over β-H elimination and selectively generate higher olefins *via* this mechanism. In this manner, 1-octene is produced after elimination occurs on the chromacyclononane intermediate. On the other hand, if rates of β-H elimination are similar for each metallacycle, this would result in a Schulz-Flory distribution of olefins. A recent example of such instance has been reported by Gibson and coworkers, whereby a chromium catalyst is capable of oligomerizing ethylene in a non-selective fashion *via* the metallacyclic mechanism.[47,48]

The work presented herein represents a significant portion of efforts towards the development of novel catalysts for the selective oligomerization of ethylene to 1-hexene and 1-octene, as well as the investigation of important facets of the process, including the dependence on ethylene pressure and reaction temperature, catalyst decomposition and solvent effects. Specifically, this work has provided valuable insights into donor ability and solvent effects that significantly improve catalyst stability and activity, which are critical in the development of a commercial ethylene tetramerization catalyst system.

Results and Discussion

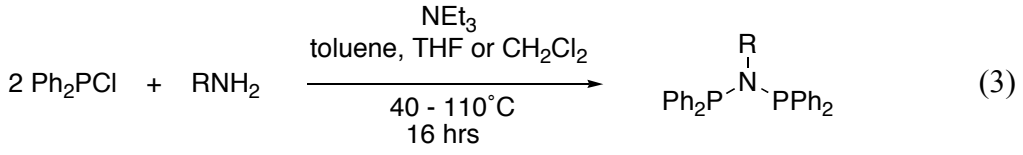
A Chromium Diphosphine System for Selective and Catalytic Ethylene Oligomerization

As mentioned earlier, it was claimed that successful catalysis required that the PNP ligand of the original BP Chemicals ethylene trimerization system possess two critical features, i.e. a nitrogen-containing backbone and ether functionalities in the *ortho* positions of the aryl groups on phosphorous (Figure 2). Investigation of these claims first led to the preparation of the modified diphosphine ligand containing a methylene moiety in the backbone (see Appendix 1). The role of the ether donor functionality was probed by switching its position on the ligand framework. Previous studies in the Bercaw laboratories have shown that the original trimerization catalyst based on the PNP ligands as well as model systems developed thereafter exhibited low stability over time. Indeed, catalyst lifetime could generally not exceed 20-30 minutes. Additionally, catalytic runs were highly irreproducible. It was therefore also a means of improving these shortcomings that a new ligand framework was designed.

Synthesis of PNP Ligands with Ether Groups Tethered to Nitrogen

The new ligands feature an ether functionality tethered to the backbone nitrogen atom, leaving the aryl groups on phosphorous as simple phenyls. Synthesizing the PNP ligands was quite straightforward and involved the condensation of two equivalents of chlorodiphenylphosphine with the appropriate amine in the presence of excess

triethylamine to neutralize the liberated acid (Eq. 3). The reaction solvent can vary somewhat, from toluene to tetrahydrofuran, however most reactions were performed in CH_2Cl_2. The reactions were typically run under refluxing conditions. A series of ligands was prepared whereby the length of the tether as well as its rigidity were tuned (Figure 5; **15-18**). In order to evaluate the importance of the donor functionality, two ligands lacking an ether functionality were prepared (**19-20**).



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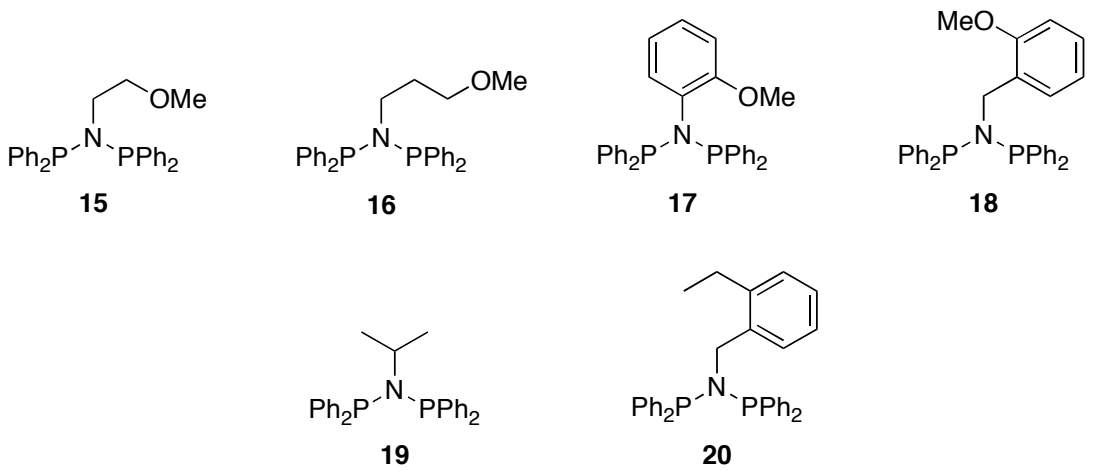


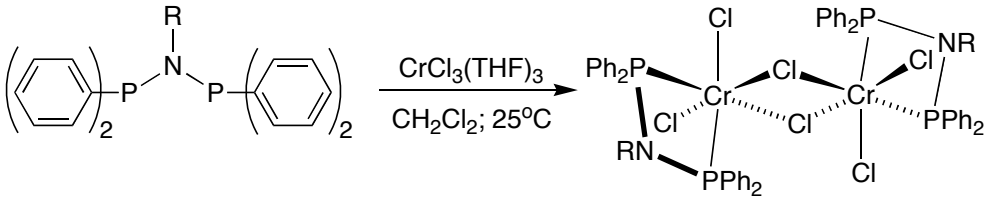
Figure 5. PNP ligands synthesized.

Preparation and Characterization of PNP Chromium Complexes

The synthesis of the catalyst precursors was also facile. Addition of chromium trichloride *tris*(tetrahydrofuran) to a methylene chloride solution of the ligand afforded, after several triturations, the desired complexes

$[CrCl_2[P,P\text{-}\kappa^2\text{-}(C_6H_5)_2PN(R)P(C_6H_5)_2](\mu_2\text{-}Cl)]_2$ (**21**-**26**) as bright bluish-purple chloro-bridged dimers in good yield (Scheme 5). Repeated triturations in methylene chloride are necessary to ensure that no tetrahydrofuran remains coordinated to the chromium center. Higher affinity towards THF coordination also implies that stirring the PNP chromium complexes in THF results in the dissociation of the ligand and formation of $(THF)_3CrCl_3$. The catalyst precursors are insoluble in common organic solvents, such as toluene, while only slightly soluble in chlorinated solvents.

Because the complexes are paramagnetic, NMR could not be used for characterization. However, X-ray crystallography has been useful in determining the solid-state structure of these complexes. Crystallographic analysis for complex **21** revealed an edge-sharing bioctahedral arrangement in the solid state, similar to a complex reported by Bollman and co-workers (Figure 6).[45] Similarly to $[CrCl_2[P,P\text{-}\kappa^2\text{-}(C_6H_5)_2PN(C_6H_5)P(C_6H_5)_2](\mu_2\text{-}Cl)]_2$, the Cr-P bond *trans* to the terminal chloride (2.4862(6) Å) is slightly longer than the Cr-P bond *trans* to the bridging chloride (2.4251(6) Å). The dimeric structure was initially surprising because it was expected that the tethered ether group might act as a hemilabile donor such that the ligand would exhibit a κ^3 coordination mode in the solid state, similar to species **8** discussed earlier (Figure 3). In an effort to isolate a monomeric complex with a coordinated ether group, an X-ray structure determination of **24** was obtained. It was thought that the longer and more rigid tether would help favor coordination of the ether group, however the solved structure revealed a similar chloro-bridged dimeric configuration (Figure 7).



15: R = $(CH_2)_2OCH_3$
16: R = $(CH_2)_3OCH_3$
17: R = $(o\text{-}OCH_3)C_6H_4$
18: R = $CH_2(o\text{-}OCH_3)C_6H_4$
19: R = $CH(CH_3)_2$
20: R = $CH_2(o\text{-}CH_2CH_3)C_6H_4$

21: R = $(CH_2)_2OCH_3$
22: R = $(CH_2)_3OCH_3$
23: R = $(o\text{-}OCH_3)C_6H_4$
24: R = $CH_2(o\text{-}OCH_3)C_6H_4$
25: R = $CH(CH_3)_2$
26: R = $CH_2(o\text{-}CH_2CH_3)C_6H_4$

Scheme 5. Synthesis of catalyst precursors **21**-**26**.

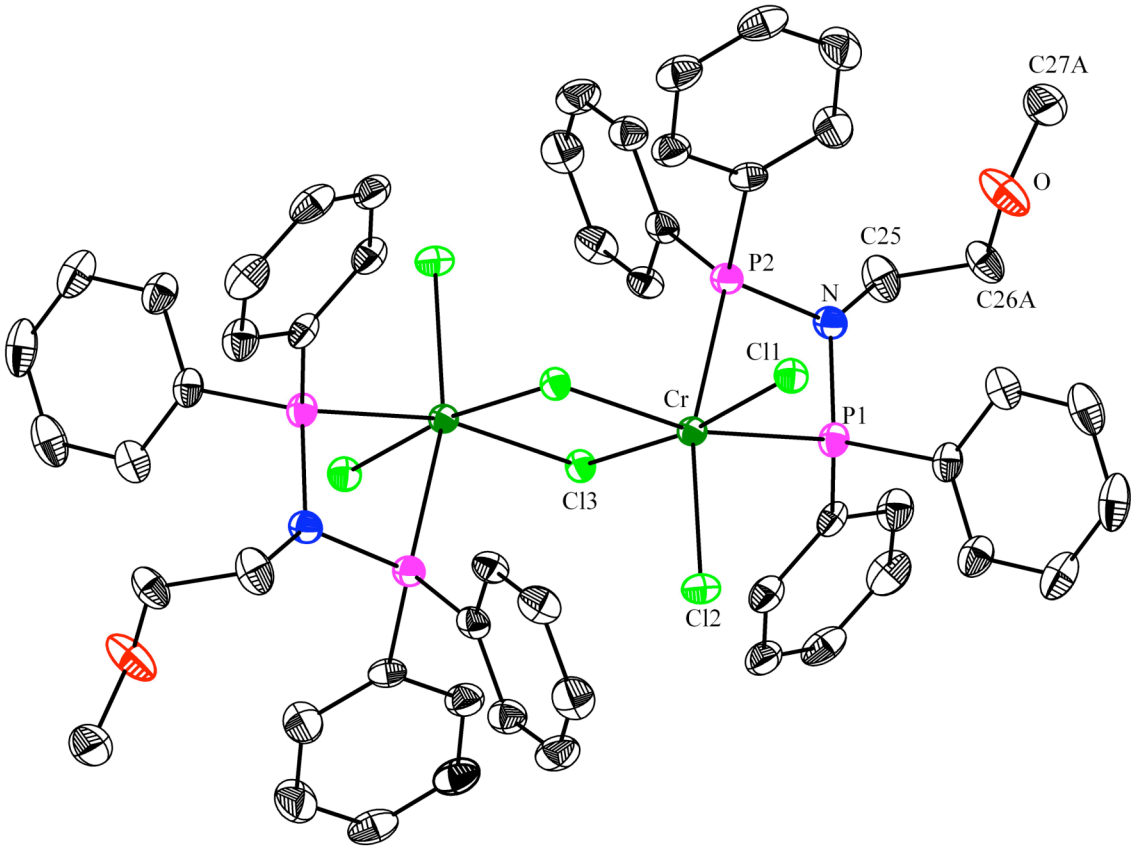


Figure 6. Structural drawing of **21** with displacement ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (°): Cr-P1, 2.4251(6); Cr-P2, 2.4862(6); Cr-Cl1, 2.2701(5); Cr-Cl2, 2.2900(5); Cr-Cl3, 2.3679(5); Cr-Cl3', 2.3939(5); P1-Cr-P2, 66.837(18); P1-N-P2, 105.01(8); Cl3-Cr-Cl3', 85.488(17).

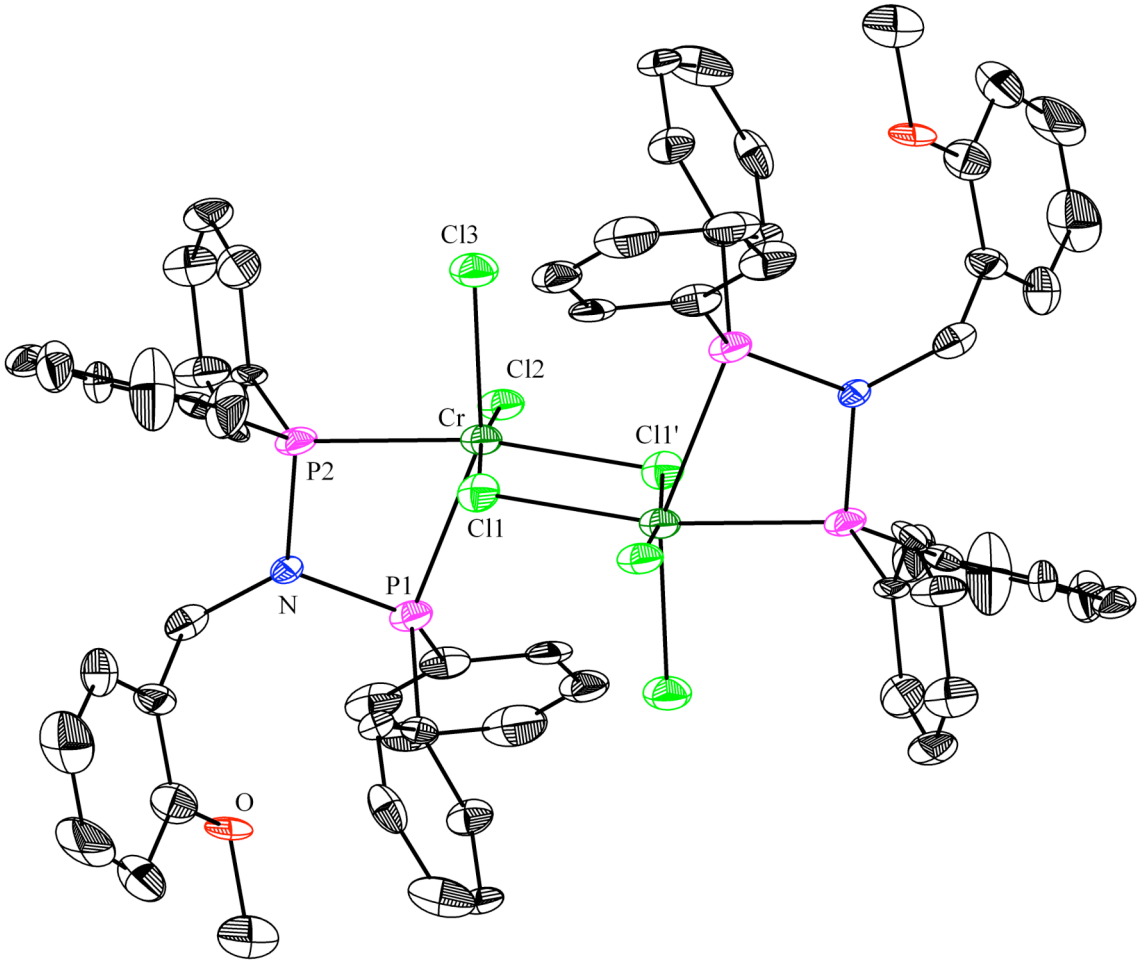
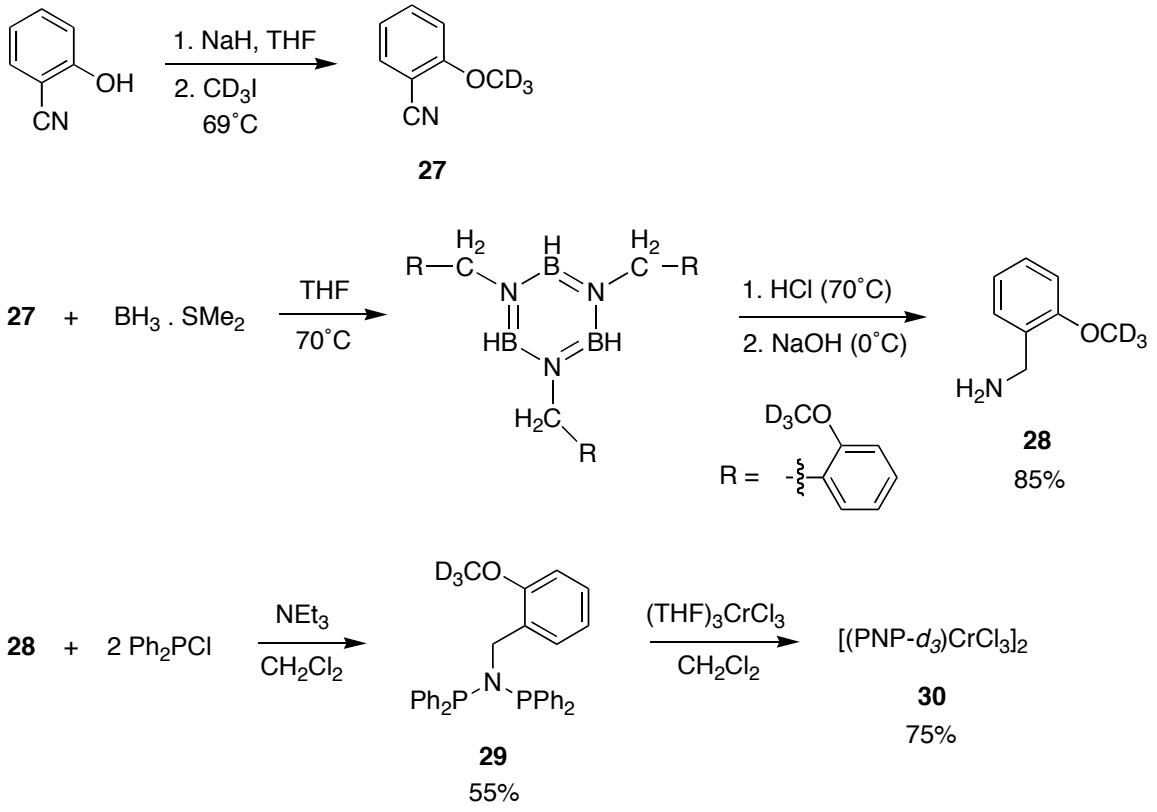


Figure 7. Structural drawing of **24** with displacement ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (°): Cr-P1, 2.548(4); Cr-P2, 2.427(4); Cr-Cl1, 2.379(4); Cr-Cl1', 2.398(4); P1-Cr-P2, 66.64(12); P1-N-P2, 106.2(5); Cl1-Cr-Cl1', 83.84(12).

While monomeric species in the solid state could not be obtained with the above systems, it was expected that a dynamic exchange between monomeric and dimeric configurations could occur in solution. ^{2}H NMR can be a very useful tool in the characterization of paramagnetic complexes. It has been shown previously[25] and in this work (Appendix 1) that at low temperature, where a dynamic exchange between coordinated and uncoordinated ether groups is frozen out, uncoordinated methoxy groups appear in the diamagnetic region upfield of the spectrum, while the coordinated methoxy group appears as a broad peak far downfield. Deuterium labeling at the methoxy position

provided an easy access to species suitable for ^{2}H NMR spectroscopy. The synthesis of deuterium-labeled chromium complex **30** is summarized in Scheme 6. 2-Cyanophenoxide was first methylated with CD_3I to generate 2-cyanoanisole-d_3 (**27**), which was reduced using borane-dimethyl sulfide following a procedure by Brown and coworkers.[49] Hydrolysis of the resulting borazine derivative generated the desired primary amine **28** in good yield. Finally, the deuterium-labeled PNP ligand was obtained upon treatment with Ph_2PCl, followed by metalation onto $(THF)_3CrCl_3$ to generate the desired complex **30**.



Scheme 6. Synthesis of deuterium-labeled PNP ligand **29** and the corresponding chromium complex **30**.

The solution-phase ^{2}H NMR spectrum of complex **30** failed to provide conclusive evidence for either the presence or absence of a monomeric species in a dynamic

exchange with the dimeric complex (Figure 8). Because **30** contains only one methoxy group potentially available for coordination to the chromium center, as opposed to four in the case of **8**, it is expected that the paramagnetic region of the spectrum will be particularly broad due to the low concentration of potentially coordinated methoxy groups. Despite no spectroscopic or structural evidence for the presence of a monomeric species, it is likely that during catalytic conditions, after activation with a large excess of methylaluminoxane (MAO), the active species is in fact monomeric. Moreover, evidence for the participation of the tethered ether donor in stabilizing the chromium center during catalysis has been provided by the comparison of catalytic runs using catalysts derived from **21**-**24** and **25**-**26**, as well as **32** (See following discussion).

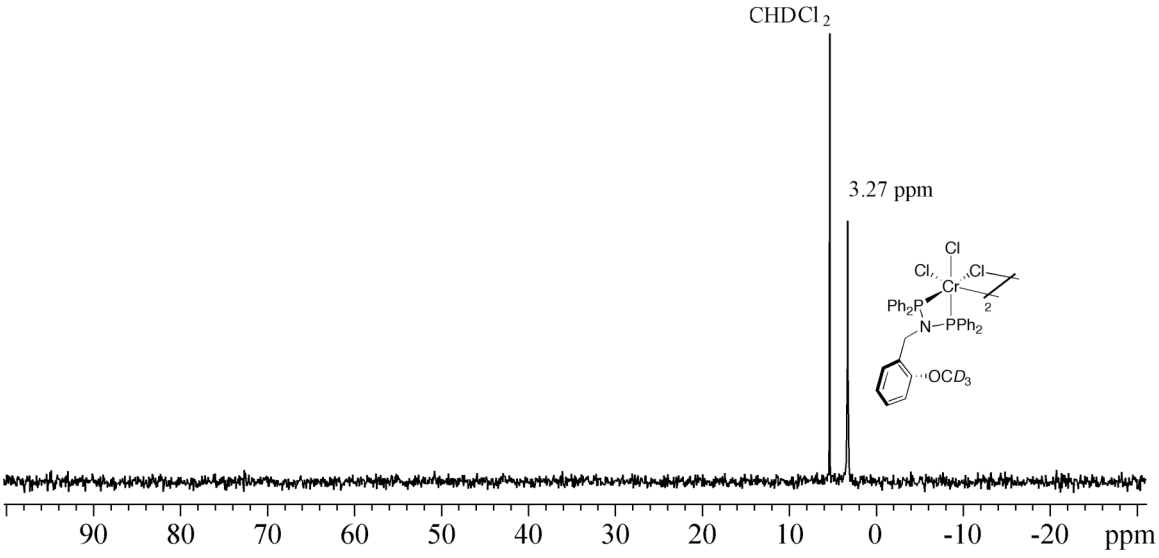


Figure 8. Solution-state ^{2}H NMR spectrum of **30** in CD_2Cl_2; uncoordinated OCD_3 peak appears at 3.27 ppm, while there is no evidence for a peak far downfield corresponding to the a coordinated methoxy group.

Catalytic Runs at 1 atm of Ethylene Using Precatalysts 21-24

Complexes **21-24** were tested as precatalysts in the selective oligomerization of ethylene. Low-pressure reactions (1 atm ethylene) were conducted on a high-vacuum line, where ethylene consumption could be monitored over time using a mercury manometer. In a typical catalytic run, the reaction flask, initially assembled in the glovebox, whereby the precatalyst is suspended in the solvent, is degassed on the vacuum line before an atmosphere of ethylene is introduced. Once the solution is saturated with ethylene, methyaluminoxane (MAO) is syringed into the flask. The solution immediately turns green indicating the formation of the active species. Ethylene consumption is extracted from the rate at which the mercury contained in the manometer is displaced over time. After the reaction is close to completion, i.e. > 95% of the catalyst has decomposed, the reaction mixture is quenched with acidic methanol. The organic fraction is collected, filtered through activated alumina to remove traces of water and chromium species, and a sample used to obtain GC and GC-MS data is collected. The solid polyethylene residue from the reactions is washed with acidic methanol, dried under vacuum and weighed.

The first experiment run used precatalyst **21**. Analysis of the product distribution showed that in addition to 1-hexene being formed, 1-octene was produced in significant quantities. A 90-minute reaction produced 361 $g_{product}/g_{Cr}$, of which 60 %wt was 1-hexene and 30 %wt 1-octene, representing 106 and 52 turnovers, respectively. Although the catalyst exhibited unprecedented selectivity in 1-octene, both activity and stability were low. The lack of stability of the active species was presumed to be due to the short ether

tether, which is unable to properly act as a stabilizing donor during catalysis. In an experiment involving the catalyst derived from **22** on the other hand, ethylene consumption remained constant for the entirety of the reaction (tested up to 4.5 hrs reaction time, Figure 9). Productivity remained low however, even though catalyst stability was remarkably high.

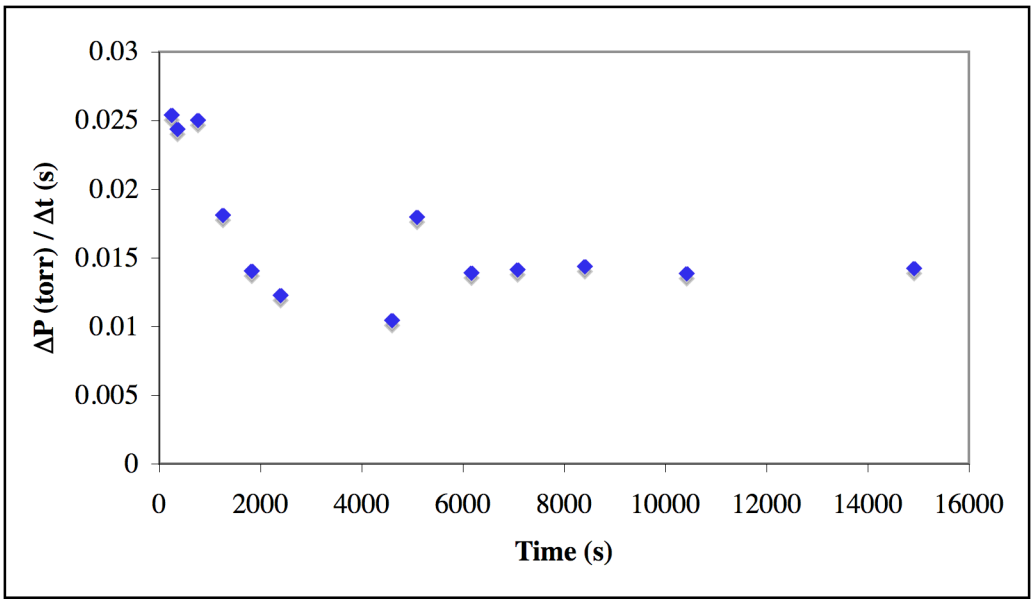


Figure 9. Ethylene consumption over time at 1 atm ethylene using precatalyst **22**.

Activity is significantly improved when the tether on the ligand is more rigid, such as in the reaction using **23**. However, as in the case of **21**, stability was lost and the typical catalyst decay was observed. Plotting ethylene consumption over time showed that initial activity was more than doubled, when comparing a catalyst derived from **23** with that from **21** (Figure 10). Complex **24** possesses both features that seem to be important in providing catalyst stability and improving its activity. Indeed, the methoxy benzylene linker is as long as that of **22** but contains the phenyl moiety, which provides the necessary rigidity for activity. Reactions at 1 atm ethylene have clearly shown that

excellent activity can be achieved with this system, which remained stable for several hours (Figure 11).

The new ligands developed herein, and in particular **18**, therefore allow the preparation of catalytic systems that are highly active for the selective oligomerization of ethylene to 1-hexene and 1-octene. A unique feature displayed by two of the systems is the remarkable stability of the catalysts, which had been up to then elusive. As mentioned previously, it was shown that the original PNP chromium catalyst for ethylene trimerization as well as the model systems developed thereafter suffered from very low stability.[10,44]

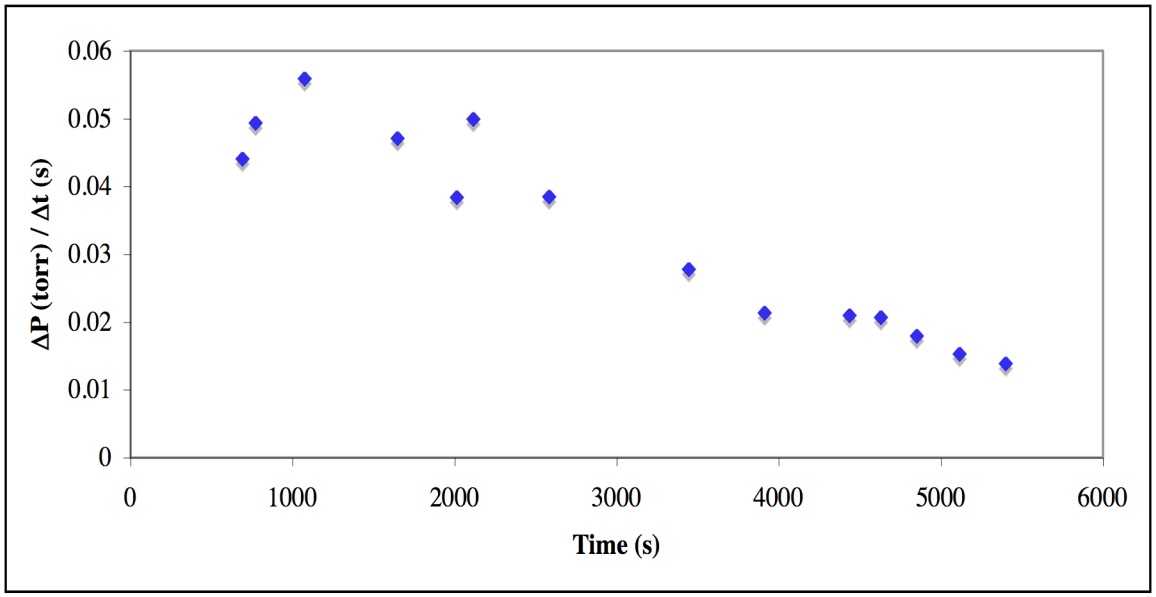


Figure 10. Ethylene consumption over time at 1 atm ethylene using precatalyst **23**.

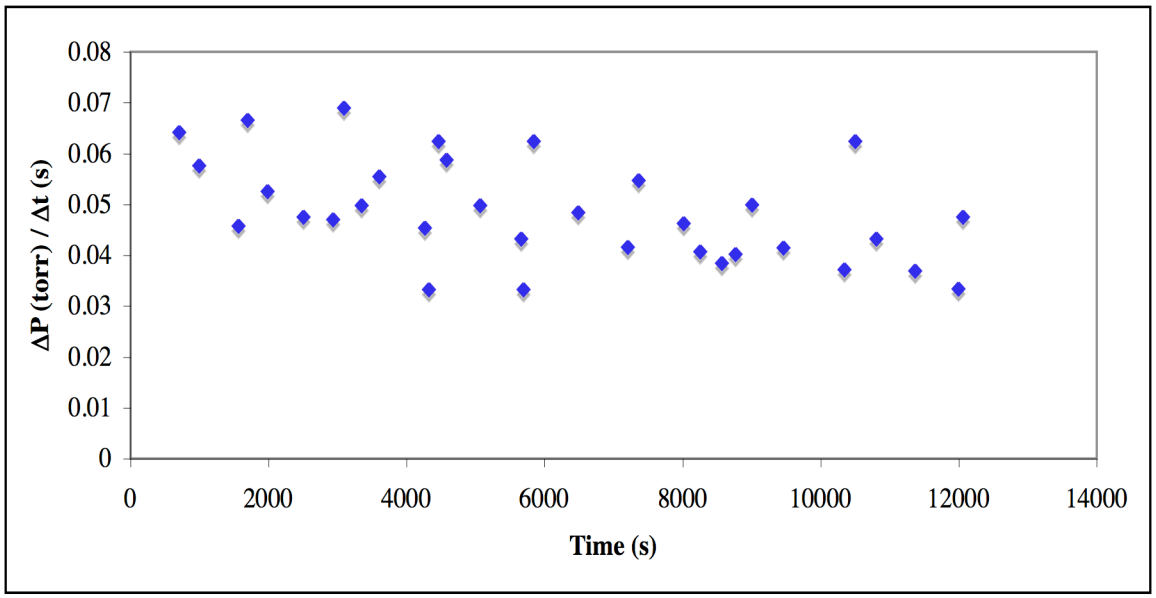


Figure 11. Ethylene consumption over time at 1 atm ethylene using precatalyst **24**.

A summary of reactions performed at 1 atm of ethylene using precatalysts **21**-**24** is shown in Table 3. Entries 1-4 show results for each catalyst under the same reaction conditions. While productivity is low for systems containing a linear tether (≤ 400 $g_{product}/g_{Cr}$ for both **21** and **22**), adding rigidity to the linker significantly improves activity (> 900 $g_{product}/g_{Cr}$ for **23** and **24**). In all cases, polymer formation is kept to a minimum. This is critical because an accumulation of polyethylene, an undesired byproduct, can coat the sides of the reactor. Selectivity in C_6 and C_8 products is remarkably high at > 85 %wt in all cases. Another important aspect of the reaction lies in the purity of both 1-hexene and 1-octene in the C_6 and C_8 fractions, respectively. In this respect, 1-octene is generally more pure than 1-hexene, due to the formation of cyclic C_6 products, as will be discussed in a later section of this chapter. Heavier olefins formed during the reaction are the result of cotrimerization processes involving generated 1-hexene and 1-octene with ethylene. At least at low pressure of ethylene, no chromacycloundecane is formed during

the oligomerization reaction, as 1-decene is not present in the product distribution obtained from analysis of the GC trace. As can be seen in longer reactions involving **24**, an increase in higher olefin formation is due to the higher concentration of 1-hexene and 1-octene at higher conversions. Longer reaction times do not significantly affect selectivity however, as polymer formation remains low and purity in 1-hexene is preserved. A slight decrease in the purity of 1-octene is observed over 20 hours (Table 3, entry 6).

Catalytic Runs at Higher Pressures of Ethylene

The highly active and stable catalyst derived from **24** was further studied. Reactions at higher pressures of ethylene (4-12 atm) were carried out in thick-glass vessels attached to a high-pressure manifold. Table 4 summarizes the results of the oligomerization of ethylene in chlorobenzene using **24**. As expected, productivity increased with higher ethylene pressures. When the pressure reached 12 atm, the reaction had to be stopped after 30 minutes because product formation was so rapid that the vessel filled up (Table 4, entry 6). A plot depicting the dependence of catalyst productivity on ethylene pressure emphasizes the significant effect of higher pressures (Figure 12), however no reliable quantitative measure of the reaction order in ethylene can be extracted from the plot because the nature of the active species as well as the fraction of chromium centers active at any given time during catalysis are not known. However, plotting the dependence of the ratio of the concentration of 1-octene to that of 1-hexene with ethylene pressure fits a line quite well, suggesting that if 1-hexene formation is n^{th}-

order in ethylene, 1-octene is then $(n+1)^{th}$-order in ethylene (Figure 13). From Figure 12, and based on kinetic studies performed by Walsh and coworkers,[8] it seems likely that 1-hexene formation is first-order in ethylene, while 1-octene formation is second-order.

Observations on selectivity are impressive. Increasing ethylene pressure over 12 atmospheres did not affect polymer formation, which remained remarkably low. Selectivity in C_6 and C_8 products seemed to decrease, however this effect was due to the significantly larger concentration of the olefin products at high ethylene pressure, which facilitated cotrimerization pathways and broadened product distribution. This was further demonstrated by comparing C_6/C_8 selectivities between entries 5 and 6, whereby at lower reaction time less higher olefins were generated. Finally, purity in both 1-hexene and 1-octene was not affected by increasing ethylene pressure, suggesting that C_6 and C_8 byproducts, i.e. internal olefins and cyclic products, are not exclusively formed at higher 1-hexene and 1-octene conversions.

Table 3. Ethylene oligomerization with complexes **21**-**24** at 1 atm of ethylene.[a]

Entry (Complex)	Time (min)	Productivity ($g_{product}/g_{Cr}$)	PE (wt%)	C-6 (wt%)[b]	C-8 (wt%)	C-10 (wt%)[c]	>C-10 (wt%)[d]	1-C6 in C6 (%)	1-C8 in C8 (%)
1 **(21)**	90	361	6	61	31	1	1	83	>90
2 **(22)**	90	403	0.5	62	34	2	2	84	99
3 **(23)**	90	924	0.3	66	27	4	3	91	97
4 **(24)**	90	1,625	<0.1	62	24	7	7	93	93
5 **(24)**	270	3,106	<0.1	54	23	12	11	93	88
6 **(24)**	1250	6,244	0.2	45	16	16	24	92	73

[a] Conditions: $[CrCl_2[P,P\text{-}\kappa^2\text{-}(C_6H_5)_2PN(R)P(C_6H_5)_2](\mu_2\text{-}Cl)]_2$ (0.02 mmol), C_6H_5Cl (50 mL), MAO (300 eq, 10 wt% in toluene), C_2H_4 (1 atm), 25 ºC . [b] In the C_6 fraction, hexene isomers appear as 0 - 0.3 wt%. [c] 1-C_{10} was not detected by GC. [d] C-12 (among which 5-methyl-1-undecene), C-14, C-16, etc.; structures not determined.

Table 4. Ethylene oligomerization with complex **24**.

Entry	P (atm)	Productivity ($g_{product}/g_{Cr}$)	PE (wt%)	C-6 (wt%)[d]	C-8 (wt%)	C-10 (wt%)	C-12 (wt%)	>C-12 (wt%)	1-C6 in C6 (%)	1-C8 in C8 (%)
1[a]	1	1,625	<0.1	62	24	7	5	1	93	93
2[a]	2.4	3,911	0.6	57	28	6	6	2	92	94
3[a]	4.1	11,684	0.4	44	33	7	11	5	90	92
4[a]	6.1	14,584	0.2	41	38	6	10	5	87	95
5[b]	8.4	42,408	0.2	30	34	8	17	12	83	93
6[c]	12	35,667	0.1	34	42	6	11	6	86	96

[a] Conditions: $[(PNP)CrCl_3]_2$ (0.02 mmol), C_6H_5Cl (50 mL), MAO (300 eq, 10 wt% in toluene), 25 ºC, 90 min . [b] Conditions: $[(PNP)CrCl_3]_2$ (0.008 mmol), C_6H_5Cl (20 mL), MAO (300 eq, 10 wt% in toluene), 90 min. [c] Conditions: same as b), reaction time of 30 min. [d] In the C_6 fraction, hexene isomers appear as 0 - 0.3 wt%.

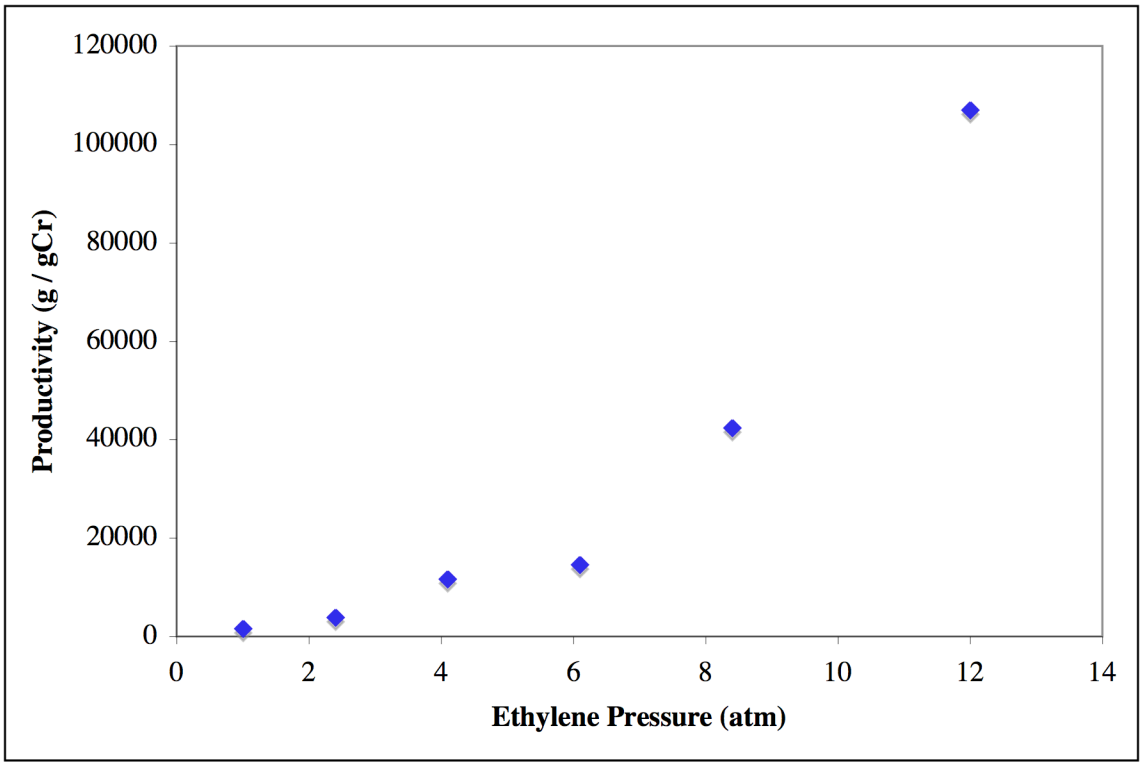


Figure 12. Productivity dependence on ethylene pressure (data point at 12 atm was extrapolated to a reaction time of 90 min, assuming the catalyst remains stable).

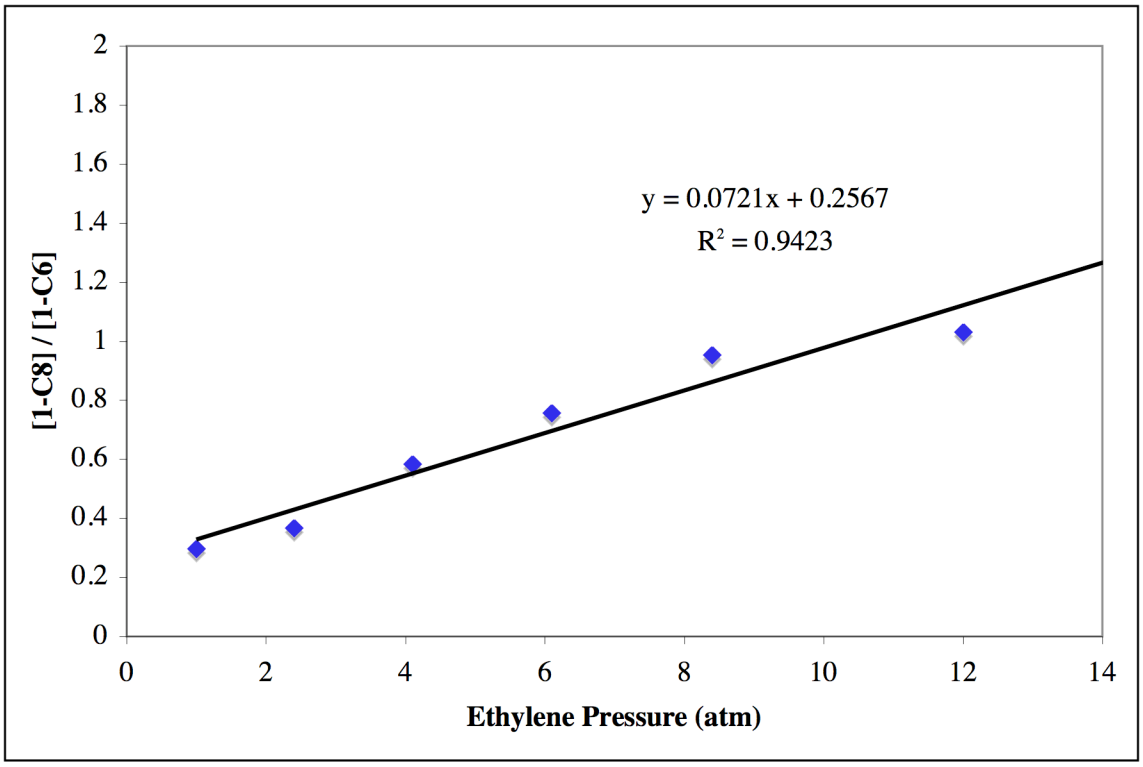


Figure 13. [1-octene] / [1-hexene] dependence on ethylene pressure.

Role of the Ether Tether in Increasing Catalyst Stability

As was demonstrated previously, the ether tether on the PNP ligands provides additional stability during catalysis by acting as a hemilabile donor to the chromium center. It was shown that when a tether of sufficient length and rigidity is employed, catalyst stability and activity are maximized. To provide further evidence for the beneficiary effect of the ether donor, precatalyst **24** was compared with two systems lacking the ether functionality, i.e. **25** and **26**. Complex **25**, typically formed *in situ*, was used extensively by Bollmann and coworkers as their most active catalyst for ethylene tetramerization.[8,45] On the other hand, complex **26** is structurally and sterically similar to

24, however the methoxy functionality has been replaced with an ethyl group. Ethylene consumption over several hours can be monitored by running oligomerization reactions at 1 atmosphere of ethylene as presented previously. Comparisons between the three systems can then be drawn to determine whether the addition of a coordinating linker to the PNP ligand is a significant factor in increasing stability during catalysis. A plot representing ethylene consumption during reactions involving each of the three catalysts is shown in Figure 14. While both systems lacking the ether group seem to be more active initially, they do not remain stable over time and start decomposing within 20 minutes, as was the case with previous ethylene trimerization catalysts discussed earlier. In contrast, the initially less active system based on **24** remains stable several hours before slow decay. The increased stability has a significant effect on total productivity (6243, 2641, and 2706 g/g_{Cr} for **24**, **25**, and **26**, respectively).

To confirm that the results reflected a general trend and were not limited to reactions at 1 atmosphere of ethylene, a similar set of experiments was carried out at higher pressure. Due to technical limitations, it was not possible to monitor ethylene consumption above atmospheric pressure. Therefore, separate experiments were performed at various reaction times. The highly reproducible nature of the reactions demonstrated throughout the course of this study justifies the method employed here to determine ethylene consumption over time at higher pressures. The results of the experiments were consistent with those found at lower pressure, as is depicted in Figure 15. While the catalyst containing the methoxy benzylene linker remained stable after 5 hours at 4 atmosphere of ethylene, both catalysts lacking a donor functionality displayed a decrease in activity suggesting decomposition of the active catalyst. The additional

stability exhibited by **24** provided a significant improvement in total productivity. After 5 hours, productivity was indeed doubled when the more stable catalyst was employed.

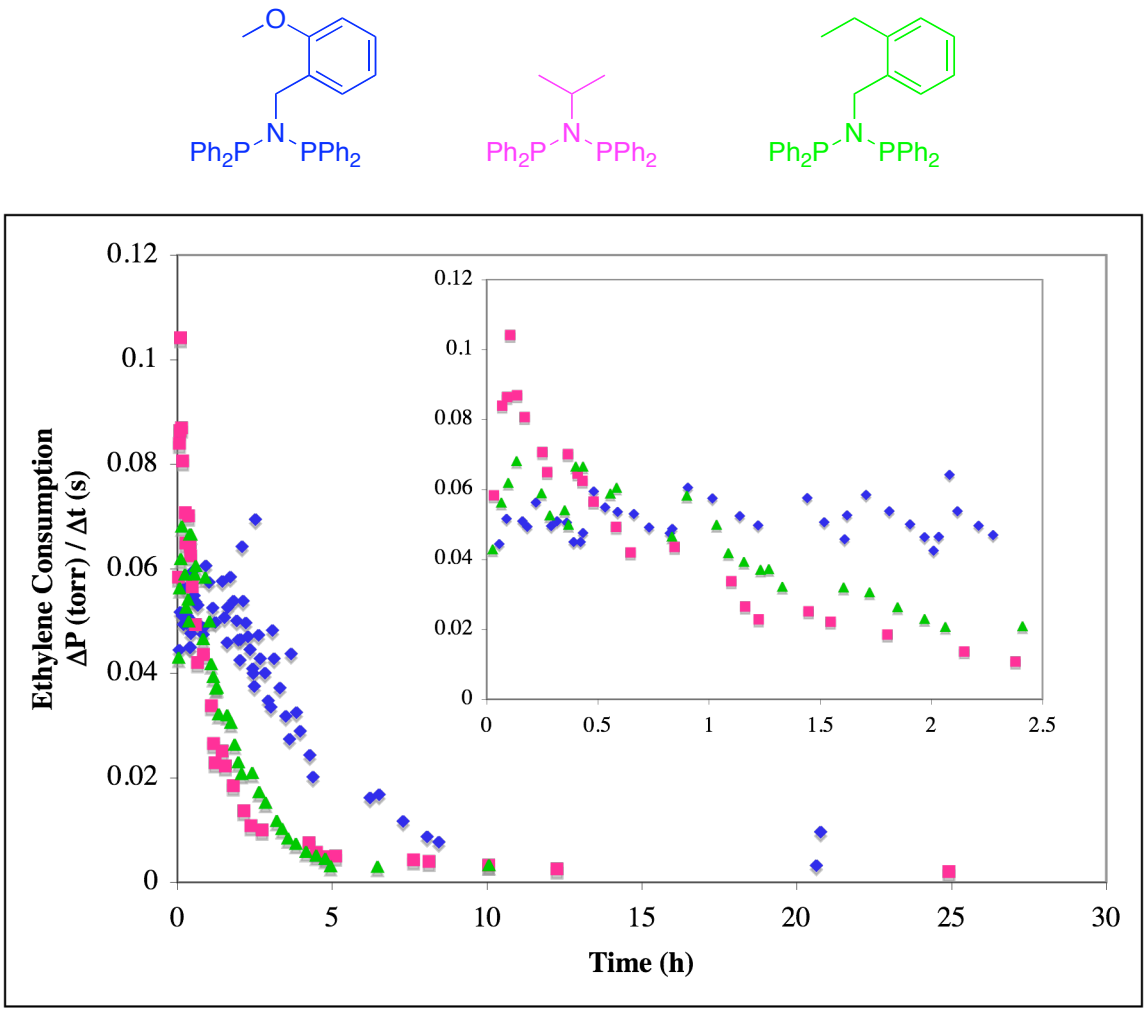


Figure 14. Stability of systems based on **24-26** at 1 atm of ethylene.

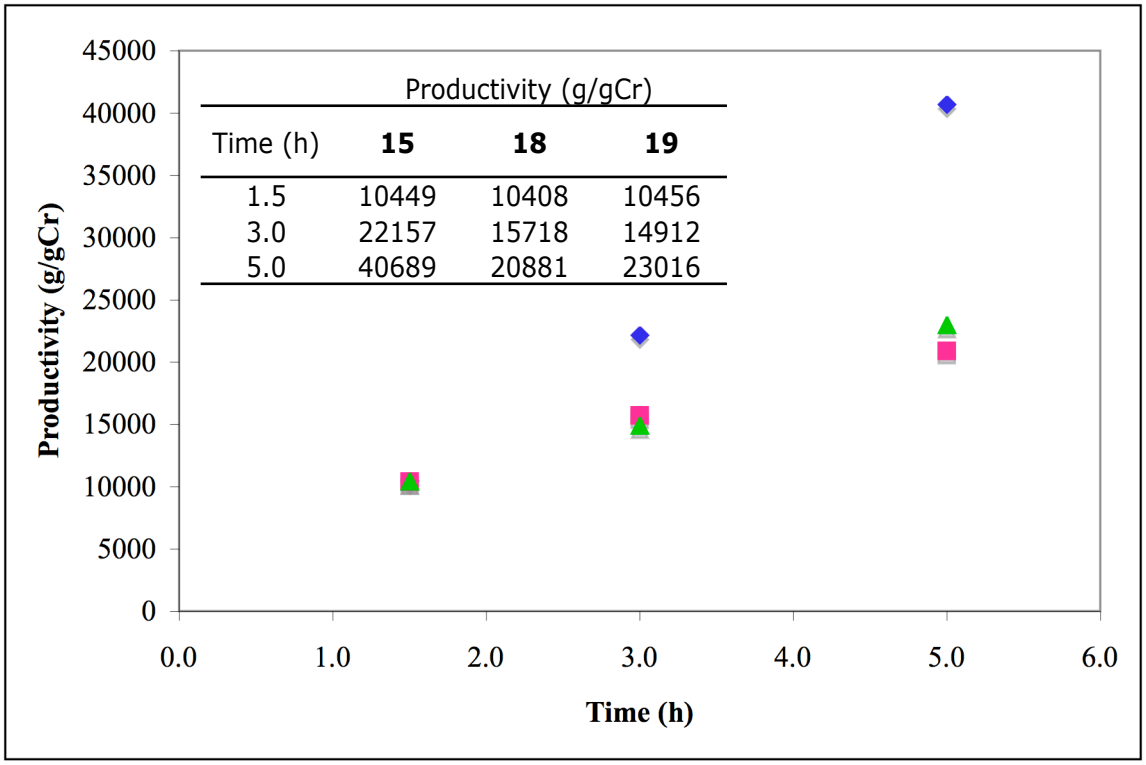
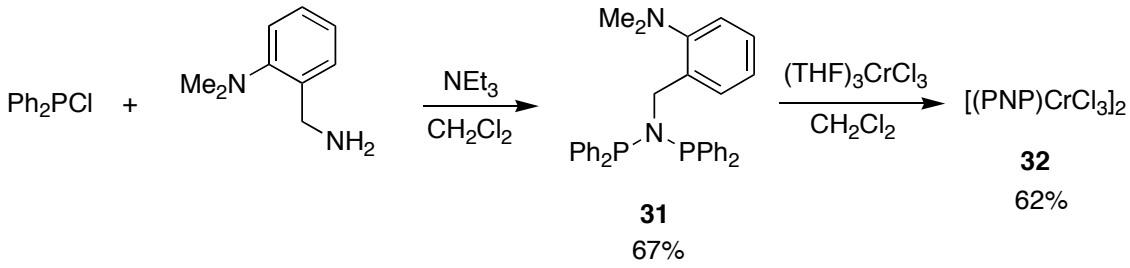


Figure 15. Comparison between catalysts **24**, **25**, and **26**: total productivity over time at 4 atm ethylene.

Modification of the Pendant Donor

While the beneficiary effect of the pendant ether group is evident when examining the catalytic performance of the catalysts, the isolation of a monomeric precursor displaying coordination of the donor functionality to chromium was still elusive. It was hypothesized that due to the weak binding of the ether functionality to the chromium center, a dimeric structure featuring chloride bridges was favorable in the solid state. A monomeric species could therefore be obtained if a stronger interaction between the donor functionality and chromium was established. A recent report shows the isolation of

a monomeric chromium complex with a molecule of acetonitrile occupying the last coordination site.[50] During their investigation of models of ethylene trimerization catalysts, Bercaw and coworkers demonstrated that chromium(III) centers display a stronger affinity for nitrogen and sulfur-based ligands than oxygen-based ones, i.e. ethers.[25] A particularly interesting example is complex **11**, which exhibits a completely different coordination mode (κ^3-N,P,N) than its close analogue **8** to accommodate the coordination of two amino groups. Inspired by this concept, a ligand analogous to **18** with a dimethylamino group in place of the ether functionality was synthesized and the corresponding chromium complex prepared following typical procedures (Scheme 7).



Scheme 7. Synthesis of ligand **31** and complex **32**.

Crystallographic data would have been highly valuable in obtaining insight on the structure of this complex, however repeated attempts at growing X-ray quality crystals of **32** were unsuccessful. Nonetheless, the precursor was tested for catalytic activity in the hopes that its behavior under catalytic conditions could provide hints on the participation of the pendant amino group. The procedure employed was as described previously and reactions were carried out at 1 and 4 atmospheres of ethylene. The catalyst generated upon activation displayed high activity towards oligomerization, with productivity slightly lower than in the case of **24** (Table 5). Selectivity trends were also consistent.

Monitoring ethylene consumption at 1 atmosphere of ethylene revealed that catalyst **32** was even more stable than **24**, where activity started to decrease only after more than 4 hours (Figure 16). The lower activity displayed by **32** is also evident from the plot, contributing to the lower total productivity of the system. While these results are inconclusive in providing strong evidence towards the formation of a monomeric species involving coordination of the amino group, they are consistent with the higher affinity of the chromium center towards nitrogen-based ligands leading to a more stable, but less active system where ethylene coordination and insertion competes with the pendant amino group.

Table 5. Catalytic performance of systems containing pendant ether and amino groups.[a]

entry (complex)	*p* (atm)	productivity ($g_{product}/g_{Cr}$)	PE (wt %)	C-6 (wt %)	C-8 (wt %)	1-C6 in C6 (%)	1-C8 in C8 (%)	1-C8 (mol)/ 1-C6 (mol)
1 (**24**)	1	13,902	0.2	30	14	87	65	0.272
2 (**32**)	1	11,756	0.4	37	16	89	73	0.277
3 (**24**)	4	9,092	0.5	41	33	85	95	0.689
4 (**32**)	4	7,572	1	43	37	83	97	0.752

[a] Conditions: $[(PNP)CrCl_3]_2$ (0.08 mmol), C_6H_5Cl (20 mL), MAO (300 eq, 10 wt% in toluene), 25 ºC, 30 hrs (at 1 atm) or 90 min (at 4 atm).

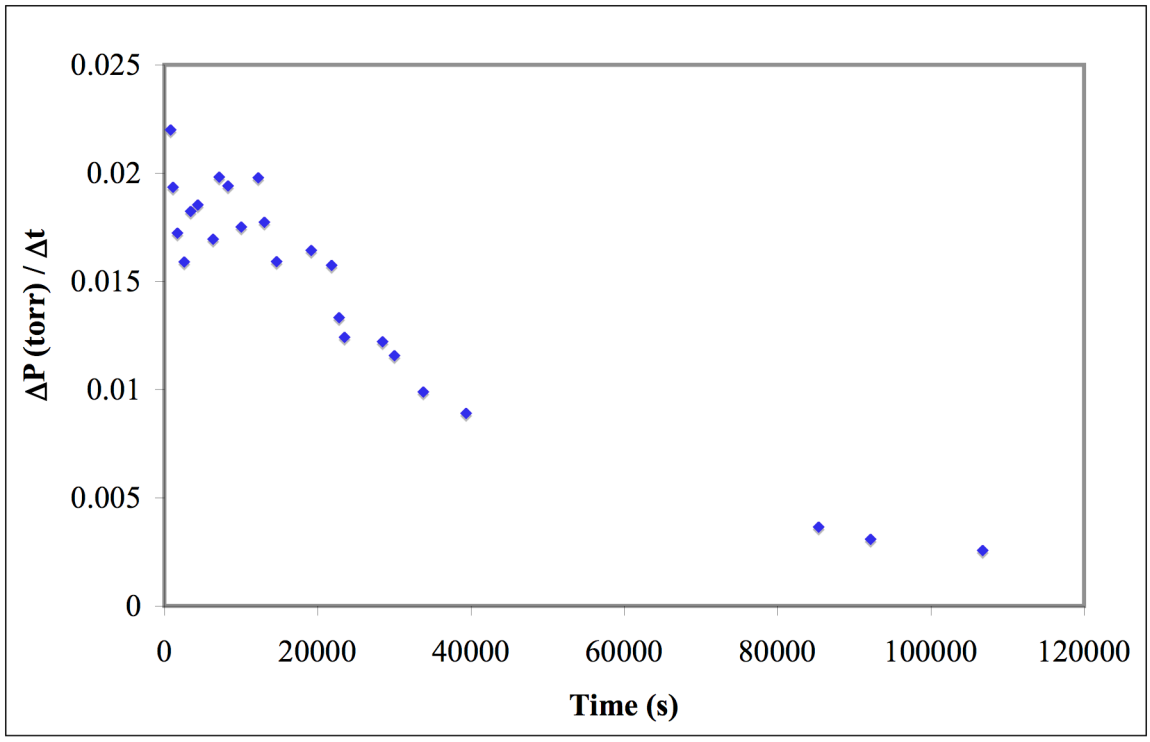
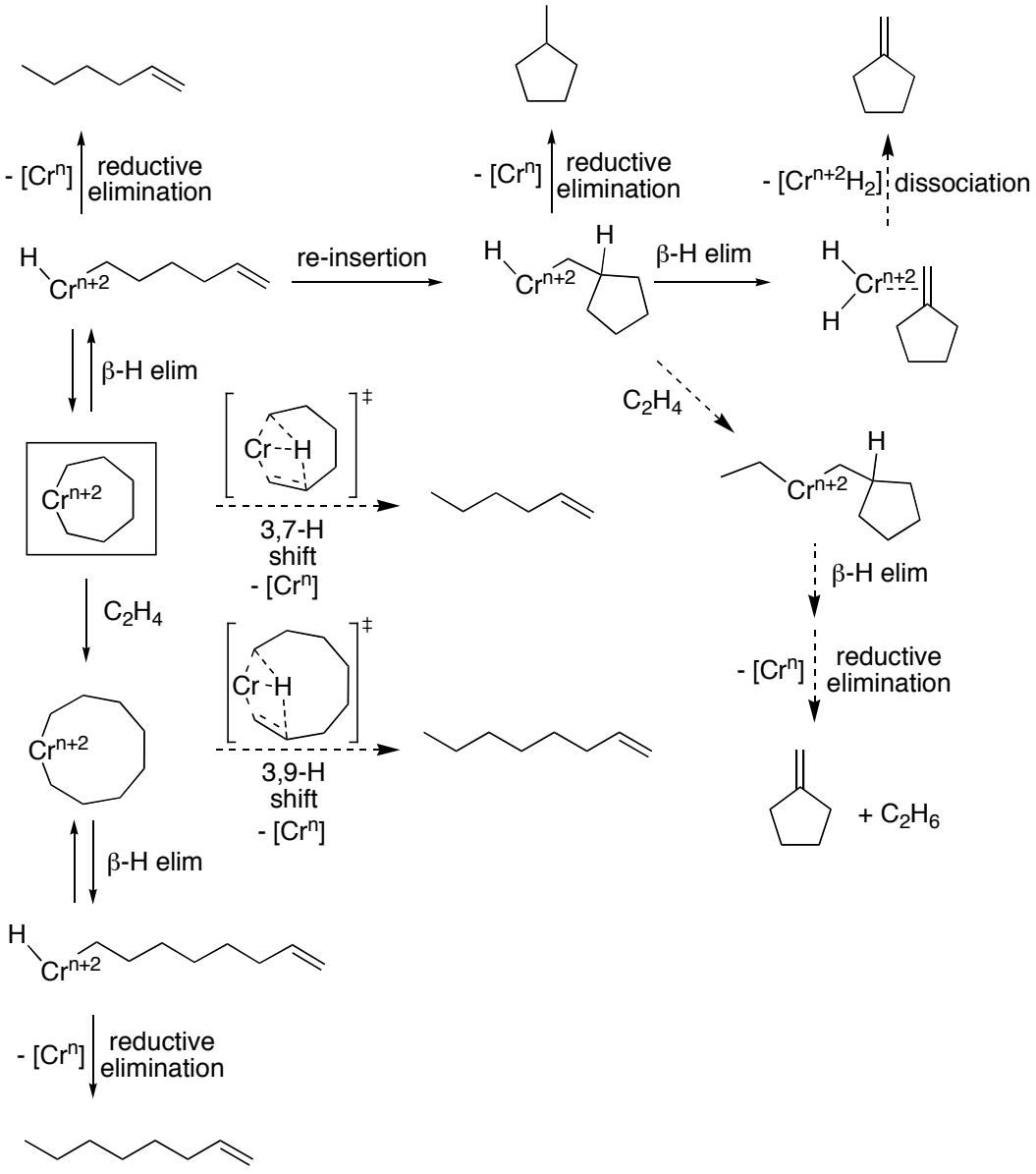


Figure 16. Ethylene consumption over time at 1 atm ethylene using precatalyst **32**.

Mechanistic Insight Obtained from the Product Mixture

Careful investigations of the product mixture from the oligomerization reactions provided valuable insights on the mechanism of tri- and tetramerization of ethylene. It was mentioned previously that two pathways for the formation of 1-hexene were proposed, one involving β-hydride elimination from the chromacycloheptane to form a hexenyl-hydride intermediate followed by reductive elimination; the other invokes a metal-assisted 3,7-hydride shift from the metallacycloheptane. A closer look at the C_6 side-products formed in the oligomerization reactions revealed that the two main side-products within the C_6 fraction, as determined by GC, are methylcyclopentane and methylenecyclopentane.

Similar observations have later been reported by Overett and coworkers.[46] Both of these products suggest the hexenyl-hydride mediated pathway. Formation of the methylcyclopentane may be readily accommodated by olefin reinsertion into the Cr-C bond followed by C-H reductive elimination, as depicted in Scheme 8. An alternative pathway could involve 2,1-reinsertion of the olefin into the Cr-H bond to afford a 2-methylchromacyclohexane that subsequently reductively eliminates methylcyclopentane. This possibility appears less likely because the analogous reductive elimination of cyclohexane from the chromacycloheptane (or cyclooctane from the chromacyclononane) is not observed. Moreover, deuterium labeling experiments do not indicate reversible 2,1-reinsertion of the olefin into the Cr-H bond.[51] Methylenecyclopentane could arise from this same cyclopentylmethyl-hydride intermediate *via* a second β-hydride elimination by either pathway shown in Scheme 8. One pathway implies the formation of an interesting chromium dihydride species as a possible intermediate. It is indeed difficult to envision formation of either of these minor products by any mechanism *not* involving a chromium hydride. Of course, it cannot be ruled out that, whereas methylcyclopentane and methylenecyclopentane arise from the hexenyl-hydride intermediate, 1-hexene is formed by the principal alternative: a concerted 3,7-hydride shift. Nonetheless, formation of these two minor products does provide some of the only support for the stepwise pathway. It should also be noted that the corresponding cyclic products in the C_8 fraction, methylcycloheptane and methylenecycloheptane, are not observed in any of the reactions performed suggesting that re-insertion from the longer alkenyl-hydride is not favorable.



Scheme 8. Proposed mechanism for the formation of cyclic C_6 products.

Temperature Dependence

Most reactions were run in water or oil baths with the temperature regulated at 25 ^{o}C. In the case of the reaction performed at 12 atmospheres of ethylene, the temperature reading of the water bath had reached 35 ^{o}C by the end of the reaction, highlighting the high exothermicity of ethylene oligomerization reactions. In an industrial setting, such reactions are typically carried out at higher temperature to lower the cost of the cooling process and overall heat management. Catalysts able to tolerate temperatures ranging from 80-120 ^{o}C are therefore highly desirable. During a collaboration with Innovene (now Ineos), catalysts **21**-**24** were tested for catalytic activity at higher temperatures and ethylene pressure. The results indicated that increasing the temperature had several negative effects on the reaction outcome. Firstly, productivity had significantly decreased, while polymer formation had greatly increased. Secondly, and more surprisingly, selectivity towards 1-hexene and 1-octene had been lost and a Schultz-Flory distribution of olefins was obtained. While it was later suggested that contamination of the reactor was the cause of the selectivity loss, catalyst **24** was tested at higher temperature in our laboratories. Two sets of comparative experiments were carried out with temperature ranging from 25-65 ^{o}C (8.4 atm ethylene, 90 minutes) in the first and 25-80 ^{o}C (12 atm ethylene, 30 minutes) in the second (Table 6). The results revealed that productivity had decreased dramatically while polymer formation increased by at least an order of magnitude. Contrary to prior assumptions however, selectivity was hardly, if at all, affected. A possible explanation involves the decomposition of the oligomerization catalyst at elevated temperatures into a chromium species capable of polymerizing

ethylene. It is important to note however that while the results shown in Table 6 seem to indicate that catalyst **24** does not constitute a viable system at high temperatures, the actual reaction temperature could not be accurately measured due to limitations with the instrument. The temperature reading from the thermometer does not reflect the true value inside the vessel, likely significantly higher due to the severe exothermicity at elevated pressures.

Table 6. Temperature effects on productivity and selectivity.[a]

Temp. (˚C)	Time (min)	*p* (atm)	Productivity (g/gCr)	PE (%wt)	C6 (%wt)	C8 (%wt)	1-C6 (%wt)	1-C8 (%wt)
25	90	8.4	44,040	0.3	31	34	84	93
65	90	8.4	6,491	9	36	32	91	91
25-35	30	12	35,667	0.1	34	42	86	96
80	30	12	6,479	22	44	23	98	94

[a] Conditions: $[(PNP)CrCl_3]_2$ (0.08 mmol), C_6H_5Cl (20 mL), MAO (300 eq, 10 wt% in toluene)**.**

Investigating Catalyst Decomposition

Little is known about the nature of the decomposition products in the ethylene oligomerization reaction or the factors that lead to decomposition. The challenge stems from several features of the system that hinder proper characterization. Perhaps most importantly, the true identity of the active catalyst remains unknown despite numerous attempts at determining it. Furthermore, addition of large excess of activators, such as

aluminoxanes, renders the analysis of any chromium products present at the end of the reaction very difficult.

Several steps were undertaken during the course of this study that provide hints on the possible nature of catalyst decomposition products. In examining the portion of the ethylene consumption plots at one atmosphere that reflect catalyst decay, and when assuming that ethylene consumption is proportional to the concentration of active catalyst in solution, it is possible to determine the order in chromium during decomposition by fitting the data points to a straight line. Systems, both featuring a donor functionality and lacking one, display second-order decomposition in chromium; a plot of the inverse of ethylene consumption *versus* time gives a straight line (Figure 17). A similar treatment for first-order decomposition (a plot of the natural log of ethylene consumption *versus* time) does not fit a straight line over the course of the reaction (30 hours). This is in sharp contrast with observations from previous investigations of ethylene trimerization reactions, which suggested that catalyst decomposition is first-order in chromium.[10] It is in fact likely that decomposition follows second-order kinetics during ethylene trimerization as well. The data recorded previously covered only the first 20 minutes of the reaction, while it was shown in the present study that data points collected after about an hour do not fit the straight line anymore.

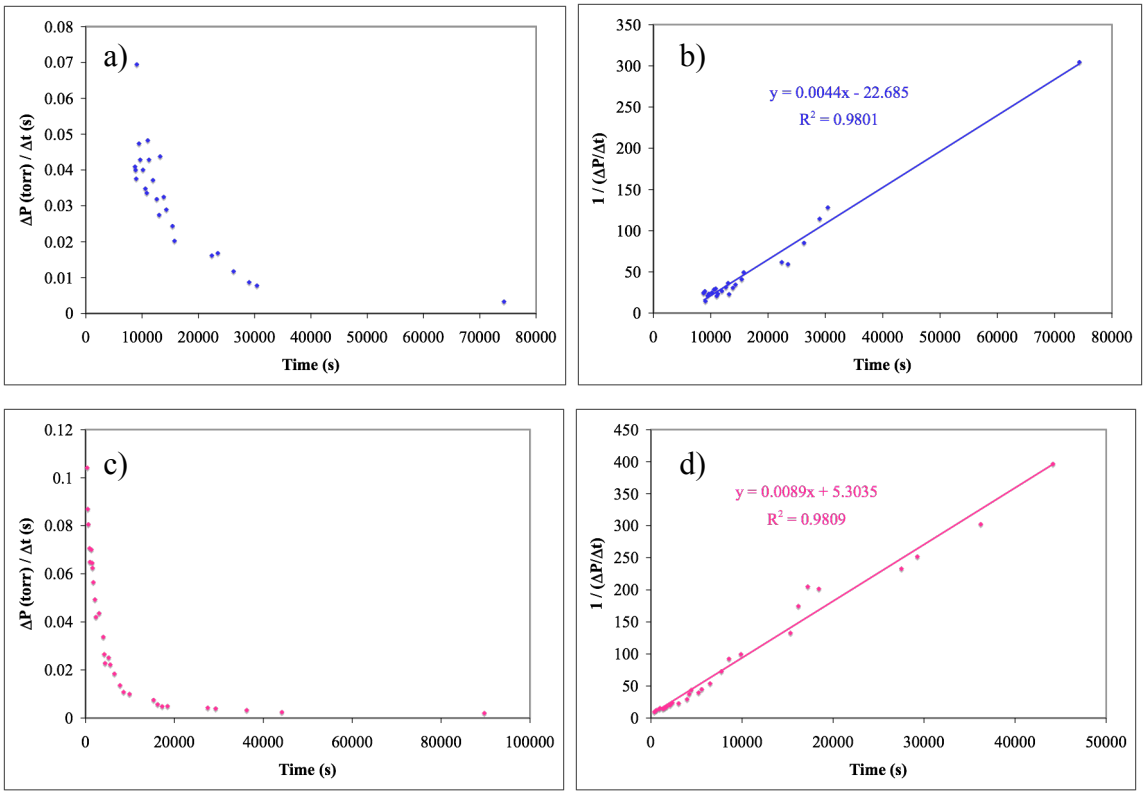


Figure 17. a) Catalyst decomposition for **24**. b) Second-order fit for **24**. c) Catalyst decomposition for **25**. d) Second-order fit for **25**.

In order to confirm these results, the concentration of catalyst was reduced by half in a reaction at 1 atmosphere of ethylene (Figure 18). As expected, stability was significantly improved and the catalyst remained stable 4 hours before slow decay. Of course, total productivity was therefore increased, as is depicted in Table 7. Attempts at further lowering catalyst concentration were thwarted by experimental limitations (sub-miligram quantities of catalyst precursor), and solubility issues prevented increasing catalyst concentration.

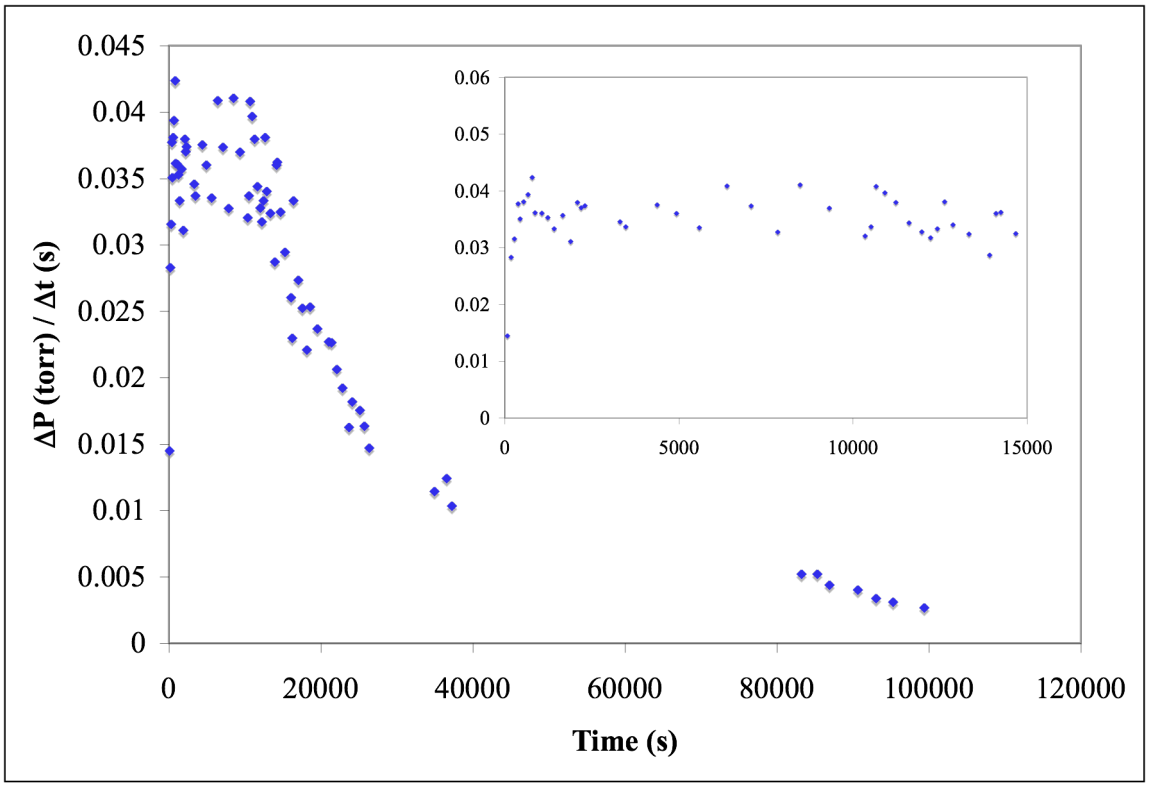


Figure 18. Increased stability at lower catalyst concentration.

Table 7. Varying catalyst concentration at 1 atm ethylene.

[Cr] Conc. (mM)	Productivity (g/g_{Cr})	Time before Decay (hrs)	Half-life (hrs)
0.4	6,244	2	4
0.2	14,388	4	7

With respect to the nature of the catalyst decomposition product, a simple experiment was carried out, which aimed at determining whether diphosphine ligand dissociation during catalysis was the primary decomposition pathway. ^{1}H NMR of a C_6D_5Cl solution of **24** revealed several very broad peaks attributed to the ligand, while a ^{31}P NMR spectrum showed no signal, typically observed for a paramagnetic complex. The J-Young NMR tube was charged with MAO and placed on a high vacuum line where

an atmosphere of ethylene was introduced. After vigorous shaking, ^{31}P NMR spectra were recorded after 5, 20, and finally 27 hours, when over 99% of the active catalyst was expected to have decomposed. No signal was ever observed, suggesting that diphosphine dissociation did not occur. ^{31}P NMR of a sample containing the free PNP ligand and MAO in C_6H_5Cl revealed a peak, although slightly broadened, at the expected chemical shift, indicating that PNP ligand dissociated during catalyst should be observed in the ^{31}P NMR spectrum. Furthermore, the NMR reaction was worked up following the typical procedure and a GC trace was obtained, which revealed the formation of several turnovers of 1-hexene and 1-octene, confirming that a reaction had indeed taken place.

The possibility of diphosphine dissociation was further investigated. Assuming that ligand dissociation played a role in accelerating catalyst decomposition, an excess of PNP ligand should retard catalyst decay and increase total productivity. Two catalytic runs, one containing **24**, and the other a 1:1 mixture of **24** and the free ligand **18**, were compared at 1 atmosphere of ethylene. An ethylene consumption plot revealed that not only did adding excess ligand not improve catalyst lifetime, it seemed to accelerate decomposition (Figure 19). Moreover, the less stable system resulted in a decrease in total productivity, as depicted by the turnover numbers in 1-hexene and 1-octene in Table 8. These results imply that catalyst decomposition does not involve disphosphine dissociation, as was proposed above. In fact, it may be possible that decomposition involves disproportionation of the PNP chromium catalyst to an inactive *bis*(PNP) chromium species, which would be consistent with the observed behavior when excess ligand is present. Interestingly, while stability, and therefore productivity, are

significantly influenced by excess ligand, no effect on polymer formation or olefin product selectivity was observed.

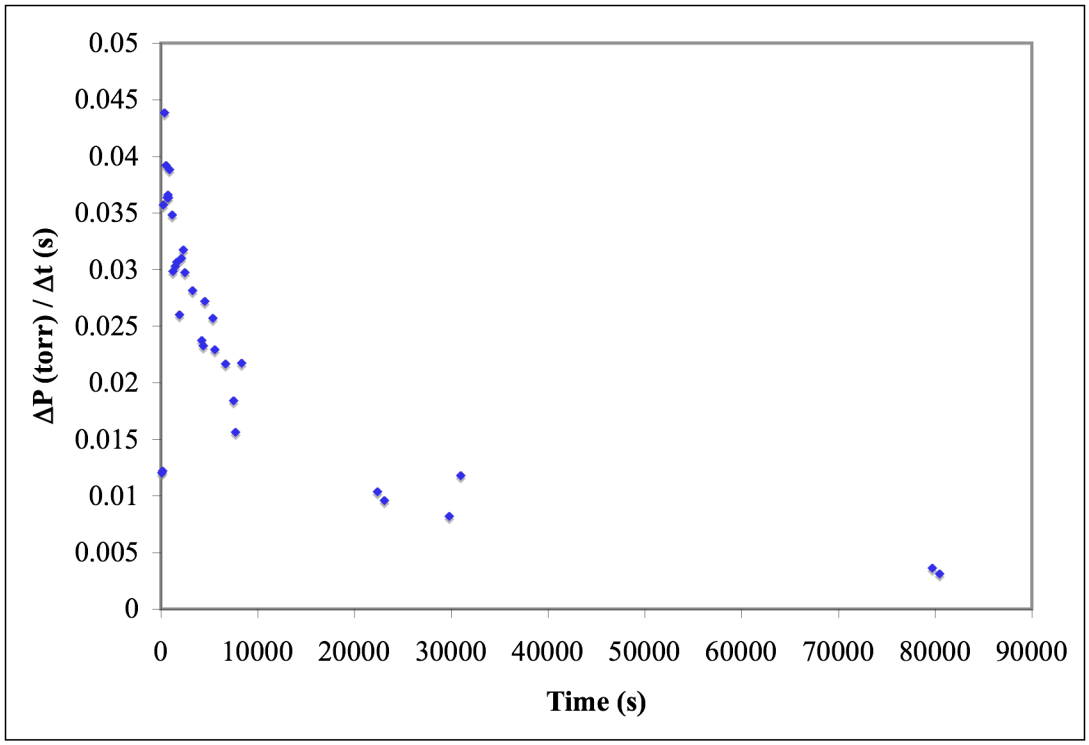


Figure 19. Ethylene consumption plot in a reaction containing a 1:1 mixture of **24** and free ligand **18**.

Table 8. Decrease in olefin turnovers with excess ligand present.

Precatalyst Combination	1-C6 (TON)	1-C8 (TON)
[(PNP)Cr] + PNP	2,254	518
[(PNP)Cr]	3,440	751

Solvent Effects in the Chromium-Catalyzed Ethylene Oligomerization

Reactions performed initially and reported above were carried out in chlorobenzene as the solvent. The catalyst precursors are slightly soluble in this solvent, while not at all in non-polar solvents. However, typical oligomerization solvents employed, in industrial settings primarily, but also by various academic laboratories studying this type of reactions are toluene, as well as mixtures of alkanes, such as hexanes or dodecane. As described previously, reactions using **24** in chlorobenzene were shown to be highly active and selective for the formation of 1-hexene and 1-octene with little production of undesired polyethylene. In contrast, comparative reactions in less polar toluene resulted in a dramatic decrease in productivity and a high formation of polyethylene. Moreover, reactions in toluene showed more favorable formation of 1-octene, compared to 1-hexene, than in chlorobenzene. A control reaction, whereby a dodecane solution of chlorobenzene and dry MAO (toluene was first removed *in vacuo*) was allowed to stir for several hours at temperatures ranging from 25-60 ^{o}C, showed that no reaction occurs between MAO and chlorobenzene, as was confirmed by GC analysis. This result confirmed the stability of this solvent under typical oligomerization reaction conditions. In 1,2-dichlorobenzene catalysts display greater stability than in chlorobenzene (Figure 20), however with slightly lower activity as depicted in Table 9.

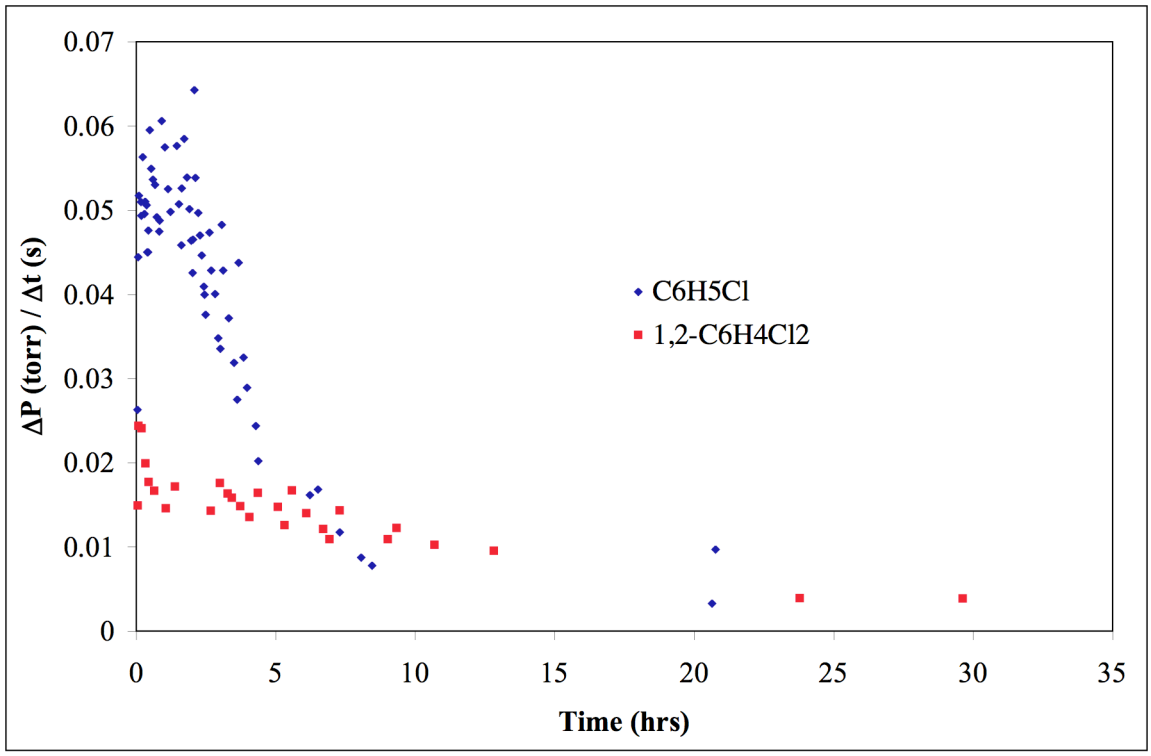


Figure 20. Comparison between C_6H_5Cl and 1,2-$C_6H_4Cl_2$ reactions at 1 atm ethylene.

Table 9. Comparison between C_6H_5Cl and 1,2-$C_6H_4Cl_2$ reactions at 1 atm ethylene.

Solvent	Productivity (g/g_{Cr})	Time before Decay (hrs)	Half-life (hrs)
C_6H_5Cl	6,244	2	4
1,2-$C_6H_4Cl_2$	4,011	5	12

It was not clear initially whether the beneficial effects of chlorobenzenes were due to weak solvation *via* the chlorine atom or, more generally, higher solvent polarity. Unfortunately, a successful reaction under comparable conditions in the non-coordinating polar solvent α,α,α-trifluorotoluene was not possible due the rapid reaction of this solvent with MAO. With the aim of sorting out the surprisingly large solvent effects

observed during oligomerization reactions, a more thorough investigation of the role of the solvent was undertaken. A series of seven solvents, varying in polarity as well as coordinating ability, was investigated in oligomerization reactions using **24** at 4 atmospheres of ethylene. A summary of the results is shown in Table 11. In contrast to the highly active and selective reactions in chlorobenzene, reactions in non-polar, non-coordinating solvents, such as toluene and dodecane, resulted in significantly lower productivity and stability with a considerable increase in polymer formation (Table 11, entries 2-3). Benzene, as expected, performed similarly (entry 4). As observed previously, there is a striking difference in the preferred formation of 1-octene compared to 1-hexene at only 4 atmospheres of ethylene. This preference is amplified at higher pressures as was discussed above. On the other hand, reaction in fluorobenzene, with a dielectric constant similar to that of chlorobenzene (Table 10), resulted in very high productivity while 1-octene formation was favored over 1-hexene (Table 11, entry 6). Interestingly, reaction in the more polar 1,2-difluorobenzene generated slightly less products while the preferential formation of 1-octene was accentuated further (entry 7). From the literature, it can be inferred that ethylene solubility in the solvents studied is not a major contributor to the trends observed.[52-55] Indeed, ethylene solubility is greatest in linear alkanes, such as dodecane or hexane. Its solubility is significantly lower in chlorobenzene and benzene, while slightly higher in toluene, at least at pressures under which the reactions were carried out. Furthermore, upon activation with aluminoxane, the catalyst is fully soluble throughout the reaction in all solvents tested, with the exception of dodecane, in which a few green particles are suspended at the end of the reaction. A recent theoretical report on the role of MAO during the trimerization and tetramerization

reactions demonstrated that the favorable formation of dissociated ion-pair complexes, and consequent formation of more active cationic chromium species, is a prerequisite for catalysis to proceed (Figure 21).[56] Moreover, there is presumably a competitive coordination of the counteranion, which hinders ethylene coordination and insertion into the chromacycle. It is predicted that solvent polarity influences the ion-pair separation, which is supported by our results. In accordance with van Rensburg's report, non-polar solvents (Table 11, entries 2-4) would favor shorter ion-pair separation impairing catalyst performance. On the other hand, it seems that when the reaction medium is too polar, the ion-pair separation becomes too large, which in turn lowers activity, as is the case with 1,2-dichlorobenzene and 1,2-difluorobenzene.

Table 10. Dielectric constants of the solvents investigated.[57]

Solvent	ε
dodecane	2.0
benzene	2.3
toluene	2.4
C_6H_5F	5.5
C_6H_5Cl	5.6
1,2-$C_6H_4Cl_2$	10.1
1,2-$C_6H_4F_2$	13.4

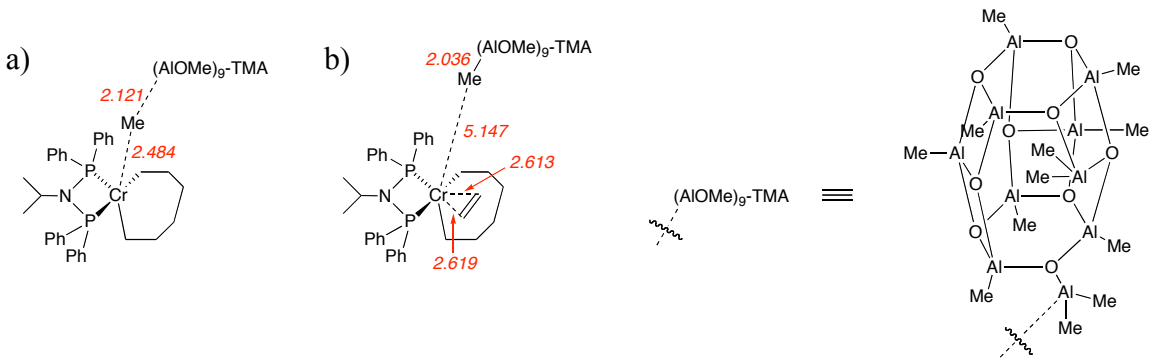


Figure 21. Calculated geometries of chromacycloheptanes interacting with a model counteranion a) before coordination of the fourth molecule of ethylene and b) after (from ref. 56).

Similar reactions were run using precatalyst **25** to determine if the pendant ether donor played a role in the observed trends (Table 12). The general tendencies discussed above were preserved in large part in runs using **25**. While reactions carried out in non-polar solvents did not generate much product (Table 12, entries 2-4), those in halobenzenes showed significantly higher productivity (entries 1 and 5-7). Furthermore, the trend in the relative preference in the formation of 1-octene over 1-hexene in this set of experiments mirrors that of Table 11. Indeed, non-coordinating solvents seem to favor 1-octene formation when compared to chlorobenzenes. It should be noted that activity values in Table 12 are significantly higher than the values from Table 11. This observation seems surprising considering the discussion earlier in the chapter, which established that under these reaction conditions, **24** and **25** should display similar productivity (Figure 15). The reason for the discrepancies stems from the nature of the MAO activator used for the reactions, details of which will be discussed in the next section.

Table 11. Solvent comparison in ethylene oligomerization using precatalyst **24**.[a]

entry	solvent	productivity ($g_{product}/g_{Cr}$)	PE (wt%)	C-6 (wt%)	C-8 (wt%)	C-10 (wt%)	>C-10 (wt%)	1-C6 in C6 (%)	1-C8 in C8 (%)	1-C8 / 1-C6 (molar)
1	C_6H_5Cl	9,092	0.5	41	33	7	18	85	95	0.689
2	toluene	1,203	20	28	49	1	1	64	99	1.99
3	dodecane	<150	>80	<10	<10	<1	<1	NA	NA	*ca.* 1.00
4	C_6H_6	1,288	17	31	49	1	3	69	99	1.72
5	1,2-$C_6H_4Cl_2$	7,250	1	39	29	11	19	86	93	0.601
6	C_6H_5F	10,711	0.1	32	42	5	21	79	98	1.20
7	1,2-$C_6H_4F_2$	7,035	3	27	49	3	17	74	99	1.86

[a] Conditions: **24** (0.008 mmol), solvent (20 mL), MAO (300 eq., 10% in toluene), C_2H_4 (4 atm), 25 ^{o}C, 90 min.

Table 12. Solvent comparison in ethylene oligomerization using precatalyst **25**.[a]

entry	solvent	productivity ($g_{product}/g_{Cr}$)	PE (wt%)	C-6 (wt%)	C-8 (wt%)	C-10 (wt %)	>C-10 (wt %)	1-C6 in C6 (%)	1-C8 in C8 (%)	1-C8 / 1-C6 (molar)
1	C_6H_5Cl	17,616	0.3	39	25	12	24	94	88	0.439
2	toluene	1,241	6	37	54	1	2	88	99	1.25
3	dodecane	<200	>50	<20	<30	<1	<1	NA	NA	*ca.* 1.50
4	C_6H_6	2,307	2	40	54	1	3	88	99	1.14
5	1,2-$C_6H_4Cl_2$	10,204	0.6	37	32	8	22	92	95	0.668
6	C_6H_5F	20,270	0.1	26	36	6	32	90	96	1.10
7	1,2-$C_6H_4F_2$	17,980	0.2	21	33	7	39	88	95	1.24

[a] Conditions: **25** (0.008 mmol), solvent (20 mL), MAO* (300 eq., 10% in toluene), C_2H_4 (4 atm), 25 ^{o}C, 90 min.

Results from Tables 11 and 12 seem to suggest that, while solvent polarity influences catalyst activity by enhancing ion-pair separation, the coordinating ability of the solvent is somehow responsible for the favorable formation of the smaller chromacycle, which generates 1-hexene. The selectivity changes prompted the investigation of coordinating additives during oligomerization reactions. Experiments involved the addition of coordinating organic molecules to the reaction mixture containing a non-coordinating solvent, such as benzene and fluorobenzene (Table 13). An initial attempt to add diethyl ether (200 equiv.) to the reaction mixtures resulted in a complete shutdown of the catalysis. Addition of 20 equivalents of less coordinating *N*,*N*-dimethylaniline to a reaction in benzene resulted in a slight increase in the 1-octene/1-hexene ratio and a negligible effect on productivity (Table 13, entry 1). This of course contradicted the above observation that coordinating solvents tend to favor 1-hexene formation, suggesting that either the additive does not coordinate during catalysis, or more likely that some other feature, perhaps unique to chlorobenzenes and which causes preferential formation of 1-hexene, exceeds the rather small coordinating effect favoring the formation of the larger α-olefin. Addition of 40 equivalents of *N*,*N*-dimethylaniline did not affect productivity either but resulted in further increase in the selectivity towards 1-octene (entry 2). Catalysis was again almost shut down upon addition of 200 equivalents of the additive (entry 3). Similar observations were made when 20 equivalents of the aniline were added into a fluorobenzene reaction (entry 4), as well as when the additive was replaced with anisole (entry 5). Reaction in chlorobenzene with added aniline followed a similar tendency, whereby 1-octene formation was favored

when compared to reactions in neat chlorobenzene, while productivity has decreased slightly (entry 6). Furthermore, in order to confirm that these trends were general and reflected all catalysts employed in this study, reactions using **25** were carried out under comparable conditions. The results were consistent with the above observations (entries 7-9). Additionally, a closer look at reactions using **24** and **25** further supports a coordinating effect influencing selectivity. Experiments involving complex **24**, which possesses a potentially coordinating tether, consistently display a higher preference for 1-octene than those using **25** in all conditions investigated. These results could provide further evidence towards the coordinating ability of the ether tethers from the catalysts discussed earlier in the chapter. It seems now that the ether donors can play key roles in both stabilizing the active chromium species during catalysis and in promoting higher selectivity towards 1-octene.

From these experiments, the variables affecting the selectivity between 1-hexene and 1-octene are therefore still unclear. However, it is quite interesting that in all cases investigated, addition of a potentially coordinating additive enhanced the selectivity towards 1-octene formation slightly, provided that productivity was not affected by competitive coordination of the additive. Lower productivity is likely due to such coordinative competition hindering catalyst activity, which can eventually be shut down.

Solvent mixtures were also investigated as a means of improving catalytic performance in toluene and dodecane while reducing the process cost of using expensive solvents such as chlorobenzene and 1,2-difluorobenzene. In a 1:1 mixture of chlorobenzene and toluene, the reaction performed well with intermediate productivity and 1-octene/1-hexene ratio as well as a significant decrease in polymer formation when

compared to reactions in neat toluene (Table 14, entry 1). Furthermore, an experiment was carried out in a 1:1 mixture of 1,2-difluorobenzene and dodecane to improve ethylene solubility and lower overall medium polarity (as compared to a reaction in neat 1,2-difluorobenzene). Productivity was comparable to a run in fluorobenzene, while 1-octene selectivity remained high (entry 2). These highly promising results showed that a clever choice of reaction medium allows excellent tunability of the oligomerization reaction.

Table 13. Potentially coordinating additives in the reaction mixture.[a]

entry (complex)	solvent	additive (equiv.)	productivity ($g_{product}/g_{Cr}$)	PE (wt %)	C-6 (wt %)	C-8 (wt %)	C-10 (wt %)	>C-10 (wt %)	1-C6 in C6 (%)	1-C8 in C8 (%)	1-C8/1-C6 (molar)
1 (**24**)	C_6H_6	$C_6H_5NMe_2$ (20)	2,145	6	33	57	1	3	66	99	1.91
2 (**24**)	C_6H_6	$C_6H_5NMe_2$ (40)	2,010	7	31	58	1	3	62	99	2.24
3 (**24**)	C_6H_6	$C_6H_5NMe_2$ (200)	<200	<10	*ca.* 36	*ca.* 55	<1	<1	NA	NA	*ca.* 1.86
4 (**24**)	PhF	$C_6H_5NMe_2$ (20)	17,857	<0.1	31	42	4	22	77	97	1.32
5 (**24**)	PhF	C_6H_5OMe (20)	15,563	0.1	30	45	4	21	74	98	1.52
6 (**24**)	PhCl	$C_6H_5NMe_2$ (20)	14,021	0.2	37	36	6	21	81	97	0.856
7 (**25**)	C_6H_6	$C_6H_5NMe_2$ (20)	1,920	3	36	55	1	5	88	99	1.27
8 (**25**)	PhF	$C_6H_5NMe_2$ (20)	13,852	0.1	29	43	4	24	89	98	1.23
9 (**25**)	PhF	C_6H_5OMe (20)	10,796	0.2	23	32	4	18	90	97	1.13

[a] Conditions: precatalyst (0.008 mmol), solvent (20 mL), MAO* (300 eq., 10% in toluene), C_2H_4 (4 atm), 25 ^{o}C, 90 min.

Table 14. Oligomerization reactions using solvent mixtures.[a]

entry	solvent mixture	productivity ($g_{product}/g_{Cr}$)	PE (wt%)	C-6 (wt%)	C-8 (wt%)	C-10 (wt%)	>C-10 (wt%)	1-C6 in C6 (%)	1-C8 in C8 (%)	1-C8/1-C6 (molar)
1	PhCl/toluene (1:1)	5,698	1	37	50	2	9	75	99	1.34
2	1,2-$C_6H_4F_2$/dodecane (1:1)	10,578	0.5	27	47	3	21	73	98	1.75

[a] Conditions: **24** (0.008 mmol), solvent mixture (20 mL), MAO (300 eq., 10% in toluene), C_2H_4 (4 atm), 25 ^oC, 90 min.

The Effect of the Co-Catalyst on Activity and Selectivity

It was shown from the many oligomerization experiments performed and discussed previously that the catalysts developed herein allow very reproducible results, which is in sharp contrast to older ethylene trimerization systems and models studied thereafter. Nevertheless, one aspect of these reactions that displays significant variability is the activator used to generate the catalytically active chromium species. With the composition of the methylaluminoxane solution changing over time, significant increases in productivity have been observed in the latest experiments carried out. To identify the experiments affected, the activator is labeled herein as MAO*. These observations further suggest that the nature of the activator is of considerable importance to the reaction outcome. As was briefly mentioned above, a large increase in productivity to 17616 $g_{product}/g_{Cr}$ was observed in a chlorobenzene reaction using **25** (Table 12, entry 1), while a reaction using **24** under similar conditions generated 9092 $g_{product}/g_{Cr}$ (Table 11, entry 1). It was expected from previous studies (Figure 15) that at 4 atmospheres of ethylene, the catalysts should generate comparable amounts of products. It should be noted that reactions from Table 12 were carried out several months after those in Table 11, when a significant change in the composition of the MAO solution could be expected. To confirm this possibility and verify the consistency of the results, the same reaction as in Table 11, entry 1, was carried out at the same time as the data collected in Table 12; the productivity was then found to be 17062 $g_{product}/g_{Cr}$ (Table 15, entry 1), demonstrating that the nature of the MAO had indeed changed.

Interestingly however, selectivity remained mostly unchanged (Table 15, entries 1-2). This was further supported when a solution of partially fluorinated MAO in toluene (F-MAO, 10 wt%) was used as the co-catalyst (entries 3-5). Productivity increased by 20-50% while selectivity was not affected. These observations remained consistent in reactions using both catalysts in both chloro- and fluorobenzene. This is in sharp contrast to reports by McGuiness and coworkers in which various co-catalysts, albeit quasi-stoichiometric and non-aluminoxane, were compared in reactions showing significant differences in activity and selectivity.[58] Nevertheless, initial reports on ethylene tetramerization revealed that selectivity is not affected in reactions utilizing various aluminoxanes,[45] in line with the results presented herein.

Table 15. Oligomerization reactions using different activators.[a]

entry (complex)	aluminoxane	solvent	productivity ($g_{product}/g_{Cr}$)	PE (wt%)	C-6 (wt%)	C-8 (wt%)	C-10 (wt%)	>C-10 (wt%)	1-C6 in C6 (%)	1-C8 in C8 (%)	1-C8/1-C6 (molar)
1 (**24**)	MAO*	PhCl	17,062	0.2	38	31	7	23	82	95	0.718
2 (**24**)	MAO*	PhF	15,904	0.2	30	42	4	24	73	97	1.39
3 (**24**)	F-MAO	PhCl	13,103	1	37	28	10	23	85	92	0.622
4 (**24**)	F-MAO	PhF	12,670	0.6	30	43	4	23	74	98	1.43
5 (**25**)	F-MAO	PhCl	20,349	0.4	34	21	14	30	94	84	0.410

[a] Conditions: precatalyst (0.008 mmol), solvent (20 mL), aluminoxane (300 eq., 10% in toluene), C_2H_4 (4 atm), 25 °C, 90 min.

Conclusions

A series of chromium(III) complexes supported by PNP diphosphine ligands have been synthesized. The ligands feature ether or amine tethers of various lengths and rigidity. In the solid state, the complexes display a chloro-bridged dimeric geometry with the donor functionality not coordinated to chromium. Upon activation with MAO, these chromium complexes are active catalysts for the selective trimerization and tetramerization of ethylene to 1-hexene and 1-octene, respectively. It was shown that ligand modification has a considerable influence on the reaction outcome. While longer ether tethers increase catalyst lifetime by acting as hemilabile donors that stabilize the chromium center, adding rigidity to the linker enhances catalyst activity. Furthermore, the complexes containing an ether tether display higher stability than similar species lacking the donor functionality, which in turns results in higher total productivity. Increasing ethylene pressures favors 1-octene formation over 1-hexene. The detection of minor C_6 products, methylcyclopentane and methylenecyclopentane, may suggest that 1-hexene arises *via* a stepwise mechanism involving a hexenyl-hydride, rather than a concerted loss by a 3,7-hydride shift from the chromacycloheptane. Higher reaction temperatures result in lower productivity and a significant increase in polymer formation, presumably due to the decomposition of the oligomerization catalyst to a chromium species capable of polymerizing ethylene. Catalyst decomposition is second-order in chromium and was shown not to involve PNP ligand dissociation. Moreover, it was shown that ethylene oligomerization reactions exhibit striking solvent effects such that simple modifications

of the reaction medium can significantly alter the outcome of the reaction. It is clear that solvent polarity affects activity, presumably by assisting ion-pair separation, which generates a more effective cationic active species and reduces competitive coordination of the counteranion. An additional surprising observation is the 1-hexene/1-octene selectivity dependence on the reaction solvent. While apparently non-coordinating solvents such as toluene and fluorobenzenes favor the latter in contrast to chlorobenzenes, experiments run with coordinating additives consistently exhibit enhanced 1-octene selectivity. While it is not yet clear why coordinating additives increase 1-octene selectivity, these experiments are supported by the comparison of oligomerization reactions using a catalyst containing a potentially coordinating donor functionality tethered to the PNP ligand and a catalyst lacking one. Indeed, higher selectivity towards the larger α-olefin is observed in all cases studied involving the system featuring the coordinating functionality. Solvents can be mixed resulting in highly tunable media allowing optimization of catalyst performance, such as productivity and selectivity, while lowering potential process cost. Finally, modifications of the aluminoxane co-catalyst were shown to contribute significantly towards catalyst activity while selectivity remained unchanged.

Experimental Section

General Considerations. All air- and moisture-sensitive compounds were manipulated using standard vacuum line, Schlenk, or cannula techniques or in a glovebox under a

nitrogen atmosphere. All gases were purified by passage over MnO on vermiculite and activated molecular sieves. Solvents for air- and moisture-sensitive reactions were dried over sodium benzophenone ketyl, calcium hydride, or by the method of Grubbs.[59] Chloroform-*d* was purchased from Cambridge Isotopes and dried over activated molecular sieves. Dichloromethane-d_2 was purchased from Cambridge Isotopes and distilled from calcium hydride. Other materials were used as received. *o*-Ethylbenzylamine hydrochloride was purchased from Rare Chemicals. N-[2-(Aminomethyl)phenyl]-N,N-dimethylamine was purchased from Peakdale Molecular. Other amine starting materials, 2-cyanophenol, MAO (10% wt. in toluene), chlorodiphenylphosphine and $(THF)_3CrCl_3$ were purchased from Aldrich. F-MAO (10% wt. in toluene) was obtained from Albemarle.

Instrumentation. ^1H and ^{31}P NMR spectra were recorded on a Varian Mercury 300 spectrometer at 299.868 MHz and 121.389 MHz respectively, at room temperature. ^2H NMR spectra were recorded on a Varian INOVA-500 spectrometer at 76.848 MHz at room temperature. All ^1H NMR chemical shifts are reported relative to TMS, and ^1H (residual) chemical shifts of the solvent are used as secondary standard. ^{31}P NMR chemical shifts are reported relative to an external H_3PO_4 (85%) standard. GC measurements were taken on an Agilent 6890 Series GC using an Agilent HP-5 column. Elemental analyses were performed by Desert Analytics, Tuscon, AZ. X-ray crystallography was carried out by Dr. Michael W. Day and Lawrence M. Henling using an Enraf-Nonius CAD-4 diffractometer.

Synthesis of $(C_6H_5)_2PN(CH_2CH_2OCH_3)P(C_6H_5)_2$ (15). Chlorodiphenylphosphine (4.5 mL, 24 mmol, 2.3 equiv.) was dissolved in dry toluene (150 mL). Under an atmosphere

of argon, an excess of triethylamine (5.0 mL, 36 mmol) was syringed into the reaction flask, which was stirred for 5 minutes. 2-Methoxyethylamine (0.9 mL, 10 mmol) was then syringed dropwise under argon. A precipitate immediately formed. The reaction mixture was then allowed to stir for 36 hrs at 110 ºC. The ammonium salt was filtered off and the solvent and the excess triethylamine and chlorodiphenylphosphine were removed *in vacuo* to leave a yellow residue. The residue was passed through a silica gel plug using a CH_2Cl_2 (15%) / petroleum ether (85%) mixture as the eluent. Removing the solvent afforded 2.905 g of a fine white powder in 63% yield. ^{1}H NMR (RT, 300 MHz, $CDCl_3$): δ = 2.90 (2H, t, J_{HH} = 7.4 Hz, C*H*$_2$O), 3.02 (3H, s, OC*H*$_3$), 3.47 (2H, m, C*H*$_2$), 7.29 – 7.44 (20H, m, Ar*H*). ^{31}P NMR (RT, 121 MHz, $CDCl_3$): δ = 64.6 ppm (s). MS (FAB+): 444 (M+H).

Synthesis of $(C_6H_5)_2PN(CH_2CH_2CH_2OCH_3)P(C_6H_5)_2$ (16). Chlorodiphenylphosphine (4.9 mL, 26 mmol, 2.5 equiv.) was dissolved in dry toluene (150 mL). Under an atmosphere of argon, an excess of triethylamine (8.0 mL, 58 mmol) was syringed into the reaction flask, which was stirred for 5 minutes. 3-Methoxypropylamine (1.1 mL, 11 mmol) was then syringed dropwise under argon. A precipitate immediately formed. The reaction mixture was then allowed to stir for 36 hrs at 110 ºC. The ammonium salt was filtered off and the solvent and the excess triethylamine and chlorodiphenylphosphine were removed *in vacuo* to leave a yellowish residue. The residue was passed through a silica gel plug using a CH_2Cl_2 / petroleum ether (1:1) mixture as the eluent. Removing the solvent and trituration with petroleum ether afforded 3.564g of a fine white powder in 75% yield. ^{1}H NMR (RT, 300 MHz, $CDCl_3$): δ = 1.39 (2H, br tt, J_{HH} = 8.1 Hz, J_{HH} = 6.3 Hz, C*H*$_2$), 3.03 (2H, t, J_{HH} = 6.3 Hz, C*H*$_2$O), 3.10 (3H, s, OC*H*$_3$), 3.27 – 3.44 (2H, m,

NCH_2), 7.28 – 7.46 (20H, m, ArH). ^{31}P NMR (RT, 121 MHz, $CDCl_3$): δ = 63.1 ppm (s). MS (FAB+): 458 (M+H).

Synthesis of $(C_6H_5)_2PN((o\text{-}OCH_3)C_6H_4)P(C_6H_5)_2$ (17). Chlorodiphenylphosphine (5.8 mL, 31 mmol, 2.3 equiv.) was dissolved in dry THF (150 mL). Under an atmosphere of argon, an excess of triethylamine (9.0 mL, 65 mmol) was syringed into the reaction flask, which was stirred for 5 minutes. *o*-Anisidine (1.5 mL, 14 mmol) was then syringed dropwise under argon. A precipitate immediately formed and the mixture turned deep yellow. The reaction mixture was then allowed to stir for 24 hrs at 62 ºC. The reaction can only afford about 75% conversion (longer reaction times do not increase conversion). The solvent and the excess trimethylamine and chlorodiphenylphosphine were removed *in vacuo*. The yellow residue was dissolved in CH_2Cl_2 and washed with 10% NaOH. The organic fraction was dried over $MgSO_4$ and the solvent removed after filtration, which afforded a yellow oil. After dissolving the oil in a minimum amount of CH_2Cl_2, petroleum ether was added and a white powder crashed out at room temperature to give 4.642 g of the desired compound in 70% yield. ^{1}H NMR (RT, 300 MHz, $CDCl_3$): δ = 3.29 (3H, s, OCH_3), 6.79 – 6.71 (1H, m, ArH), 7.01 – 7.11 (1H, m, ArH), 7.16 –7.51 (20H, m, ArH), 7.55 – 7.65 (1H, m, ArH), 7.73 – 7.83 (1H, m, ArH). ^{31}P NMR (RT, 121 MHz, $CDCl_3$): δ = 65.5 ppm (s). MS (FAB+): 491 (M+H).

Synthesis of $(C_6H_5)_2PN(CH_2(o\text{-}OCH_3)C_6H_4)P(C_6H_5)_2$ (18). Chlorodiphenylphosphine (4.6 mL, 24.7 mmol, 2.5 equiv.) was dissolved in dry CH_2Cl_2 (150 mL). Under an atmosphere of argon, an excess of triethylamine (7.0 mL, 50.6 mmol) was syringed into the reaction flask, which was stirred for 5 minutes. 2-methoxybenzylamine (1.3 mL, 9.9 mmol) was then syringed dropwise under argon. A precipitate immediately formed and

the mixture turned deep yellow. The reaction mixture was then allowed to stir for 14 hrs at 37 °C. The solvent and the excess trimethylamine and chlorodiphenylphosphine were removed *in vacuo*. The yellow residue was dissolved in CH_2Cl_2 and washed with 10% NaOH. The organic fraction was dried over $MgSO_4$ and the solvent removed after filtration, which afforded an off-white solid. After dissolving the solid in a minimum amount of CH_2Cl_2, acetonitrile was added and a white powder crashed out at room temperature to give 3.366 g of the desired compound in 67% yield. ^{1}H NMR (RT, 300 MHz, $CDCl_3$): δ = 3.70 (3H, s, OC*H*$_3$), 4.47 (2H, t, J_{HP} = 9.2 Hz, C*H*$_2$), 6.66 – 6.84 (3H, m, NCH$_2$Ar*H*), 7.09 – 7.18 (1H, m, NCH$_2$Ar*H*), 7.22 – 7.32 (12H, m, Ar*H*), 7.35 – 7.44 (8H, m, Ar*H*). ^{31}P NMR (RT, 121 MHz, $CDCl_3$): δ = 59.9 ppm (s). MS (Direct Insertion Probe EI): 505.17.

Synthesis of $(C_6H_5)_2PN(CH(CH_3)_2)P(C_6H_5)_2$ (19). Chlorodiphenylphosphine (4.0 mL, 21.5 mmol, 2.3 equiv.) was dissolved in dry CH_2Cl_2 (150 mL). Under an atmosphere of argon, an excess of triethylamine (5.5 mL, 39.8 mmol) was syringed into the reaction flask, which was stirred for 5 minutes. isopropylamine (0.8 mL, 9.4 mmol) was then syringed dropwise under argon. The reaction mixture was then allowed to stir for 14 hrs at room temperature. The solvent and the excess trimethylamine and chlorodiphenylphosphine were removed *in vacuo*. The yellow residue was dissolved in Et_2O and washed with 1M NaOH. The organic fraction was dried over $MgSO_4$ and the solvent removed after filtration, which afforded an off-white oil. After dissolving the oil in a minimum amount of CH_2Cl_2, acetonitrile was added and a white powder crashed out at room temperature to give 2.823 g of the desired compound in 71% yield. ^{1}H NMR

(RT, 300 MHz, $CDCl_3$): δ = 1.15 (6H, d, J_{HH} = 6.5 Hz, $CH(CH_3)_2$), 3.76 (1H, m, $CHMe_2$), 7.25 – 7.41 (20H, m, Ar*H*). ^{31}P NMR (RT, 121 MHz, $CDCl_3$): δ = 49.5 ppm (s).

Synthesis of $(C_6H_5)_2PN(CH_2(o\text{-}CH_2CH_3)C_6H_4)P(C_6H_5)_2$ (20). Chlorodiphenylphosphine (1.9 mL, 10.1 mmol, 2.3 equiv.) was dissolved in dry CH_2Cl_2 (80 mL). Under an atmosphere of argon, an excess of triethylamine (3.5 mL, 25.3 mmol) was syringed into the reaction flask, which was stirred for 5 minutes. *o*-Ethylbenzylamine hydrochloride (0.750 g, 4.4 mmol), as a CH_2Cl_2 suspension was then added to the reaction flask. The reaction mixture was then allowed to stir for 14 hrs at room temperature. The solvent and the excess trimethylamine and chlorodiphenylphosphine were removed *in vacuo*. The yellow residue was dissolved in CH_2Cl_2 and washed with 10% NaOH. The organic fraction was dried over $MgSO_4$ and the solvent removed after filtration, which afforded an off-white oil. After dissolving the oil in a minimum amount of CH_2Cl_2, acetonitrile was added and a white powder crashed out at room temperature to give 1.474 g of the desired compound in 67% yield. ^{1}H NMR (RT, 300 MHz, $CDCl_3$): δ = 1.11 (3H, t, J_{HH} = 7.6 Hz, CH_2CH_3), 2.59 (2H, q, J_{HH} = 7.6 Hz, CH_2CH_3), 4.46 (2H, t, J_{HP} = 9.7 Hz, NCH_2Ar), 6.66 - 6.75 (1H, m, NCH_2ArH), 6.87 - 6.97 (1H, m, NCH_2ArH), 7.05 - 7.12 (2H, m, NCH_2ArH), 7.19 – 7.45 (20H, m, Ar*H*). ^{31}P NMR (RT, 121 MHz, $CDCl_3$): δ = 59.8 ppm (s). HRMS (Direct Insertion Probe EI) *m* / *z* calcd for $C_{33}H_{31}NP_2$ 503.1932, found 503.1940.

Synthesis of $[CrCl_2(15)(\mu\text{-}Cl)]_2$ (21). In the glovebox, **15** (0.335 g, 0.7554 mmol) was dissolved in CH_2Cl_2 (3 mL). $(THF)_3CrCl_3$ (0.283 g, 0.7554 mmol) was dissolved in CH_2Cl_2 (7 mL) in a separate vial. The chromium starting material solution was slowly added to the stirring solution of **15**. The mixture, which immediately turned blue, was

allowed to react for 10 minutes after which the solvent was pumped off. The residue was triturated twice with CH_2Cl_2. The remaining solid was recrystallized from CH_2Cl_2/petroleum ether to give a bright blue/violet powder. Yield: 0.344 g (76%). Anal. calcd. for $C_{54}H_{54}Cl_6Cr_2N_2O_2P_4$ (%): C, 53.89; H, 4.52; N, 2.33. Found: C, 53.63; H, 4.60; N, 2.26.

Synthesis of $[CrCl_2(16)(\mu\text{-}Cl)]_2$ (22). In the glovebox, **16** (0.494 g, 1.080 mmol) was dissolved in CH_2Cl_2 (3 mL). $(THF)_3CrCl_3$ (0.405 g, 1.080 mmol) was dissolved in CH_2Cl_2 (7 mL) in a separate vial. The chromium starting material solution was slowly added to the stirring solution of **16**. The mixture, which immediately turned blue, was allowed to react for 10 minutes after which the solvent was pumped off. The residue was triturated twice with CH_2Cl_2. The remaining solid was recrystallized from CH_2Cl_2/petroleum ether to give a blue powder. Yield: 0.599 g (90%). Anal. calcd. for $C_{56}H_{58}Cl_6Cr_2N_2O_2P_4$ (%): C, 54.61; H, 4.75; N, 2.27. Found: C, 53.42; H, 5.08; N, 1.93.

Synthesis of $[CrCl_2(17)(\mu\text{-}Cl)]_2$ (23). In the glovebox, **17** (0.364 g, 0.7406 mmol) was dissolved in CH_2Cl_2 (3 mL). $(THF)_3CrCl_3$ (0.278 g, 0.7406 mmol) was dissolved in CH_2Cl_2 (7 mL) in a separate vial. The chromium starting material solution was slowly added to the stirring solution of **17**. The mixture, which immediately turned blue, was allowed to react for 10 minutes after which the solvent was pumped off. The residue was triturated twice with CH_2Cl_2. The remaining solid was recrystallized from CH_2Cl_2/petroleum ether to give a dark blue powder. Yield: 0.119 g (25%). Anal. calcd. for $C_{62}H_{54}Cl_6Cr_2N_2O_2P_4$ (%): C, 57.29; H, 4.19; N, 2.16. Found: C, 56.11; H, 4.93; N, 1.95.

Synthesis of $[CrCl_2(18)(\mu\text{-}Cl)]_2$ (24). In the glovebox, **18** (0.547 g, 1.081 mmol) was dissolved in CH_2Cl_2 (3 mL). $(THF)_3CrCl_3$ (0.405 g, 1.081 mmol) was dissolved in CH_2Cl_2 (7 mL) in a separate vial. The chromium starting material solution was slowly added to the stirring solution of **18**. The mixture, which immediately turned blue, was allowed to react for 10 minutes after which the solvent was pumped off. The residue was triturated twice with CH_2Cl_2. The remaining solid was recrystallized from CH_2Cl_2/petroleum ether to give a bright purple powder. Yield: 0.621 g (86%). Anal. calcd. for $C_{64}H_{58}Cl_6Cr_2N_2O_2P_4$ (%): C, 57.89; H, 4.40; N, 2.11. Found: C, 57.78; H, 4.56; N, 1.98. HRMS (FAB+) *m* / *z* calcd for $C_{64}H_{58}Cl_5Cr_2N_2O_2P_4$ (M-Cl) 1291.0672, found 1292.0692.

Synthesis of $[CrCl_2(19)(\mu\text{-}Cl)]_2$ (25). In the glovebox, **19** (0.462 g, 1.081 mmol) was dissolved in CH_2Cl_2 (3 mL). $(THF)_3CrCl_3$ (0.405 g, 1.081 mmol) was dissolved in CH_2Cl_2 (7 mL) in a separate vial. The chromium starting material solution was slowly added to the stirring solution of **19**. The mixture, which immediately turned blue, was allowed to react for 10 minutes after which the solvent was pumped off. The residue was triturated twice with CH_2Cl_2. The remaining solid was recrystallized from CH_2Cl_2/petroleum ether to give a purple powder. Yield: 0.530 g (84%). Anal. calcd. for $C_{54}H_{54}Cl_6Cr_2N_2P_4$ (%): C, 55.36; H, 4.65; N, 2.39. Found: C, 53.83; H, 5.01; N, 2.26. HRMS (FAB+) *m* / *z* calcd for $C_{54}H_{54}Cl_5Cr_2N_2P_4$ (M-Cl) 1135.0461, found 1135.0598.

Synthesis of $[CrCl_2(20)(\mu\text{-}Cl)]_2$ (26). In the glovebox, **20** (0.602 g, 1.195 mmol) was dissolved in CH_2Cl_2 (3 mL). $(THF)_3CrCl_3$ (0.448 g, 1.195 mmol) was dissolved in CH_2Cl_2 (7 mL) in a separate vial. The chromium starting material solution was slowly added to the stirring solution of **20**. The mixture, which immediately turned blue, was

allowed to react for 10 minutes after which the solvent was pumped off. The residue was triturated twice with CH_2Cl_2. The remaining solid was recrystallized from CH_2Cl_2/petroleum ether to give a bright pruple powder. Yield: 0.578 g (73%). Anal. calcd. for $C_{66}H_{62}Cl_6Cr_2N_2P_4$ (%): C, 59.88; H, 4.72; N, 2.12. Found: C, 58.63; H, 5.03; N, 1.80. HRMS (FAB+) *m* / *z* calcd for $C_{66}H_{62}Cl_5Cr_2N_2P_4$ (M-Cl) 1287.1087, found 1287.0411.

Synthesis of $(C_6H_5)_2PN(CH_2(o\text{-}OCD_3)C_6H_4)P(C_6H_5)_2$ (29). In a bomb was placed NaH (1.952 g, 81.34 mmol, 1.3 equiv.) and THF (50 mL). In another bomb was dissolved 2-cyanophenol (7.454 g, 62.58 mmol) in THF (30 mL). The cyanophenol solution was slowly syringed onto the NaH suspension, which was kept at 0 ^oC. The mixture was allowed to react for an hour under heavy stirring. After the deprotonation was complete, CD_3I (4.7 mL, 75.10 mmol, 1.2 equiv.) was syringed in. The resulting mixture was allowed to react at 69 ^oC for 2 days protected from light. After reaction, the mixture was quenched with $NH_4Cl_{(aq)}$ and extracted with Et_2O, washed with H_2O, $Na_2S_2O_3$, NaOH and brine. The organic layer was dried over $MgSO_4$ and the solvent removed on the rotovap. After distillation, 7.593 g (89%) of the desired 2-cyanoanisole-d_3 (**27**) were collected and its purity confirmed by GC-MS.

The following step, consisting of the reduction of the nitrile to the amine, was modified from a reported procedure.[49] In a flask, **27** (7.300 g, 53.61 mmol) was dissolved in THF (50 mL). $BH_3{\cdot}SMe_2$ (6.35 mL, 58, 97 mmol, 1.1. equiv.) was then slowly added to the mixture under argon. The flask was sealed and the reaction stirred for 30 min at 69 ^oC, after which the flask was degassed. This was repeated twice before the mixture was allowed to react overnight at 69 ^oC. The reaction was then cooled to room temperature

and HCl (6 N, 32.2 mL) was added dropwise. The mixture was then heated to 69 ^{o}C for 2 hrs. The solution is then cooled to 0 ^{o}C and NaOH (7.237 g, 289.5 mmol) was added. The liberated amine was extracted with Et_2O (3 x 10 mL) and dried over Na_2CO_3. Distillation under full vacuum generated 6.377 g of the desired amine **28** in 85% yield and determined to be pure by GC.

Chlorodiphenylphosphine (3.7 mL, 19.61 mmol, 2.5 equiv.) was dissolved in dry CH_2Cl_2 (100 mL). Under an atmosphere of argon, an excess of triethylamine (5.5 mL, 39.8 mmol) was syringed into the reaction flask, which was stirred for 5 minutes. **28** (0.900 g, 6.419 mmol) was then syringed dropwise under argon. A precipitate immediately formed and the mixture turned deep yellow. The reaction mixture was then allowed to stir for 14 hrs at 37 ^{o}C. The solvent and the excess trimethylamine and chlorodiphenylphosphine were removed *in vacuo*. The yellow residue was dissolved in CH_2Cl_2 and washed with 10% NaOH. The organic fraction was dried over $MgSO_4$ and the solvent removed after filtration, which afforded an off-white solid. After dissolving the solid in a minimum amount of CH_2Cl_2, acetonitrile was added and a white powder crashed out at room temperature to give 1.796 g of the desired compound in 55% yield. ^{1}H NMR (RT, 300 MHz, $CDCl_3$): δ = 4.47 (2H, t, J_{HP} = 9.2 Hz, C*H*$_2$), 6.66 – 6.84 (3H, m, NCH$_2$Ar*H*), 7.09 – 7.18 (1H, m, NCH$_2$Ar*H*), 7.22 – 7.32 (12H, m, Ar*H*), 7.35 – 7.44 (8H, m, Ar*H*). ^{31}P NMR (RT, 121 MHz, $CDCl_3$): δ = 59.9 ppm (s).

Synthesis of [$CrCl_2$(29)(*μ*-Cl)]$_2$ (30). In the glovebox, **29** (0.508 g, 0.9989 mmol) was dissolved in CH_2Cl_2 (3 mL). $(THF)_3CrCl_3$ (0.374 g, 0.9989 mmol) was dissolved in CH_2Cl_2 (7 mL) in a separate vial. The chromium starting material solution was slowly added to the stirring solution of **29**. The mixture, which immediately turned blue, was

allowed to react for 10 minutes after which the solvent was pumped off. The residue was triturated twice with CH_2Cl_2. The remaining solid was recrystallized from CH_2Cl_2/petroleum ether to give a bright purple powder. Yield: 0.499 g (75%). ^{2}H NMR (RT, 77 MHz, CD_2Cl_2): δ = 3.27 ppm (s). HRMS (FAB+) *m* / *z* calcd for $C_{64}H_{52}D_6Cl_5Cr_2N_2O_2P_4$ (M-Cl) 1297.1049, found 1297.1246.

Synthesis of $(C_6H_5)_2PN(CH_2(o\text{-}N(CH_3)_2)C_6H_4)P(C_6H_5)_2$ (31). Chlorodiphenylphosphine (2.2 mL, 11.91 mmol, 2.5 equiv.) was dissolved in dry CH_2Cl_2 (150 mL). Under an atmosphere of argon, an excess of triethylamine (3.5 mL, 25.3 mmol) was syringed into the reaction flask, which was stirred for 5 minutes. N-[2-(Aminomethyl)phenyl]-N,N-dimethylamine (0.7 mL, 4.753 mmol) was then syringed dropwise under argon. The reaction mixture was then allowed to stir for 14 hrs at 37 ^{o}C. The solvent and the excess trimethylamine and chlorodiphenylphosphine were removed *in vacuo*. The yellow residue was dissolved in CH_2Cl_2 and washed with 10% NaOH. The organic fraction was dried over $MgSO_4$ and the solvent removed after filtration, which afforded an off-white solid. After dissolving the solid in a minimum amount of CH_2Cl_2, acetonitrile was added and a white powder crashed out at room temperature to give 1.645 g of the desired compound in 67% yield. ^{1}H NMR (RT, 300 MHz, $CDCl_3$): δ = 2.54 (6H, s, N(C*H*$_3$)$_2$), 4.58 (2H, t, J_{HP} = 10.2 Hz, C*H*$_2$), 6.75 – 6.82 (1H, m, NCH$_2$Ar*H*), 6.90 – 7.00 (2H, m, NCH$_2$Ar*H*), 7.06 – 7.13 (1H, m, NCH$_2$Ar*H*), 7.22 – 7.31 (12H, m, Ar*H*), 7.34 – 7.41 (8H, m, Ar*H*). ^{31}P NMR (RT, 121 MHz, $CDCl_3$): δ = 61.2 ppm (s).

Synthesis of $[CrCl_2(31)(\mu\text{-}Cl)]_2$ (32). In the glovebox, **31** (0.455 g, 0.8774 mmol) was dissolved in CH_2Cl_2 (3 mL). $(THF)_3CrCl_3$ (0.329 g, 0.8774 mmol) was dissolved in

CH_2Cl_2 (7 mL) in a separate vial. The chromium starting material solution was slowly added to the stirring solution of **31**. The mixture, which immediately turned blue, was allowed to react for 10 minutes after which the solvent was pumped off. The residue was triturated twice with CH_2Cl_2. The remaining solid was recrystallized from CH_2Cl_2/petroleum ether to give a bright purple powder. Yield: 0.364 g (62%). Anal. calcd. for $C_{66}H_{64}Cl_6Cr_2N_4P_4$ (%): C, 58.55; H, 4.76; N, 4.14. Found: C, 55.61; H, 4.85; N, 3.76.

General procedure for oligomerization of C_2H_4 (1 atm) with 21-26, 32/MAO. In the glove box, a 250 mL round bottom flask was charged with the appropriate precatalyst (0.020 mmol, 1 equiv.) in 50 mL of PhCl to give a pale bluish-purple solution. The flask was equipped with a 180° needle valve, fully degassed on the vacuum line at –78˚C. The system was allowed to warm up to 25 ºC and was backfilled with 1 atmosphere of ethylene. With a positive pressure of ethylene, the valve was replaced with a septum and MAO (10 %wt. in toluene, 3.2 mL, 300 equiv.) was syringed in. The mixture immediately turned green upon addition. Ethylene consumption was monitored using a mercury manometer. After the indicated reaction time, the mixture was quenched with HCl/MeOH. An aliquot of the organic fraction was separated and filtered through a plug of activated alumina to remove any chromium. This mixture was analyzed by GC and GC-MS. All identified products were quantified by comparison to a mesitylene standard, which was added to the reaction mixture. The reaction mixture was then filtered and any solid was washed with HCl/MeOH and dried under vacuum for 15 hours and weighed.

General procedure for oligomerization of C_2H_4 at high pressure. In the glovebox, a 225 mL high pressure glass vessel was charged with the chromium precatalyst (0.020

mmol, 1 equiv.) in 50 mL of PhCl to give a pale bluish-purple solution. The vessel was equipped with a regulator and placed on the high pressure setup. Ethylene was purged through the system after which MAO (10% wt. in toluene, 3.2 mL, 300 equiv.) was added via syringe. The mixture immediately turned green upon addition. Ethylene pressure was kept constant during the reaction (90 min), after which the system was vented and the reaction mixture quenched with HCl/MeOH. An aliquot of the organic fraction was separated and filtered through a plug of activated alumina to remove any chromium. This mixture was analyzed by GC and GC-MS. All identified products were quantified by comparison to a mesitylene standard, which was added to the reaction mixture. The reaction mixture was then filtered and any solid was washed with HCl/MeOH and dried under vacuum for 15 hours and weighed.

General procedure for oligomerization of C_2H_4 at high pressure. This procedure was followed for reactions requiring pressures higher than 8 atm ethylene. The procedure is the same as above, however a 85 mL high pressure glass vessel was employed for the reaction. Furthermore, 0.008 mmol of precatalyst, 20 mL of PhCl and 1.3 mL of MAO solution in toluene (300 equiv.) were used.

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