Chapter 2

Investigations of the Effect of Ligand Array on Polymer Molecular Weight Using Scandocene Tetramethylaluminate Complexes as Models for α-Olefin Polymerization Catalysts

Abstract

Preparation of a series of scandocene tetramethylaluminate complexes is reported. $Ind_2Sc(\mu\text{-}Me)_2AlMe_2$ (**1**), $Cp_2Sc(\mu\text{-}Me)_2AlMe_2$ (**2**), $Cp^*CpSc(\mu\text{-}Me)_2AlMe_2$ (**3**), and *meso*-$DpSc(\mu\text{-}Me)_2AlMe_2$ (**4**) have been prepared and characterized by ^1H NMR spectroscopy. These complexes all display characteristic terminal and bridging methyl resonances in solution at room temperature, indicating static structures. Complex **4** has been characterized by X-ray crystallography and shows bonding of the bridging methyl groups through both a scandium-carbon bond and a σ interaction between the carbon-hydrogen bonds and scandium. Complexes **1**-**4** oligomerize 1-pentene to form a range of oligomers. Complex **1** gives a distribution of oligomer products that more closely resembles a Poisson distribution than a Flory-Schulz distribution of products, which is typical for linear step polymerizations, indicating that this catalyst undergoes facile chain transfer reactions to reincorporate oligomer fractions that have been eliminated. Complex **2** gives a Flory-Schulz distribution of oligomer products. Complexes **3** and **4** only give very low molecular weight oligomers (dimer-pentamer). Analysis of GC-MS data shows that the tetramethylaluminate complexes initiate oligomerization from a scandium-methyl species and that the primary mechanism of chain transfer is β-hydrogen elimination, although there is some chain transfer to aluminum. Complexes **1**-**4** react with dimethylaminopyridine (DMAP) to form $(R_nCp)_2ScMe(DMAP)$ compounds (**5**, **8**, **9**), and **1** reacts with L donors (L = THF, PMe_3) to form $Ind_2ScMe(L)$ complexes (**6**, **7**). Addition of $AlMe_3$ to **1** dramatically retards its reaction with α-olefins, implying that the reaction of tetramethylaluminate catalysts with olefins is dissociative in $AlMe_3$. We observe that addition of less than two equivalents of DMAP to **1**-**4** catalyzes their reaction with α-olefins, while addition of two equivalents of DMAP slows these reactions.

Introduction

Although the effect of catalyst geometry on polymer stereochemistry for metallocene-catalyzed α-olefin polymerization has been well established,[1] the way in which ligand array affects polymer molecular weight is not well characterized. Understanding the factors that dictate polymer molecular weight is essential; current homogeneous metallocene catalysts are of minimal industrial use as they produce poly(α-olefins) of significantly lower molecular weight than polymers made by heterogeneous catalysts.[2] In order to understand the correlation between ligand array and molecular weight, the fundamental transformations that determine molecular weight must be examined. The active metallocene catalyst undergoes an initial olefin insertion into the metal-alkyl or -hydride bond (initiation), followed by repeating olefin insertions to build the polymer chain (propagation). The polymer chain is released from the active catalyst by chain transfer (termination), which may proceed via β-hydrogen transfer, β-methyl transfer, chain transfer to an aluminum cocatalyst, or chain transfer to an added transfer agent, such as H_2 or $SiHR_3$.[3] Figure 1 illustrates the polymerization mechanism with the most common chain transfer mechanism for metallocene catalysts, β-hydrogen transfer to the metal (β-hydrogen elimination). The molecular weight of the polymer produced is thus proportional to the rate of propagation (k_{prop}) relative to the rate of chain transfer (k_{CT}), as shown in Equation 1.

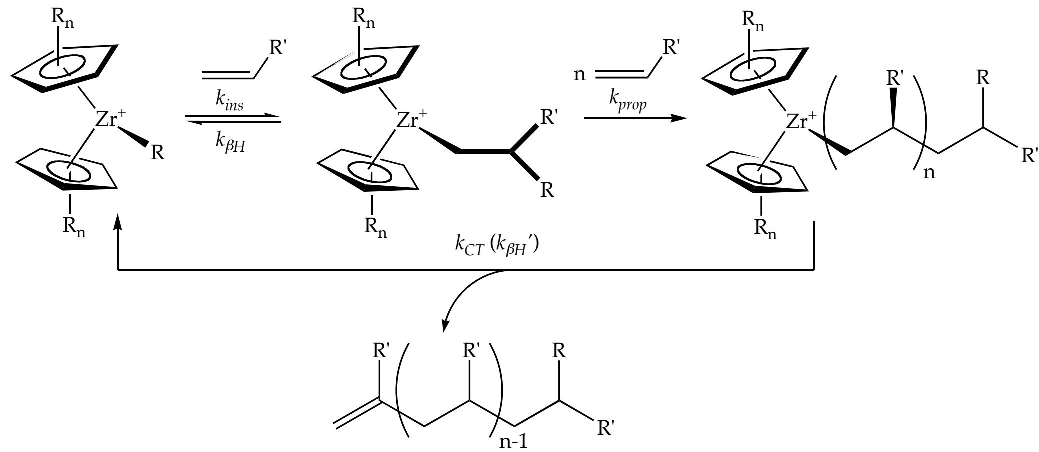


Figure 1. Fundamental steps in metallocene-catalyzed α-olefin polymerization (R = H, alkyl; R′ = alkyl).

$$\text{M.W.} \quad \alpha \quad \frac{k_{prop}}{k_{CT}} \qquad (1)$$

There has been some effort to characterize the key features of metallocene catalysts that are capable of producing polypropylene of the highest molecular weights. A series of catalysts reported by Spaleck utilizing dimethylsilyl*bis*(indenyl) ligands produce polypropylene with extremely high activities and high molecular weights.[4] Specifically, the zirconocene dichloride complex containing Spaleck's 2-methyl-4-naphthyl-substitued, dimethylsilyl*bis*(indenyl) ligand, shown in Figure 2, produces polypropylene with molecular weights (M_w) of up to 920,000 for polymerizations run at 70 °C, which are some of the highest reported for metallocene catalysts. It is believed that both the methyl substituent and the napthyl substituent and their placements are key to this system's ability to produce high molecular weight polymers. The methyl group increases the overall rigidity of the structure and disfavors 2,1-insertion of olefins by an unfavorable steric interaction with the alkyl substituent on an α-olefin (Figure 3). It is believed that 2,1-insertions deactivate the catalyst towards further α-olefin insertion, as they create a very bulky environment around the zirconium center, thus lowering catalyst activity and polymer molecular weights.[5] Both the methyl and the napthyl group may serve to sterically block conformations that allow interactions between the zirconium and the β-hydrogen of the growing polymer chain, thus making chain termination difficult. Finally, these electron-releasing substituents may lower the Lewis acidity of the active zirconium species, thus reducing its tendency for chain termination by β-hydrogen elimination.

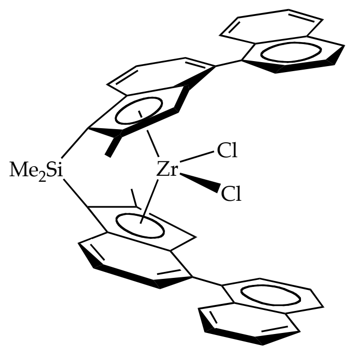


Figure 2. Spaleck's dimethylsilyl*bis*(2-methyl-4-naphthyl-indenyl)$ZrCl_2$ catalyst produces polypropylene of extremely high molecular weight.

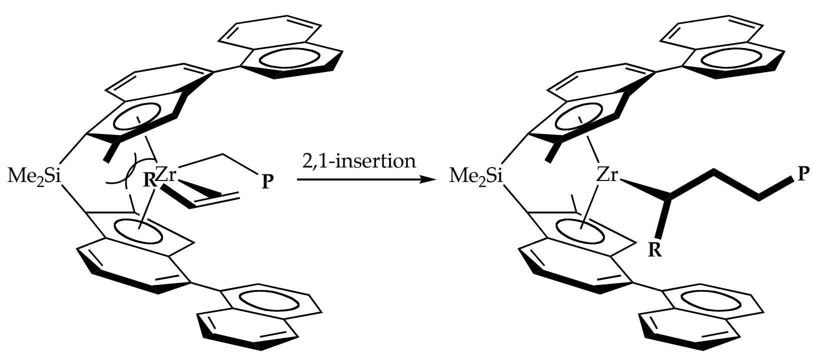


Figure 3. The 2-methyl substituents discourage 2,1-insertion of propylene by unfavorable steric interactions (**R** = alkyl, **P** = polymer chain).

It has been well established that the active species in metallocene-catalyzed α-olefin polymerizations are 14 electron, d^0 metal alkyl or hydride complexes.[6] In the case of a group 4 catalyst, the active complex, $[(R_nCp)_2MR]^+$ (R_nCp = substituted or bridged cyclopentadienyl; M = Ti, Zr, Hf; R = H, alkyl), can be generated by reaction of a metallocene dichloride $(R_nCp)_2MCl_2$ with a large excess of an activator such as methylaluminoxane

($[AlOMe]_x$, abbreviated MAO) or by abstraction of CH_3^- from a metallocene dimethyl complex $(R_nCp)_2MMe_2$ using $B(C_6F_5)_3$, $[(C_6H_5)_3C][B(C_6F_5)_4]$, or $[C_6H_5N(CH_3)_2H][B(C_6F_5)_4]$. These species are cationic and therefore only exist in the presence of one equivalent of an anion.

In the case of a group 3 catalyst, a neutral metallocene $(R_nCp)_2MR$ (M = Sc, Y; R = H, alkyl) may be used as a single component catalyst. It has been shown that neutral yttrocenes can serve as good models for active, cationic group 4 polymerization catalysts.[7] While group 3 metallocenes undergo similar transformations, they are generally less active than their group 4 counterparts.[6] As a consequence, more detailed studies of the individual reactions that occur in the process of polymerizing α-olefins are feasible. Additionally, group 3 catalysts do not possess the added complications of an ill-defined cocatalyst, which is often present in great excess, or the complications of ion-pairing effects.

Unfortunately, monomeric group 3 metallocene alkyl or hydride derivatives are often very difficult to isolate due to their extreme electrophilicity. Such compounds frequently form dimers, coordinate solvents, or form salt adducts in order to remain more electronically saturated by forming 16 or 18 electron complexes.[8] Additionally, group 3 hydride species, $(R_nCp)_2MH$, have been observed to undergo intermolecular C-H activation of the Cp rings to form bridged dimers.[9] Therefore, in order to use group 3 complexes as models for group 4 catalysts, synthetic routes must be designed to provide isolable metallocene compounds with labile ligands that can dissociate easily to allow for coordination and insertion of α-olefins.

Synthesis of group 3 tetramethylaluminate species of the form $(R_nCp)_2M(\mu\text{-}Me)_2AlMe_2$ (M = Sc, Y) is relatively straightforward,[8,10] and these complexes have been observed to insert α-olefins (Figure 4).[11] This is notable because scandocene alkyl or hydride complexes have generally been shown to dimerize α-olefins.[12,6] It is believed that these 16 electron tetramethylaluminate species react with α-olefins via initial dissociation of $AlMe_3$ to give a 14 electron, neutral group 3 methyl species that binds and inserts α-olefins as shown in Scheme 1. Alternatively, the tetramethylaluminate species may react with α-olefins via an associative mechanism whereby addition of α-olefin results in the formation of the active species. These species react with α-olefins in the presence of only one equivalent of $AlMe_3$, thus circumventing the complications created by a large excess of MAO and ion-pairing effects.

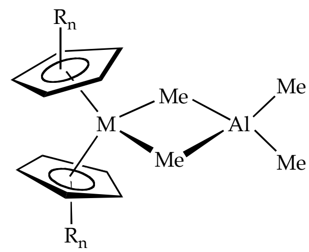
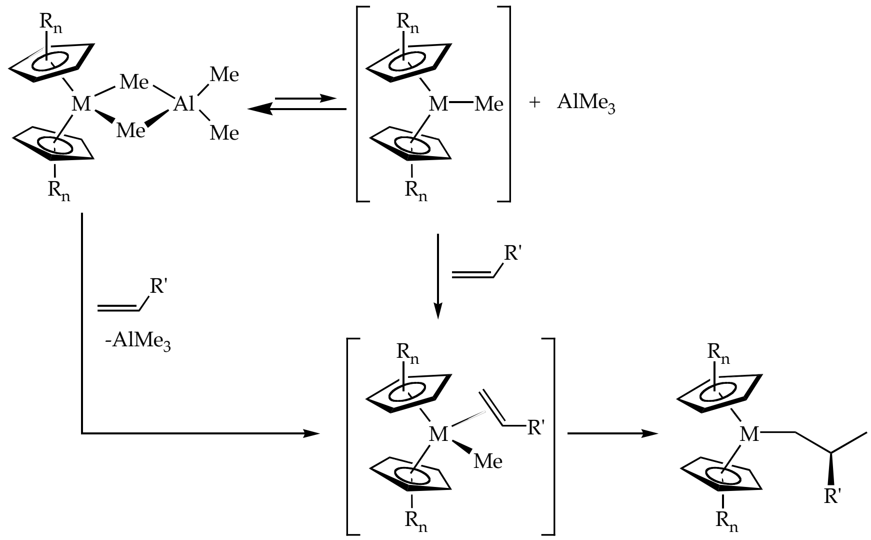


Figure 4. The general structure of a group 3 tetramethylaluminate complex.

Previous studies have shown that (RThp)M(μ-Me)$_2$AlMe$_2$ (RThp = 1,2-(Me$_2$Si)$_2$[{η^5-C$_5$H-3,5-(CHMe$_2$)$_2$}{η^5-C$_5$H$_2$-4-(R)}], R = iPr, tBu; M = Sc, Y) produces polymers of propylene and 1-pentene.[11] For example, (iPrThp)Sc(μ-Me)$_2$AlMe$_2$ produces polypropylene of M_w = 32,100 with PDI = 2.0. These results suggest that group 3 tetramethylaluminate derivatives function as precursors to group 3 alkyl or hydride complexes that can readily insert α-olefins. In an effort to gain insight into the relationship between ligand array and molecular weight, we have prepared a series of scandium tetramethylaluminate complexes with a range of ligand arrays and examined their reactivity toward α-olefins. Attempts have been made to characterize the relationship, if one exists, between ligand substitution and oligomer molecular weight. Further attempts will be made to elucidate the nature of the active species, as well as the mechanisms and rates of chain initiation, propagation, and termination. In addition, this data can be compared to molecular weight data obtained by polymerizations performed by a series of group 4 metallocene dichlorides activated by MAO to assess the validity of this model.

Scheme 1.



This study could enable a correlation to be made between ancillary ligand substitution, polymer molecular weight, and relative rates of the fundamental reactions that occur in the course of group 4 metallocene-catalyzed α-olefin polymerization. Ultimately, this knowledge may allow for tailoring of catalysts to produce polymers of desired molecular weight.

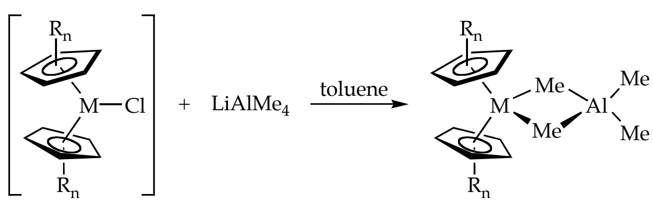
Results and Discussion

The initial goal of this study was to examine metallocene systems containing ligands similar to those used as catalysts industrially that produce polypropylene of high molecular weight. The first example of a homogeneous catalyst used to make isotactic polypropylene was Brintzinger's *rac*-[ethylene*bis*(4,5,6,7-tetrahydroindenyl)]zirconium dichloride (*rac*-(EBTHI)$ZrCl_2$).[13] In fact, many homogeneous catalysts used today for poly(α-olefin) production contain substituted or bridged indenyl ligands. Therefore, initial target molecules were group 3 *bis*(indenyl) chloride complexes as precursors to group 3 tetramethylaluminate complexes. In an attempt to gain a fundamental understanding of the effects of ligand substitution on polymer molecular weight, group 3 metallocenes containing simple cyclopentadienyl, substituted cyclopentadienyl, and bridged cyclopentadienyl ligands have also been isolated and studied.

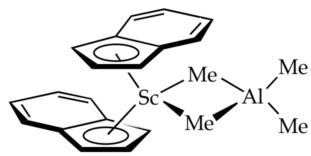
Synthesis and Characterization of Group 3 Tetramethylaluminate Catalysts

A straightforward route to well-defined group 3 alkyl species is via synthesis of tetramethylaluminate complexes. Unlinked group 3 metallocene tetramethylaluminate complexes of the form $Cp_2M(\mu\text{-}CH_3)_2Al(CH_3)_2$ (M = Y, Sc[8,10]) and $Cp^*_2M(\mu\text{-}CH_3)_2Al(CH_3)_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$; M = Sm,[14] Yb, Y[15,16]) have been reported previously. Although the yttrocene complex undergoes rapid exchange between terminal and bridging methyl groups, the scandocene complex exhibits a static structure at room temperature in solution, and distinct terminal and bridging methyl resonance are observed by ^1H NMR. These complexes may be synthesized by reaction of the desired metallocene chloride with lithium tetramethylaluminate in toluene (Scheme 2).[8a]

Scheme 2.

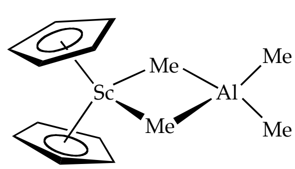


The first ligand array examined was the unlinked, *bis*-indenyl system; the initial target was $Ind_2Sc(\mu\text{-}Me)_2AlMe_2$ (**1**) (Ind = η^5-indenyl, C_9H_7). Toward this end, preparation of $[Ind_2ScCl]$ has been attempted by reaction of $ScCl_3(THF)_3$ with two equivalents of IndLi in refluxing toluene. Although the resulting yellow powder has not been fully characterized, the ^1H NMR spectrum of the complex in THF-d_8 is consistent with the formation of the desired metallocene-chloride complex as the major product. Assuming that the yellow powder is pure $[Ind_2ScCl]$, it can be reacted with 1.3 equivalents of $LiAlMe_4$ in toluene to afford a bright yellow powder, which has been isolated and characterized as **1** in 51% yield. The room temperature ^{1}H NMR spectrum of **1** in benzene-d_6 displays characteristic terminal and bridging methyl resonances at δ = -0.40 and -0.81 ppm, respectively. Observation of distinct terminal and bridging methyl resonances indicates that the structure of **1** is static in solution at room temperature.



1

This methodology has been extended for the synthesis and isolation of $Cp_2Sc(\mu\text{-}Me)_2AlMe_2$ (**2**) as an off-white powder in 52% yield from the reaction of $Cp_2ScCl(THF)$[17] and $LiAlMe_4$ in toluene.[8,10] As with **1**, the room temperature ^{1}H NMR spectrum of **2** in benzene-d_6 exhibits diagnostic terminal and bridging methyl resonances at δ = -0.32 and -0.46 ppm, respectively, indicative of a static structure at room temperature. Reaction of Cp*CpScCl[18] with $LiAlMe_4$ in toluene provides Cp*CpSc(μ-Me)$_2$AlMe$_2$ (**3**) as a pale orange powder in 50% yield. The ^{1}H NMR spectrum of **3** at room temperature in benzene-d_6 displays two terminal methyl resonances and one bridging methyl resonance at δ = -0.21, -0.39, and -0.52 ppm, respectively.



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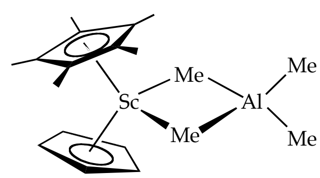
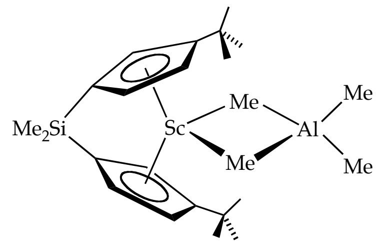


3

This synthetic route has also been extended for the preparation of the *ansa*-metallocene complex *meso*-DpSc(μ-Me)$_2$AlMe$_2$ (**4**) (Dp = $Me_2Si(\eta^5\text{-}C_5H_3\text{-}3\text{-}CMe_3)_2$).



4

Reaction of *meso*-$[DpScCl]_2$[19] with $LiAlMe_4$ in toluene affords **4** as a pale yellow powder in 35% yield. The room temperature ^1H NMR spectrum of **4** in benzene-d_6 displays only three Cp resonances, confirming the presence of exclusively the *meso* isomer of the tetramethylaluminate complex. The presence of two distinct peaks at δ = 0.60 and 0.28 ppm for the methyl groups on the dimethylsilyl linker indicates that this complex may be assigned as the *meso* isomer. The ^1H NMR spectrum of complex **4** shows a characteristic terminal methyl resonance at δ = -0.30 ppm and diagnostic bridging methyl resonances at δ = -0.46 and -0.12 ppm. The ^1H NMR data for the terminal and bridging methyl resonances for complexes **1**-**4** are summarized in Table 1.

Complex	**Terminal $-CH_3$ δ (ppm)**	**Bridging $-CH_3$ δ (ppm)**
1	-0.40	-0.81
2	-0.32	-0.46
3	-0.39, -0.21	-0.52
4	-0.30	-0.46, -0.12

Table 1. Room temperature ^1H NMR chemical shifts for the terminal and bridging methyl groups for tetramethylaluminate complexes **1**-**4** in benzene-d_6.

Cooling a saturated toluene solution of **4** to -30 °C provides X-ray quality crystals of the compound as colorless blocks. The solid state structure of **4** has been obtained and is shown in Figures 5 and 6. This complex represents the second example of a crystallographically characterized *ansa*-scandocene tetramethylaluminate, the first being (tBuThp)Sc(μ-Me)$_2$AlMe$_2$.[11] Selected bond distances for **4** and (tBuThp)Sc(μ-Me)$_2$AlMe$_2$ are listed in Table 2. The aluminum-carbon distances for the bridging methyl groups are about

0.1 Å longer than the analogous bond lengths for the terminal methyl groups. Hydrogen atoms have been found in the difference map for both **4** and (tBuThp)Sc(μ-Me)$_2$AlMe$_2$ and were refined isotropically.

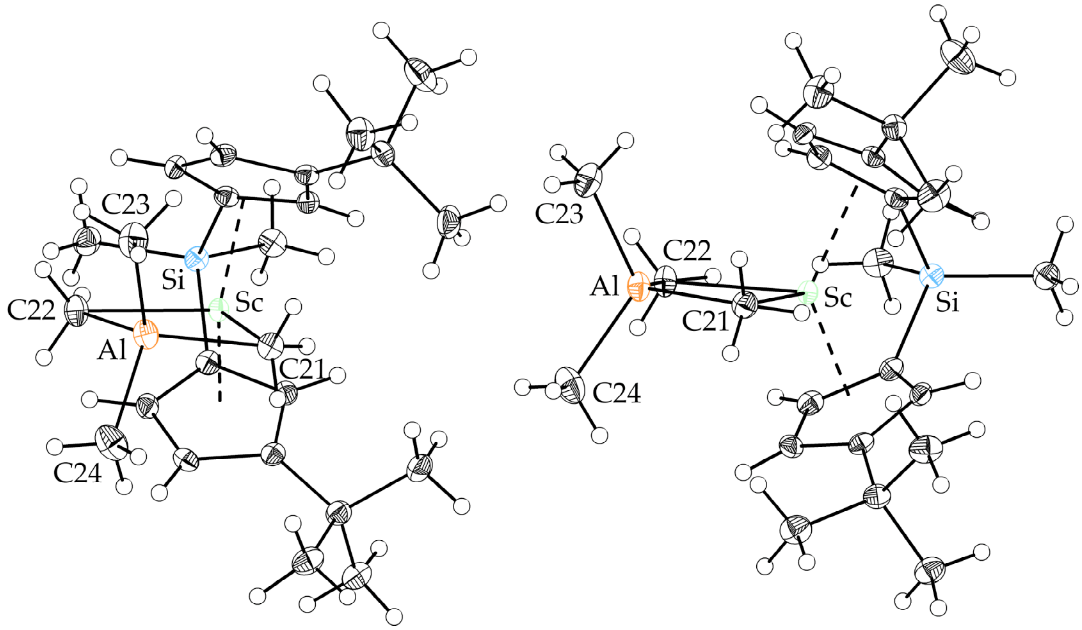


Figure 5. Side and front views of **4** shown with 50 % probability ellipsoids.

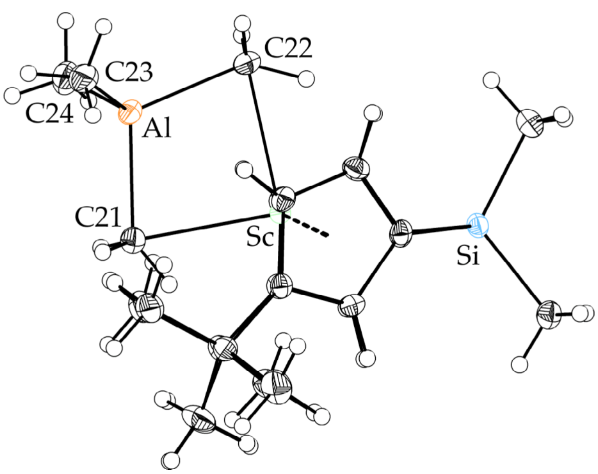


Figure 6. Top view of **4** shown with 50 % probability ellipsoids.

Although we have drawn bonding interactions between scandium and C21 and C22, these methyl groups are approximately 0.21 Å further from the scandium than would be expected for a scandium-carbon single bond to an alkyl group.[9,20] Additionally, H21B and H22B are at a distance from scandium that would suggest a bonding interaction. The C22-H22B bond length is 0.07 Å longer than the distance between this carbon and its other two hydrogens. This difference in carbon-hydrogen bond lengths is not as obvious for C21. We therefore propose that these bridging methyl groups bind to scandium through a direct scandium-carbon interaction, as well as via a σ interaction between the C-H bonds and scandium. The analogous situation, in which methyl groups bridge via a σ interaction, has been described for (tBuThp)Sc(μ-Me)$_2$AlMe$_2$,[11] as well as for [Cp*$_2$Yb(AlMe$_3$)$_2$(S-*p*-C$_6$H$_4$Me)]$_2$,[21] in which an AlMe$_3$ moiety bridges the ytterbocene fragment and the thiolate. These interactions are shown in Figure 7.

Selected Bond Length (Å)	**4**	**(tBuThp)Sc(μ-Me)$_2$AlMe$_2$**
Sc-Cent1	2.20(1)	2.239(1)
Sc-Cent2	2.19(1)	2.233(1)
Sc-C21/Sc-C26	2.4250(17)	2.414(2)
Sc-C22/Sc-C25	2.4903(17)	2.442(2)
Sc-H21B/Sc-H26C	2.133(19)	2.21(2)
Sc-H22B/Sc-H25C	2.213(14)	2.19(2)
C21-H21A/C26-H26A	0.90(2)	1.00(2)
C21-H21B/C26-H26B	0.93(2)	0.93(2)
C21-H21C/C26-H26C	0.97(2)	0.98(2)
C22-H22A/C25-H25A	0.920(17)	0.99(2)
C22-H22B/C25-H25B	0.996(15)	0.84(3)
C22-H22B/C25-H25B	0.925(17)	0.92(3)
Al-C21/Al-C26	2.0703(17)	2.087(2)
Al-C22/Al-C25	2.0601(17)	2.081(2)
Al-C23/Al-C27	1.9792(18)	1.971(2)
Al-C24/Al-C28	1.9659(19)	1.970(2)
Sc-Al	2.93(1)	2.9179(14)

Table 2. Selected bond distances for *ansa*-scandocene tetramethylaluminate complexes **4** and (tBuThp)Sc(μ-Me)$_2$AlMe$_2$.[11]

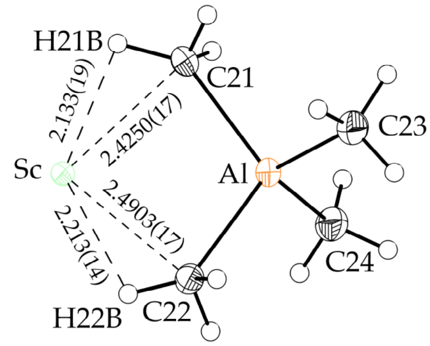


Figure 7. Molecular structure of **4** to illustrate σ interactions between scandium and methyl C-H bonds (50 % probability ellipsoids).

Attempts to utilize analogous procedures to prepare tetramethylaluminate complexes containing bridged indenyl ligands have been unsuccessful. Synthesis of ethylene*bis*(indenyl)ethylene-bridged *bis*-indenyl (EBI) scandium chloride has been attempted as a precursor for an EBI-tetramethylaluminate complex. Although NMR tube reactions of $ScCl_3(THF)_3$ with $Li_2EBI(THF)_n$ (n = 3 or 4) in THF-d_8 indicate the formation of a mixture of *rac*- and *meso*-[EBIScCl], it is clear that protio ligand, $EBIH_2$, is also present. Efforts to isolate either of these desired metallocene products have consistently resulted in the isolation of protio ligand. In fact, attempts to extract the desired metallocenes with extremely dry solvents, such as toluene or diethyl ether, facilitates the formation of protio ligand.

Attempts to form the desired compound by adding a THF solution of $Li_2EBI(THF)_n$ dropwise to a solution of $ScCl_3(THF)_3$ in THF, following methodology used to isolate a mixture of *rac*- and *meso*-[(EBI)LuCl][$LiCl(Et_2O)_2$],[22] have also resulted in isolation of protio ligand. Similar results have been obtained when the dipotassio salt of the ligand, K_2EBI, was used. A similar route has been attempted with the dimethylsilyl*bis*(indenyl) (SBI) ligand. The reaction of $ScCl_3(THF)_3$ with Li_2SBI in benzene-d_6 or THF-d_8 also gives protio ligand rather than the desired metallocene product. Results suggest that although these complexes can be made, they are relatively unstable and therefore react via facile decomposition pathways.

Oligomerizations of α-Olefins Using Group 3 Tetramethylaluminate Catalysts

A series of oligomerizations of α-olefins has been carried out with **1**-**4**. In all cases a small amount of the catalyst (5-15 mg) was combined with a large excess (5,000-10,000 equivalents) of 1-pentene. The reactions were kept in water baths which had been previously equilibrated to 19.5 °C. Each reaction was quenched separately with methanol, and each catalyst was tested at various time intervals. The organic fractions of these samples have been analyzed using GC-MS.

Catalyst **1** makes a large range of oligomers of 1-pentene, from dimer to 17-mer (85 carbons). In this case the distribution of oligomers includes higher oligomers at longer reaction times. In fact it is possible that oligomers higher than 17-mer are formed by the catalyst after 24 hours; however, these samples cannot be eluted from the GC column using standard methods. The distributions of oligomers formed by **1** at different time intervals are shown in Figure 8. The distribution more closely resembles a Poisson distribution than a Flory-Schulz distribution, which is more typically observed for linear step polymerization reactions.[23]

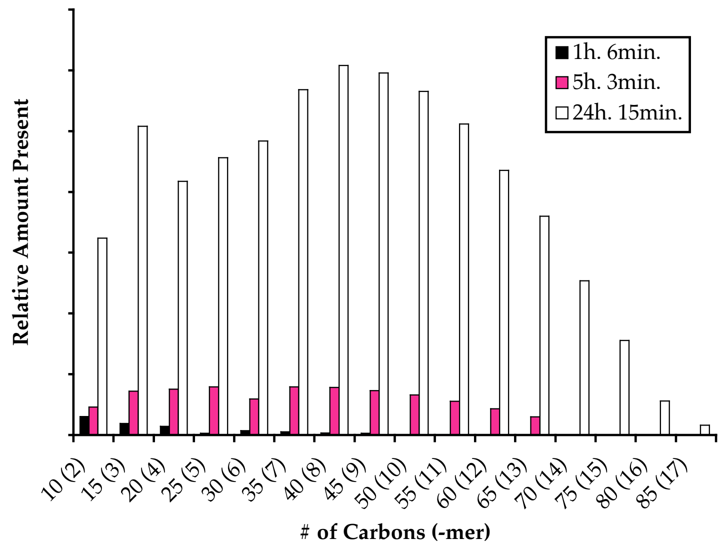
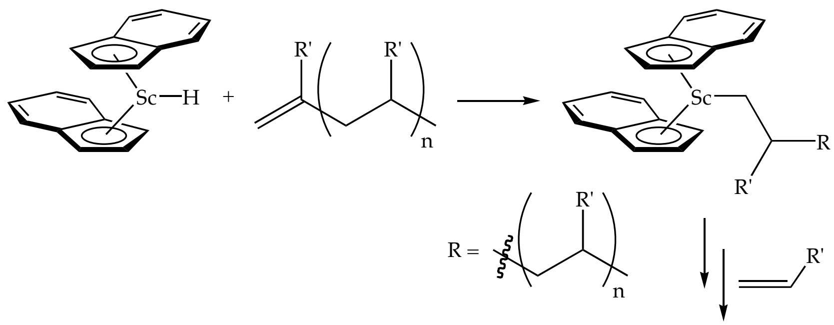


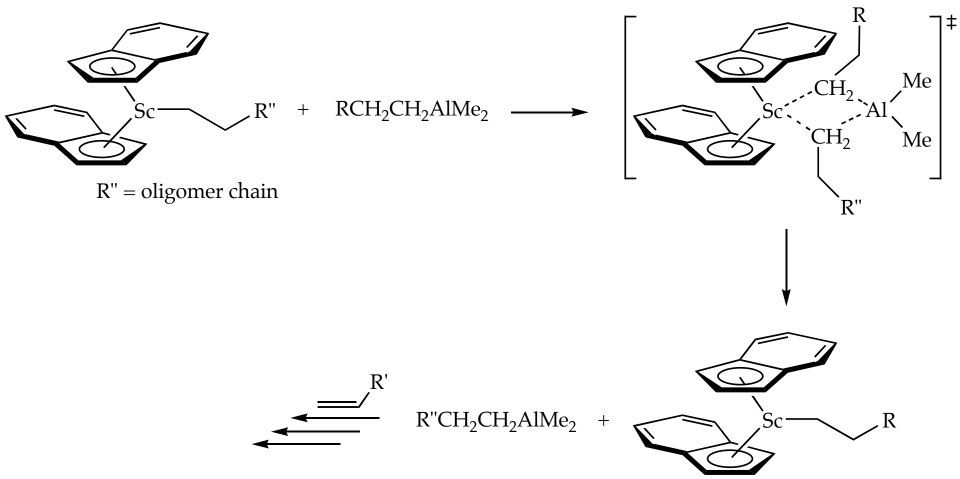
Figure 8. Relative amounts of oligomers of 1-pentene formed by catalyst **1** at different time intervals.

The observation of higher oligomer molecular weights at longer reaction times suggests that the active catalyst is able to react with oligomers that have been eliminated by chain transfer and continue propagation with these species to make longer oligomer chains at a rate that is competitive with monomer insertion. Thus at longer reaction times, longer oligomer chains are formed by reincorporation of eliminated oligomers. The catalyst may react by insertion of oligomers with olefinic end-groups into a scandium-hydride active species, as shown in Scheme 3. These oligomers are formed by chain transfer via β-hydrogen elimination and are *gem*-disubstituted olefins. It has been noted that insertion of *gem*-disubstituted olefins by early metal metallocenes is generally a much slower process than insertion of α-olefins.[24] Alternatively the catalyst may undergo a chain transfer reaction with an aluminum species bound to an oligomer chain (Scheme 4). Although results suggest that RCH_2CH_2-$AlMe_2$ may undergo chain transfer back to scandium, previous reports suggest that this type of species is too sterically hindered to react with another [$Ind_2ScCH_2CH_2R''$] species.[25] However, a recent report discusses the ability of *rac*-[$Me_2Si(2\text{-Me-Ind})_2$]$Y(\mu\text{-}R)_2AlR_2$ (R = Me, Et, iBu) to undergo reversible reaction with THF to form *rac*-[$Me_2Si(2\text{-Me-Ind})_2$]YR(THF) adducts and alkyl group exchange with trialkyaluminum reagents.[26] This suggests the possibility of facile chain transfer reactions in these systems. Their results show that the bulkier alkyl group is preferentially transferred to the aluminum alkyl.

Scheme 3.



Scheme 4.



Catalyst **2** produces oligomers from dimer to undecamer (55 carbons). Unlike **1**, **2** produces a Flory-Schulz distribution of oligomers, which remains the same at different reaction times, indicating that oligomers that have been formed and eliminated do not reinsert (Figure 9). Thus, over time the same range of oligomer molecular weights is observed with greater amounts of each oligomer being produced at longer reaction times.

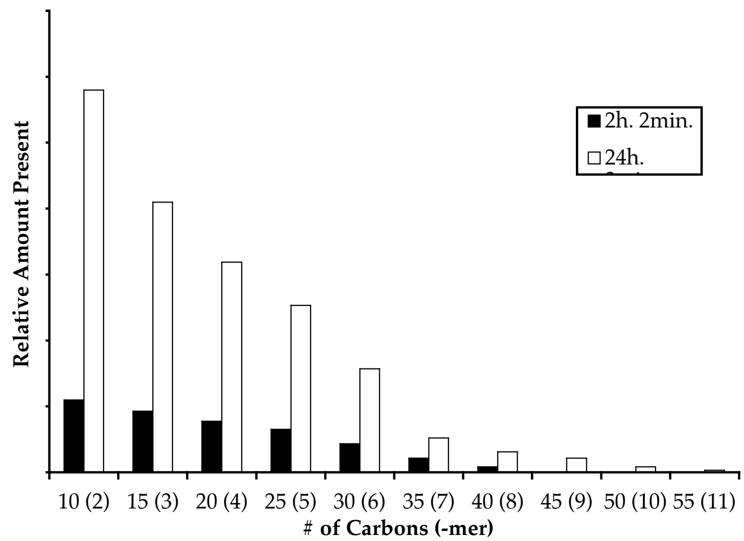


Figure 9. Relative amounts of oligomers of 1-pentene formed by catalyst **2** at different time intervals.

Catalyst **3** makes oligomers from dimer to pentamer (25 carbons). Like **2**, **3** makes the same distribution of oligomers at different reaction times. The distributions of oligomers formed by **3** at different time intervals are shown in Figure 10. Finally, **4** makes predominantly dimer, with a small amount of trimer and tetramer. This result is in agreement with previous results that indicate that $[DpScH]_2$ reacts with excess α-olefin to make exclusively head-to-tail dimers.[18a] A comparison of the oligomers formed by each of the catalysts after 24 hours is shown in Figure 11.

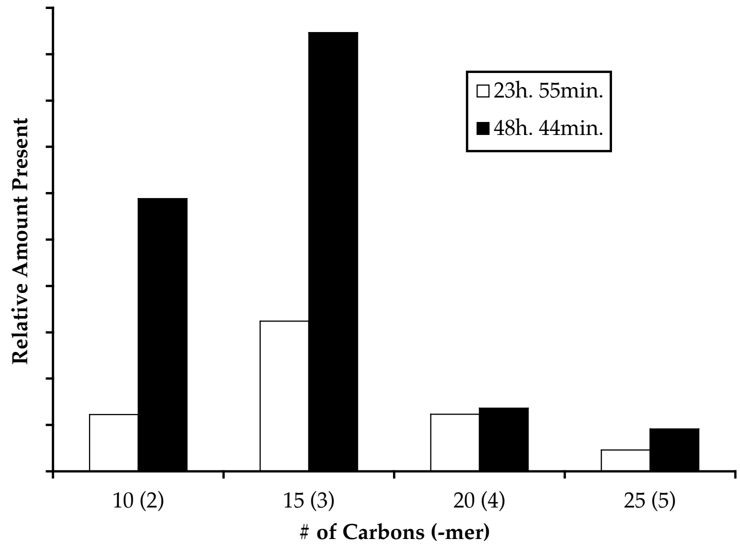


Figure 10. Relative amounts of oligomers of 1-pentene formed by catalyst **3** at different time intervals.

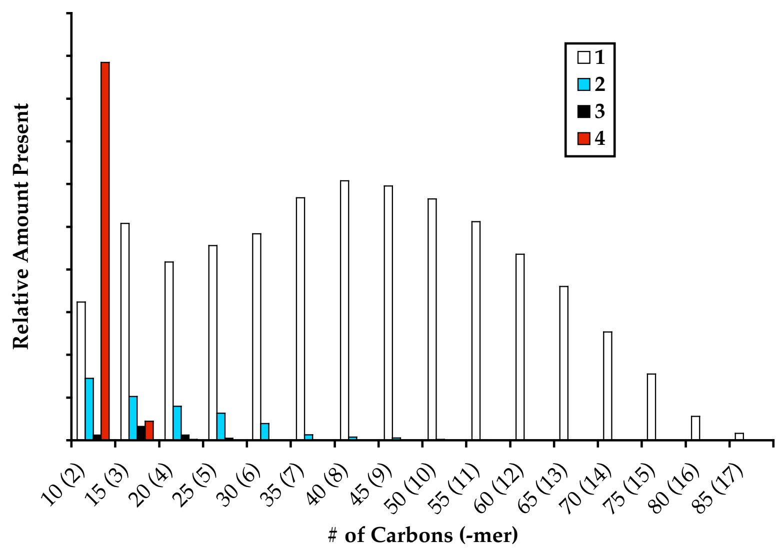
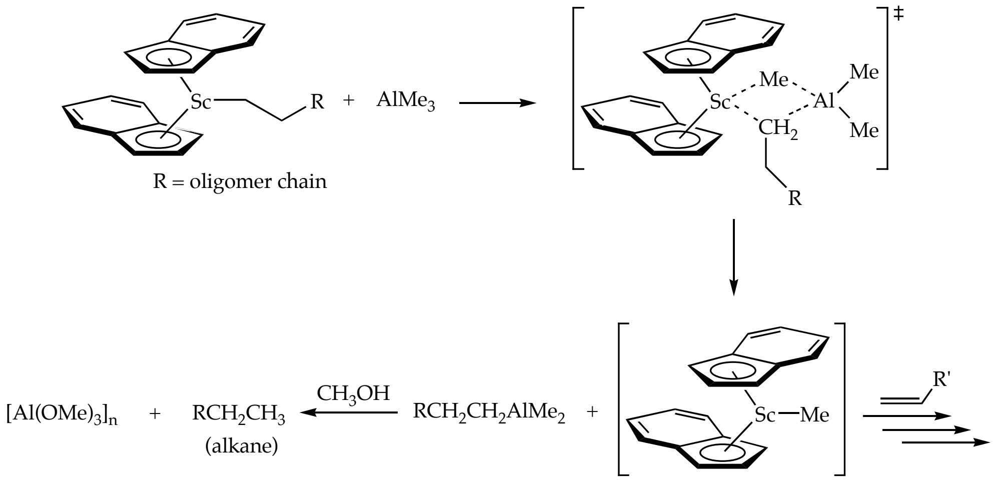


Figure 11. Relative amounts of oligomers of 1-pentene formed by catalysts **1**-**4** after 24 hours.

Using GC-MS it is possible to identify the individual species present in the low molecular weight oligomer fractions (C_{10}-C_{11}). By analyzing the components of oligomer fractions, insight can be gained into the mechanism by which the tetramethylaluminate catalysts initiate and terminate. For example, it is hypothesized that a [$(CpR_n)_2ScMe$] species coordinates and inserts olefin to initiate oligomerization. Therefore, it is expected that an additional methyl group would be present at one end of some oligomer chains (see Scheme 1). In fact, it is possible to identify oligomers in the mass spectrum from the sample made with **1** that elute from the GC column at the same time as the dimer fraction that are eleven carbon chains, indicative of a dimer of 1-pentene plus an additional methyl group ($C_{11}H_{22}$). Analogous fragments can also be found by an examination of the mass spectra of higher oligomers.

In addition, it is possible to recognize fragments using GC-MS data that are potentially oligomer end groups in an attempt to understand mechanisms of chain termination. Mass spectral data suggests that most of the oligomers formed possess one degree of unsaturation, indicative of olefinic end groups. This implies that the primary mechanism of chain transfer is β-hydrogen elimination. Data also suggests that some termination occurs via chain transfer to aluminum. The mass spectrum of the C_{10}-C_{11} fraction formed in oligomerizations of 1-pentene catalyzed by **1** contains a small amount of alkane species, $C_{10}H_{22}$. This alkane has likely been formed by chain transfer to aluminum via the mechanism illustrated in Scheme 5. Chain transfer to aluminum proceeds via a σ-bond metathesis route to form RCH_2CH_2-$AlMe_2$ (R = oligomer chain) and [Ind_2ScMe], which is capable of reinserting olefin. The formed RCH_2CH_2-$AlMe_2$ species remains in the oligomerization mixture until the reaction is quenched; addition of methanol yields the alkane, methane, and $[Al(OMe)_3]_n$. Alternatively, alkanes may be obtained when a growing polymer chain attached to scandium is quenched with methanol.

Scheme 5.



Oligomer samples created by **3** contain a large amount of alkanes. In fact, based on the mass spectra of these oligomers, it appears that within the dimer fraction there is an excess of alkane relative to alkene. This result may explain the low molecular weights of the oligomers produced by **3**. It is possible that this catalyst undergoes facile chain transfer to aluminum, thus increasing k_{CT} relative to k_{prop} and decreasing the molecular weights of the oligomers formed. Alternatively k_{prop} may be relatively small if the [Cp*CpScR] species is very slow to insert olefin due to the high stability of this scandium-alkyl species. Quenching this scandium alkyl species with methanol would generate alkane.

Overall it is clear that **1** creates oligomers of the highest molecular weight, **2** creates oligomers of slightly lower molecular weight, **3** creates oligomers of even lower molecular weight, and **4** is only able to create dimer, trimer, and tetramer. A correlation has been observed between catalyst activity and oligomer molecular weight. For example, **1** is able to convert some monomer to oligomers as high as nonamers (45 carbons) after only one hour of reaction with 5,000 equivalents of 1-pentene. Unlike **1**, after one hour under similar conditions, **2** has not converted any of the monomer into oligomers. Thus, the more active catalyst is able to produce oligomers of higher molecular weight. In fact, due to its high activity, **1** may be ultimately able to insert sterically hindered *gem*-disubstituted olefins.

Reactivity of Group 3 Tetramethylaluminate Complexes With Lewis Bases

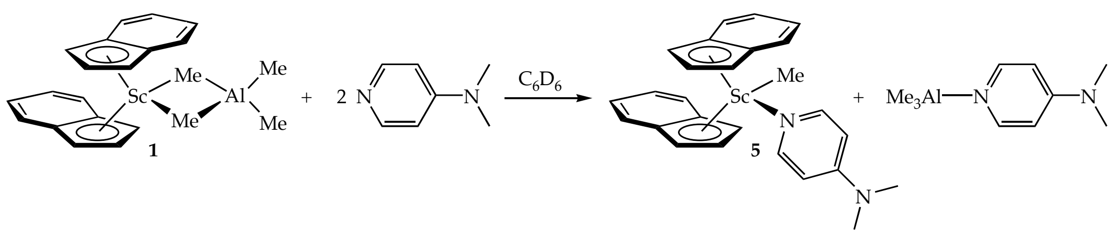
In addition to examining the range of oligomers formed by different tetramethylaluminate catalysts, we wish to understand the general mechanism by which these catalysts react with α-olefins. As discussed previously, it is believed that a 14 electron, d^0 alkyl species, $[(R_nCp)_2ScMe]$, initiates oligomerization by coordinating and inserting olefin. Unfortunately, attempts to identify the active species, $[(R_nCp)_2ScR]$ (R = H, alkyl), or to observe free $AlMe_3$ by monitoring the reaction of a tetramethylaluminate complex with an α-olefin by ^1H NMR have been unsuccessful. The only identifiable species in the reaction mixture are unreacted tetramethylaluminate complexes and α-olefins and eventually the product oligomers.

Because we have been unable to examine the individual steps in the reaction of the tetramethylaluminate complexes with olefins, we decided to use Lewis base reagents (L) to act as models for the olefin, as they may be capable of displacing $AlMe_3$ from a tetramethylaluminate complex without undergoing further reaction. These reactions would leave a $[(R_nCp)_2ScMe]$ species, which could be either a $(R_nCp)_2ScMe(L)$ adduct or a methyl-bridged dimer, $[(R_nCp)_2ScMe]_2$. The dissociated $AlMe_3$ may dimerize to form Al_2Me_6, or it may bind the Lewis base to form L-$AlMe_3$. The reactions of L (L = pyridine or THF) with $Cp_2Sc(\mu\text{-}Me)_2AlMe_2$ to form $Cp_2ScMe(L)$ complexes and half an equivalent of Al_2Me_6 have been reported previously.[8b] An examination of the different species formed in these types of reactions may elucidate the nature of the active species in the reaction of $(CpR_n)_2Sc(\mu\text{-}Me)_2AlMe_2$ with α-olefin.

In an attempt to determine which of these species are favored in reactions with different Lewis bases, a series of experiments have been performed in which solutions of **1**, **2**, **3**, or **4** in benzene-d_6 have been combined with various bases in amounts ranging from 0.5-3 equivalents. The reagents include 4-dimethyl-aminopyridine (DMAP), THF, and PMe_3. These samples have been examined by ^1H NMR and ^{31}P NMR where possible to gain insight into the number of species present and the identities of these species.

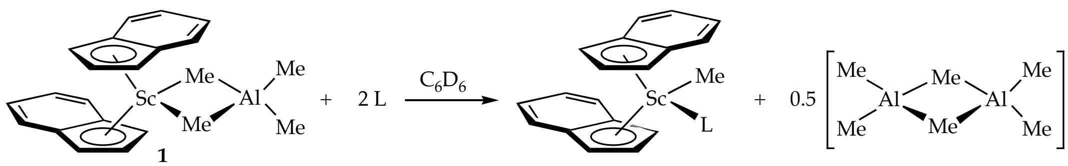
Addition of DMAP to **1** affords $Ind_2ScMe(DMAP)$ (**5**) and DMAP-$AlMe_3$ (Scheme 6). The room temperature ^1H NMR of **5** shows a characteristic Sc-Me resonance at δ = -0.42 ppm. Independent examination of DMAP-$AlMe_3$ by ^1H NMR is consistent with assignment of this species as a product of the reaction of **1** with DMAP. This result is in contrast to previous results that indicate that Cp^*_2ScR (R = H, CH_3, C_6H_5, $CH_2C_6H_5$) reacts cleanly with pyridine to afford the orthometallated (C, N-η^2) pyridine complex and eliminate alkane via σ bond metathesis.[20]

Scheme 6.



Alternatively, the reaction of **1** with either THF or PMe_3 affords a slightly different product mixture. While ^1H NMR of the reaction of **1** with THF indicates the formation of $Ind_2ScMe(THF)$ (**6**) with a characteristic Sc-Me resonance at δ = -0.68 ppm, it appears that the dissociated $AlMe_3$ dimerizes rather than reacting with added THF (Scheme 7). Addition of PMe_3 to **1** affords $Ind_2ScMe(PMe_3)$ (**7**), which has a characteristic Sc-Me peak at δ = -1.38 and a characteristic Sc-PMe_3 peak at δ = 0.52 ppm in the room temperature ^1H NMR spectrum. This complex also displays a ^{31}P NMR resonance at δ = -47.8 ppm for the phosphorus bound to scandium. In these cases, addition of greater than one equivalent of either THF or PMe_3 leads to broadening of peaks in the room temperature ^{1}H and ^{31}P NMR spectra, suggesting exchange between coordinated and free ligand (L).

Scheme 7.



The reaction of **2** with DMAP affords Cp_2ScMe(DMAP) (**8**) and DMAP-$AlMe_3$. The room temperature ^{1}H NMR of compound **8** displays a characteristic Sc-Me resonance at δ = 0.20 ppm. Addition of less than one equivalent of DMAP to a solution of **2** in benzene-d_6 provides a mixture of **2**, Cp_2ScMe(DMAP), and DMAP-$AlMe_3$. The reaction can be driven to completion by addition of two equivalents of DMAP. Attempts to separate Cp_2ScMe(DMAP) from DMAP-$AlMe_3$ have been unsuccessful. The reaction of **3** with DMAP has been examined, and its ^{1}H NMR spectrum indicates the formation of (Cp*Cp)ScMe(DMAP) (**9**) and DMAP-$AlMe_3$ (see Scheme 6). Compound **9** exhibits a representative Sc-Me peak at δ = 0.18 ppm. The ^{1}H NMR data for the scandium-methyl groups for complexes **5**-**9** are summarized in Table 3. Analogous reactivity with DMAP has been observed for **3** and **4**.

Complex	**Sc-CH_3 δ (ppm)**
5	-0.42
6	-0.68
7	-1.38
8	0.20
9	0.18

Table 3. Room temperature ^{1}H NMR chemical shifts for the scandium-methyl groups for $(CpR_n)_2ScMe(B)$ complexes **5**-**9** in benzene-d_6.

The different reactivity with $AlMe_3$ observed for DMAP as compared to THF and PMe_3 suggests that aluminum, a hard Lewis acid, prefers to bind nitrogen, a hard Lewis base, over softer Lewis bases like oxygen and phosphorus.[27] In these latter cases the dissociated $AlMe_3$ prefers to dimerize rather than coordinate to softer Lewis bases.

Effect of Lewis Acids and Bases on the Activity of Group 3 Tetramethylaluminate Complexes for α-Olefin Consumption

In order to provide support for the proposed mechanism of reactivity of tetramethylaluminate species, experiments have been carried out to determine the way in which Lewis acids and bases change the activities of **1-4** towards α-olefins. The $(R_nCp)_2ScMe(L)$ complexes **5-9** may be more or less reactive towards olefins than the tetramethylaluminate complex, depending on the relative abilities of $AlMe_3$ and the base to dissociate from scandium to form the active species. The activity of each catalyst alone has been determined by monitoring the reaction of the catalyst with 40 equivalents of α-olefin via ^{1}H NMR to ascertain the time necessary for that catalyst to consume all of the monomer. For these experiments, either propylene or 1-butene was used; all comparisons of activities for a given catalyst are for reactions performed with the same monomer. All experiments were carried out at room temperature unless otherwise indicated. Independently, **1** consumes 40 equivalents of propylene within 18 hours; **2** consumes 40 equivalents of 1-butene within 48 hours; **3** consumes approximately 24 of 40 equivalents of 1-butene after 41 days; and **4** is able to consume 40 equivalents of propylene within 72 hours. This data is summarized in Table 4.

Catalyst	Monomer	Time to Consume 40 Equivalents of α-Olefin
1	propylene	< 18 hours
2	1-butene	< 48 hours
3	1-butene	> 41 days
4	propylene	72 hours

Table 4. Activities of catalysts **1-4**.

Overall, there is a correlation between the activity of a catalyst and the molecular weight of oligomers formed by that catalyst. According to Equation 1, an increase in k_{prop} relative to k_{term} for a given catalyst results in the formation of higher molecular weight oligomers by that catalyst. A catalyst that shows high activity is able to consume α-olefins at a rapid rate; the α-olefins react with a $(R_nCp)_2ScR$ species (R = Me, H) to initiate oligomer formation or with a $(R_nCp)_2ScP$ species (P = oligomer chain) to propagate and build a longer oligomer.

The addition of a Lewis acid such as $AlMe_3$ to a tetramethylaluminate complex should slow the reaction of the catalyst with α-olefins (Scheme 1) if this reaction is dissociative in $AlMe_3$. Addition of five equivalents of $AlMe_3$ to **1** followed by the addition of 40 equivalents of propylene renders the catalyst unreactive toward olefin after five days. Addition of 0.5 equivalents of $AlMe_3$ to **1** significantly slows its reaction with 40 equivalents of propylene such that it is able to consume only 3% of the monomer within 48 hours and only 7% of the monomer after 27 days. These results are consistent with reactivity of the tetramethylaluminate species via dissociation of $AlMe_3$ prior to olefin coordination and insertion.

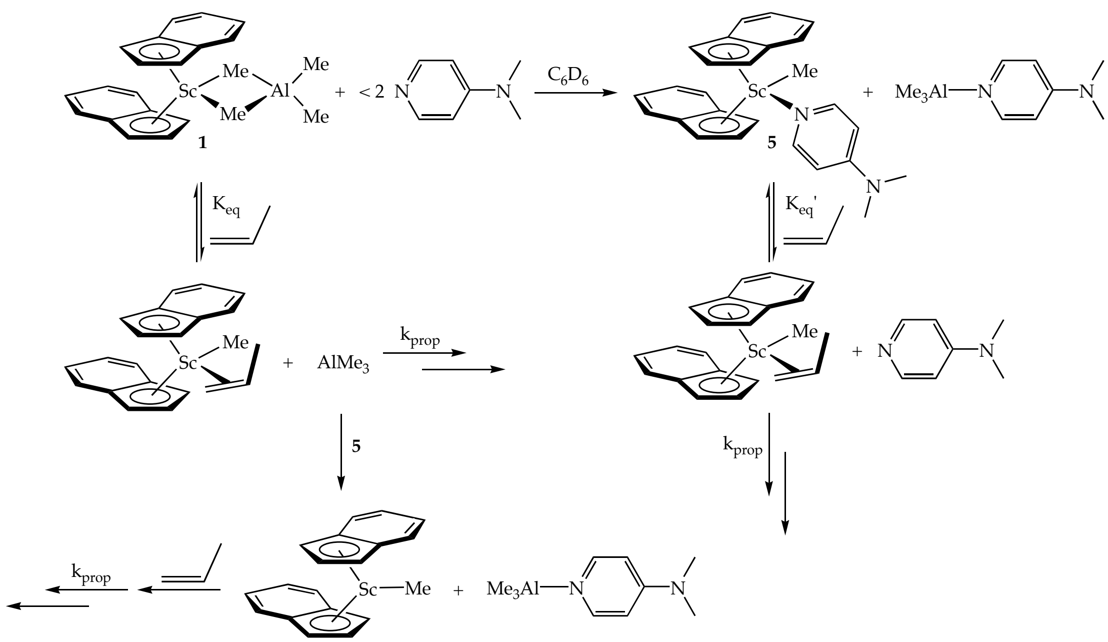
The activities of each of the tetramethylaluminate catalysts have been examined independently, in the presence of two equivalents of DMAP, and in the presence of less than one equivalent of DMAP. This data is summarized in Table 5. In the presence of a stoichiometric amount of DMAP (two equivalents), all of the catalysts consume α-olefin much more slowly than they do without added base. Conversely, in the presence of a catalytic amount of DMAP (less than two equivalents), the catalysts consume α-olefin much more rapidly than they do in the absence of any additives. In fact, a benzene-d_6 solution of catalyst **1** in the presence of 0.5 equivalents of DMAP consumes 40 equivalents of α-olefin within 15 minutes.

Catalyst	Monomer	Equiv. of DMAP	Reaction Time[a]
1	propylene	0	< 18 hours
1	propylene	2	2% consumed after 6 days
1	propylene	0.5	< 15 minutes
1	propylene	0.1	30 minutes
2	1-butene	0	< 48 hours
2	1-butene	2	none consumed after 13 days
2	1-butene	1.4	18 days
2	1-butene	0.1	< 33 hours
3	1-butene	0	60% consumed after 41 days
3	1-butene	2	none consumed after 41 days
3	1-butene	0.1	50 hours
4	1-butene	0	72 hours
4	1-butene	2	none consumed after 17 days
4	1-butene	0.1	24 hours

Table 5. Activities of catalysts **1-4** independently, in the presence of a stoichiometric amount of DMAP, and in the presence of catalytic amounts of DMAP. [a]Time to consume 40 equivalents of α-olefin.

These results suggest that multiple equilibrium processes are occurring in a reaction mixture containing a tetramethylaluminate complex, DMAP, and α-olefin. We have shown that addition of less than one equivalent of DMAP to a solution of **1** results in a mixture of **1**, **5**, and DMAP-$AlMe_3$. The proposed explanation of the observed reactivity in the presence of a catalytic amount of DMAP is shown in Scheme 8. There is some equilibrium between either **1** or **5** and a scandium-methyl olefin adduct, which proceeds through dissociation of $AlMe_3$ or DMAP, respectively, followed by coordination of olefin. We assume that this scandium-methyl olefin complex reacts rapidly to insert olefin and continue propagation. Our results also suggest that the equilibrium constant for dissociation of DMAP from Ind_2ScMe (K_{eq}') is smaller than the equilibrium constant for $AlMe_3$ dissociation (K_{eq}), as once **5** is formed, its reaction with olefin is slower than reaction of **1**. The free $AlMe_3$ that is liberated from **1** may react rapidly with DMAP that is coordinated to scandium in **5**, possibly through an interaction with the nitrogen lone pair of the dimethylamine moiety, to generate DMAP-$AlMe_3$. This reaction also generates Ind_2ScMe, which should react very rapidly with olefin, as these 14 electron species are known to be very reactive.[8] This suggests that $AlMe_3$ prefers to bind DMAP *versus* scandium. Thus, as long as both complexes **1** and **5** are present in solution, the overall reaction of **1** with olefin proceeds more rapidly than the same reaction in the absence of DMAP by promoting the formation of a scandium-methyl species. However, in the case of addition of two equivalents of DMAP to **1**, only **5** and DMAP-$AlMe_3$ are present in solution, and **5** reacts more slowly than **1** with olefin.

Scheme 8.



Conclusions

A series of tetramethyaluminate complexes, **1-4**, have been isolated, and they all display static structures at room temperature. The reactivity of **1-4** with α-olefins has been examined. Although oligomer molecular weights and catalyst activities vary with ligand array, the reasons for these effects have not been determined. Catalyst **1** is observed to produce a Poisson distribution of oligomers, suggesting that it undergoes facile chain transfer reactions to reincorporate eliminated oligomers. Tetramethyaluminate species were chosen for this study because it was believed that they react with α-olefins in a well-behaved fashion. Some of the mechanistic aspects of the tetramethyaluminate species have been determined. GC-MS data shows that some α-olefin insertions occur into a scandium-methyl bond, while most insertions occur into scandium-hydride bonds. We find that the primary mechanism of chain termination is via β-hydrogen elimination, although some termination occurs through chain transfer to aluminum.

An attempt to prepare novel scandium-methyl complexes has allowed for study of the relative affinity of scandium for different ligands including $AlMe_3$, DMAP, THF, PMe_3, and a bridging scandium-methyl bond. Our results show that $[(R_nCp)_2ScMe]$ complexes prefer to bind Lewis bases rather than to coordinate $AlMe_3$ or to dimerize. We observe a correlation between the molecular weight of oligomers formed by a given catalyst and its activity toward the consumption of α-olefin. Addition of $AlMe_3$ to complex **1** results in a dramatic decrease in its reactivity towards olefins, suggesting that the tetramethylaluminate catalysts react with olefins via initial dissociation of $AlMe_3$. Studies of the reactivities of tetramethylaluminate complexes with olefins in the presence of various amounts of Lewis bases show that catalytic amounts of DMAP can greatly increase the rates of reaction of the tetramethylaluminate species with α-olefins. In fact, in the presence of a catalytic amount of DMAP **1** is able to consume an excess of α-olefin at a remarkably rapid rate. Alternatively, addition of stoichiometric amounts of Lewis bases to these reactions slows the rates of consumption of olefins.

Experimental

General Considerations. All manipulations were performed using standard high vacuum line, Schlenk, and glove box techniques as described previously.[28] All gases were purified by passage over MnO on vermiculite and activated molecular sieves. Ethereal solvents were stored over sodium benzophenone ketyl, and hydrocarbon solvents were stored over titanocene.[29] Propylene was dried over triisobutylaluminum, 1-butene was dried over 4 Å molecular sieves, and 1-pentene was dried over $LiAlH_4$. $ScCl_3(THF)_3$,[30] *meso*-$[DpScCl]_2$,[18a] $Cp_2ScCl(THF)$,[17] and Cp*CpScCl[18a] were all prepared as previously reported. All other reagents were used as received.

Instrumentation. Most ^1H spectra and all ^{31}P and ^{27}Al NMR spectra were recorded on a Delta JEOL 400 spectrometer at 400.1, 161.9, and 104.3 MHz, respectively. Some ^1H spectra were recorded on a Bruker AM 500 spectrometer at 500.1 MHz, and ^{13}C spectra were recorded on an Inova 500 spectrometer at 125.8 MHz. All ^1H and ^{13}C NMR chemical shifts are relative to TMS, and ^1H (residual) or ^{13}C chemical shifts of the solvent are used as a secondary standard. ^{31}P NMR shifts are relative to an external H_3PO_4 standard, and ^{27}Al NMR shifts are relative to an external $Al(NO_3)_3(H_2O)_9$ standard. Elemental analysis was performed by Fenton I. Harvey at the California Institute of Technology Elemental Analysis Facility. GC-MS was done at the California Institute of Technology with the assistance of Peter G. Green. X-ray crystallography was carried out by Dr. Michael W. Day and Lawrence M. Henling.

Synthesis of [Ind_2ScCl]. In the glove box a 50 mL round-bottom flask equipped with a Teflon stir bar, a reflux condenser, and a 180° needle valve was charged with $ScCl_3(THF)_3$ (2.005 g, 5.452 mmol) and IndLi (1.395 g, 11.42 mmol). On the vacuum line, approximately 27 mL of toluene was added to the flask via vacuum transfer, and the mixture was stirred and warmed to room temperature, forming a bright yellow solution. The solution was heated to reflux. Within 1 hour the solution turned orange. The mixture was refluxed for 32 hours, and the toluene was removed *in vacuo* and replaced with petroleum ether. The solution was stirred overnight, and the petroleum ether was removed under vacuum. The flask was equipped with a swivel frit assembly, Et_2O is added, and the material was filtered and washed with recycled solvent to give an orange-brown Et_2O-soluble material and leave behind a bright yellow powder. The Et_2O was removed *in vacuo*, petroleum ether was added, the solution was stirred, the petroleum ether was removed, and the solids were dried under vacuum for an additional 2 hours. It was assumed that the bright yellow material is Ind_2ScCl, and 1.577 g of this product was isolated (93.1% yield).

Synthesis of $Ind_2ScMe_2AlMe_2$ (1). In the glove box [Ind_2ScCl] (1.577 g, 5.074 mmol) and $LiAlMe_4$ (0.622 g, 6.62 mmol) were placed in a 25 mL flask equipped with a Teflon stir bar and a swivel frit assembly. Approximately 17 mL of toluene was added to the flask via vacuum transfer to give a bright yellow solution. The solution was left to stir at room temperature overnight, during which time it turned a pale orange. Toluene was removed, pentane was added, and the material was filtered and washed many times with recycled solvent to give a pentane-soluble orange-yellow powder. Pentane was removed *in vacuo*, and the solids were dried for 2 hours. The apparatus was taken into the glove box and 0.939 g of the desired product was isolated (47.5% yield). ^1H NMR (RT, 300 MHz, C_6D_6): δ = -0.81 (s, 6H, μ-CH_3), -0.42 (s, 6H, Al-CH_3), 5.64 (t, 2H, Cp*H*), 5.67 (d, 4H, Cp*H*), 6.85 (dd, 4H, benzo), 7.22 (dd, 4H, benzo). ^{13}C NMR (RT, 500 MHz, C_6D_6): δ = -5.75 (μ-CH_3), 20.67 (Al-CH_3), 103.02, 120.99 (Cp), 124.00, 124.75, 127.08 (benzo). Anal. Calcd for $C_{22}H_{26}ScAl$: C, 72.92; H, 7.23. Found: C, 73.68; H, 7.53.

Synthesis of $Cp_2ScMe_2AlMe_2$ (2). A procedure analogous to that used to prepare **1** was followed, using $Cp_2ScCl(THF)$ (0.787 g, 2.78 mmol) and $LiAlMe_4$ (0.435 g, 4.63 mmol). The product was recrystallized from petroleum ether, and 0.382 g of the desired product was isolated (52.4% yield). ^1H NMR (RT, 300 MHz, C_6D_6): δ = -0.46 (s, 6H, μ-CH_3), -0.32 (s, 6H, Al-CH_3), 5.67 (s, 10H, Cp*H*). ^{27}Al NMR (RT, 400 MHz, C_6D_6): δ = 159.0 (s, *Al*$(CH_3)_4$)

Synthesis of Cp*CpScMe$_2$AlMe$_2$ (3). A procedure analogous to that used to prepare **1** was followed, using Cp*CpScCl (0.683 g, 2.43 mmol) and $LiAlMe_4$ (0.275g, 2.92 mmol). The product was recrystallized from pentane to give 0.4070 g of **3** as an orange powder (50.3% yield). ^1H NMR (RT, 300 MHz, C_6D_6): δ = -0.52 (s, 6H, μ-CH_3), -0.39 (s, 3H, Al-CH_3), -0.21 (s, 3H, Al-CH_3), 1.65 (s, 15H, $C_5(CH_3)_5$), 5.78 (s, 5H, Cp*H*).

Synthesis of $DpScMe_2AlMe_2$ (4). A procedure analogous to that used to prepare **1** was followed, using $[DpScCl]_2$ (0.360 g, 0.948 mmol) and $LiAlMe_4$ (0.321 g, 3.41 mmol) to generate 0.147 g of the desired product (35.9% yield). ^{1}H NMR (RT, 300 MHz, C_6D_6): δ = -0.46 (s, 3H, μ-CH_3), -0.30 (s, 6H, Al-CH_3), -0.12 (s, 3H, μ-CH_3), 0.28 (s, 3H, Si-CH_3), 0.60 (s, 3H, Si-CH_3), 1.11 (s, 9H, ^{t}Bu), 5.48 (s, 2H, Cp*H*), 5.93 (d, 2H, Cp*H*), 6.17 (d, 2H, Cp*H*). Anal. Calcd for $C_{24}H_{42}ScSiAl$: C, 66.94; H, 9.83. Found: C, 65.13; H, 10.56. X-ray quality crystals were grown by cooling a toluene solution of **4** to –30 ºC for months.

General Procedure for Oligomerizations of 1-Pentene with 1-4. In the glove box a 25 mL flask equipped with a Teflon stir bar and a 180° needle valve was charged with 5-15 mg of catalyst. On the high vacuum line 5,000 equivalents of 1-pentene were measured into a calibrated centrifuge tube. The 1-pentene was added to the flask containing the catalyst via vacuum transfer while the flask was cooled with liquid N_2 to ensure that the reaction does not commence before all of the 1-pentene has been added. When the addition was complete, the flask was sealed, the mixture was warmed by a room temperature water bath, and it was left to stir under vacuum at room temperature. After the oligomerization has proceeded for the designated amount of time, the flask was filled with argon, and the reaction was quenched by the addition of 5 mL of methanol. Water was then added to allow for separation of the organic layer, and the organic layer was analyzed by GC-MS.

General Procedure for Reaction of $(R_nCp)_2ScMe_2AlMe_2$ with $AlMe_3$ or Lewis Bases (L). In the glove box an NMR tube equipped with a Teflon valve was charged with 5-15 mg of a tetramethylaluminate complex and approximately 0.5 mL of C_6D_6. In the case of $AlMe_3$, the desired amount of material was added to the tube via syringe in the glove box. In the case where L = DMAP, the desired amount of material was added to the tube either as a solid or via syringe from a 0.6065 M solution in the glove box. In cases where L = THF, PMe_3, or pyridine, the desired amount of material was measured into a calibrated gas bulb and added to the NMR tube via vacuum transfer. The products of the reactions were analyzed by ^{1}H NMR.

Characterization of $Ind_2ScMe(DMAP)$ (5). ^{1}H NMR (RT, 300 MHz, C_6D_6): δ = -0.42 (s, 3H, Sc-CH_3), 1.88 (s, 6H, N-CH_3), 5.52 (d, 2H, DMAP), 6.01 (d, 2H, Cp*H*), 6.12 (d, 2H, Cp*H*), 6.40 (dd, 2H, Cp*H*), 6.90 (dd, 2H, benzo), 7.04 (dd, 2H, benzo), 7.19 (d, 2H, benzo), 7.33 (d, 2H, benzo), 7.60 (d, 2H, DMAP).

Characterization of $Ind_2ScMe(THF)$ (6). ^{1}H NMR (RT, 300 MHz, C_6D_6): δ = -0.68 (s, 3H, Sc-CH_3), 0.90 (m, 4H, THF), 2.69 (b, 2H, THF), 3.27 (br, 2H, THF), 5.94 (br, 4H, Cp*H*), 6.17 (t, 2H, Cp*H*), 6.96 (br, 4H, benzo), 7.56 (br, 4H, benzo).

Characterization of $Ind_2ScMe(PMe_3)$ (7). ^{1}H NMR (RT, 300 MHz, C_6D_6): δ = -1.38 (s, 3H, Sc-CH_3), 0.52 (d, 9H, Sc-P(CH_3)$_3$), 5.77 (t, 2H, CpH), 5.99 (d, 4H, CpH), 7.00 (dd, 4H, benzo), 7.31 (dd, 4H, benzo). ^{31}P NMR (C_6D_6): δ = -47.8 (s, Sc-*P*(CH_3)$_3$).

Characterization of $Cp_2ScMe(DMAP)$ (8). ^{1}H NMR (RT, 300 MHz, C_6D_6): δ = 0.20 (s, 3H, Sc-CH_3), 1.90 (s, 6H, N-CH_3), 5.58 (d, 2H, DMAP), 6.20 (s, 10H, Cp*H*), 7.62 (d, 2H, DMAP).

Characterization of Cp*CpScMe(DMAP) (9). ^{1}H NMR (RT, 300 MHz, C_6D_6): δ = 0.18 (s, 3H, Sc-CH_3), 1.99 (s, 15H, C_5(CH_3)$_5$), 2.06 (s, 6H, N-CH_3), 5.68 (d, 2H, DMAP), 6.18 (d, 5H, Cp*H*), 7.61 (d, 2H, DMAP).

General Procedure for Determination of Rate of Catalyst Consumption of α-Olefin. In the glove box an NMR tube equipped with a Teflon valve was charged with 5-15 mg of catalyst and approximately 0.5 mL of C_6D_6. On the vacuum line 40 equivalents of α-olefin (propylene, 1-butene, or 1-pentene) were measured into a calibrated gas bulb and added to the NMR tube via vacuum transfer. The tube was attached to a mechanical rotator to ensure constant mixing, and the reaction was monitored by ^{1}H NMR to determine when it has gone to completion.

Crystallography. Crystal data, intensity collection, and refinement details are presented in Table 6 for compound **4**.

Data Collection and Processing. Data for compound **4** were collected on a Bruker SMART 1000 area detector running SMART.[31] The diffractometer was equipped with a Crystal Logic CL24 low temperature device, and all data sets were collected at 98 K. The diffractometer used graphite-monochromated MoKα radiation with $\lambda = 0.71073$ Å. The crystals were mounted on a glass fiber with Paratone-N oil. Data were collected as ω-scans at 5 ϕ settings. The detector was 5 cm (nominal) distant at a θ angle of -28°. The data were processed with SAINT.[31]

Empirical Formula	$C_{22}H_{42}AlSiSc$
Formula Weight (g/mol)	406.59
Crystallization Solvent	Toluene
Crystal Habit	Block
Crystal Size (mm^3)	0.33 X 0.18 X 0.17
Crystal Color	Colorless
Preliminary Photos	Rotation
Type of Diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature (K)	98(2)
θ Range for 6358 Reflections Used in Lattice Determination (°)	2.23 to 28.02
Unit Cell Dimension a (Å)	14.1347(8)
Unit Cell Dimension b (Å)	9.6651(5)
Unit Cell Dimension c (Å)	18.2290(10)
β (°)	90.2630(10)
Volume (Å^3)	2490.3(2)
Z	4
Crystal System	Monoclinic
Space Group	$P2_1/n$
Calculated Density (Mg/m^3)	1.084
F(000)	888
Data Collection Program	Bruker SMART v5.054
θ Range for Data Collection (°)	1.82 to 28.26
Completeness to θ = 28.26° (%)	94.1

Index Ranges	$-18 \le h \le 18$, $-12 \le k \le 12$, $-23 \le l \le 23$
Data Collection Scan Type	ω scans at 5 ϕ settings
Data Reduction Program	Bruker SAINT v6.022
Reflections Collected	35,234
Independent Reflections	5800 ($R_{int} = 0.0528$)
Absorption Coefficient (mm^{-1})	0.382
Absorption Correction	None
Structure Solution Program	SHELXS-97 (Sheldrick, 1990)
Primary Solution Method	Direct Methods
Secondary Solution Method	Difference Fourier Map
Hydrogen Placement	Difference Fourier Map
Structure Refinement Program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data/Restraints/Paramaters	5800/0/412
Treatment of Hydrogen Atoms	Unrestrained
Goodness-of-Fit[a] on F^2	1.867
Final R Indices[b] ($I > 2\sigma(I)$, 4716 Reflections)	R1 = 0.0340, *w*R2 = 0.0626
R Indices[b] (All Data)	R1 = 0.0447, *w*R2 = 0.0636
Type of Weighting Scheme Used	Sigma
Weighting Scheme Used	$w = 1/\sigma^2(Fo^2)$
Max Shift/Error	0.001
Average Shift/Error	0.000
Largest Diff. Peak and Hole (e/Å^3)	0.483 and –0.227

Table 6. X-ray experimental data for **4**. [a]Goodness-of-Fit (S) is based on F^2; F set to zero for negative F^2. [b]R-factors (R) are based on F and weighted R-factors (*w*R) are based on F^2.

Structure Analysis and Refinement. Crystallographic data for the structure of **4** (CCDC 192902) have been deposited with the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2, 1EZ, UK, and copies can be obtained on request, free of charge, by quoting the deposition number 192902. Structure factors are available electronically by e-mail: xray@caltech.edu.

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