

Supported Constrained-Geometry Catalysts on Cross-Linked (Aminomethyl)polystyrene: Studies of Ethylene and 1-Octene Polymerizations

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The reaction of TiCl_4 with (chlorodimethylsilyl)(trimethylsilyl)cyclopentadiene results in the chemoselective elimination of Me_3SiCl and cleanly affords ((chlorodimethylsilyl)cyclopentadienyl)titanium trichloride (**2**). Likewise, the reaction of TiCl_4 with (chlorodimethylsilyl)(trimethylsilyl)tetramethylcyclopentadiene (**6**) also results in the chemoselective elimination of Me_3SiCl and cleanly affords ((chlorodimethylsilyl)tetramethylcyclopentadienyl)titanium trichloride (**7**). This observation is in sharp contrast to the reaction of **6** with ZrCl_4 , which results in the chemoselective elimination of Me_3SiCl but affords a mixture of half-sandwich and zirconocene complexes. Support of complex **2** or **7** on (aminomethyl)polystyrene (AMPS, 1% cross-linking, 1.3 wt % N, 0.928 mmol of N/g of support), where the mole ratio of amine content of the support to precursor catalysts was selected to be 3:1, leads to the assembly of the constrained-geometry catalyst (CGCs) **8** or **9**, respectively. From the ^{29}Si NMR, the presence of a single silicon species was observed in complex **9**, which has been attributed to the CGC form. However, for **8** two silicon resonances were observed, one of which has been attributed to the CGC form and the other to a titanium amide moiety. The Ti:Si:Cl ratio for both **8** and **9** was found to be 1:1:4 through elemental analyses. Complexes **8** and **9**, in conjunction with MAO as the cocatalyst, were tested for ethylene homopolymerization and ethylene/1-octene copolymerization. The thermal properties and the molecular weights of the resulting polymers were determined. The observation of ethylene-*co*-1-octene provides independent evidence for the formation of supported CGC from the synthetic protocol.

Introduction

Numerous efforts are being directed toward the synthesis of single-site catalyst (SSC) architectures for the polymerization of olefins to produce high-density polyethylene and branched polyethylene as well as isotactic and syndiotactic polypropylenes.^{1–4} One subclass of SSCs comprises the constrained-geometry catalysts (CGCs), containing a cyclopentadienyl ring and an amido ligand, linked together with a dimethylsilyl unit.^{5–10} These catalysts are alternatives to the well-known Brintzinger and Kaminsky *ansa*-metallocenes.

Due to their open nature, CGCs are able to very efficiently polymerize α -olefins. Polyolefins made using these catalyst systems in homogeneous media have been studied extensively.¹¹

There are several different strategies by which the CGCs have been synthesized. One route is to synthesize $[\text{C}_5\text{R}_4\text{HSiMe}_2\text{NHR}']$ (**1**; R = CH_3 , H) from $(\text{C}_5\text{R}_4\text{H})\text{SiMe}_2\text{Cl}$ and $\text{R}'\text{NHLi}$ with subsequent removal of lithium chloride. The basic ligand framework of constrained-geometry catalysts can then be obtained by metathetical reaction of the dilithium salt of **1** with MCl_4 (M = Ti, Zr) (Scheme 1, method A).^{5,8,12} This route leads to a low yield of **3A**, which has subsequently been improved by the use of $\text{TiCl}_3(\text{THF})_3/\text{PbCl}_2$,¹³ while **3B** is obtained in good yield. Other preparations include amine elimination from the reaction of homoleptic metal amides with **1** (Scheme 1, method B).^{14,15} In this preparative method, the eliminated amine is found to coordinate to the metal center. Reduced ethylene polymerization activity has been observed when these catalyst systems have been

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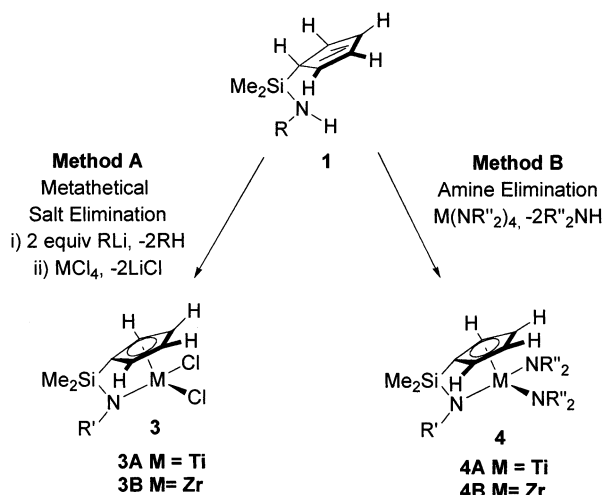
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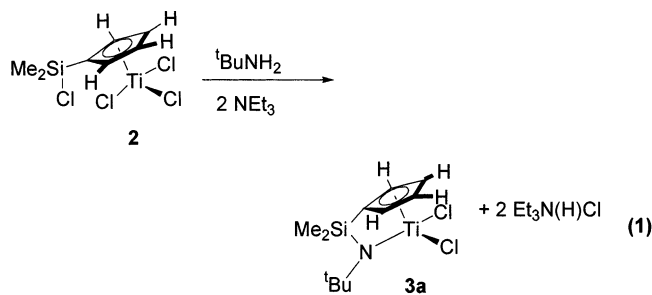
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Scheme 1. Synthetic Routes to Constrained-Geometry Catalysts



used, and this could be attributed to inefficient activation of these metal amides by the cocatalyst and presence of coordinated amines.^{16,17}

An alternate synthesis involves the initial formation of the chlorodimethylsilyl-substituted mono(cyclopentadienyl)titanium complex **2**, which on subsequent reaction with *tert*-butylamine affords the CGC **3** (eq 1).^{18,19} To date, this synthetic approach to CGC forma-



tion has been studied only in the case of the reaction of precursor catalyst **2** with *tert*-butylamine. The scope of this synthetic approach to the formation of CGCs has been limited by the availability of suitable precursors.

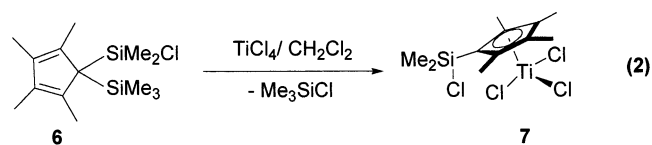
Commercial polymerization processes using soluble SSCs have been utilized to synthesize elastomers and low-crystallinity polyolefins, which remain soluble throughout the polymerization process. In gas-phase, slurry, or bulk polymerization, the polyolefin produced is insoluble in the fluidizing gas or reactor diluent/fluid. Therefore, to operate in a continuous process, catalyst particles of uniform size and shape need to be fed continually into the reactor, thus making it necessary to support the catalyst on an insoluble solid matrix.²⁰ Metallocenes have been supported on organic, typically polymeric, and inorganic materials. Cyclopentadienyls containing silyl moieties have been used as anchoring

points for metallocene complexes on silica supports.^{21,22} In general the polymerization activity of these supported metallocenes has not been as high as that for the corresponding homogeneous systems. Interestingly, polyolefins of ultrahigh molecular weight and increased crystallinity have been observed when metallocene-supported systems have been utilized.^{23–25} In contrast to the large number of studies correlating the structure of the metallocene or CGC with the resulting catalyst performance and resulting polymer properties,^{10,26} the systematic investigation of heterogenized CGCs is not nearly as comprehensive.^{27–29}

Adaptation of the assembly protocol of Royo to the use of primary amine functionalized solid supports with precursor catalysts should provide a synthetic route to CGCs. Toward this goal, we have synthesized chlorodimethylsilyl trimethylsilyl derivatives of cyclopentadienes and investigated the silyl elimination chemistries with TiCl₄ and ZrCl₄ to provide precursor catalysts. Their reaction with (aminomethyl)polystyrene (AMPS) results in the formation of heterogenized CGCs. The immobilized CGCs have been investigated for ethylene homopolymerization and ethylene/1-octene copolymerization.

Results and Discussion

(Trimethylsilyl)tetramethylcyclopentadiene was deprotonated using MeLi in a mixture of ether and toluene at room temperature with constant stirring overnight. The addition of an equimolar amount of (CH₃)₂SiCl₂ affords (chlorodimethylsilyl)(trimethylsilyl)tetramethylcyclopentadiene (**6**, mixed-silyl tetramethylcyclopentadiene), which was isolated by the removal of solvents in vacuo to yield a dark yellow viscous liquid in good yield and high purity. For the reactions of **6** with MCl₄ (M = Ti, Zr) there exists the question of chemoselectivity of the chloroalkylsilane eliminated. Literature precedence for the reaction of the mixed-silyl cyclopentadiene ((CH₃)₃Si)((CH₃)₂SiCl)C₅H₄ with TiCl₄ demonstrated that there is chemoselective elimination of (CH₃)₃SiCl and exclusive formation of **2**.¹⁸ Compound **6** on treatment with TiCl₄ in dichloromethane at room temperature for 3 days resulted in the exclusive formation of **7** as a dark red solid in good yield (eq 2). In the ¹H NMR



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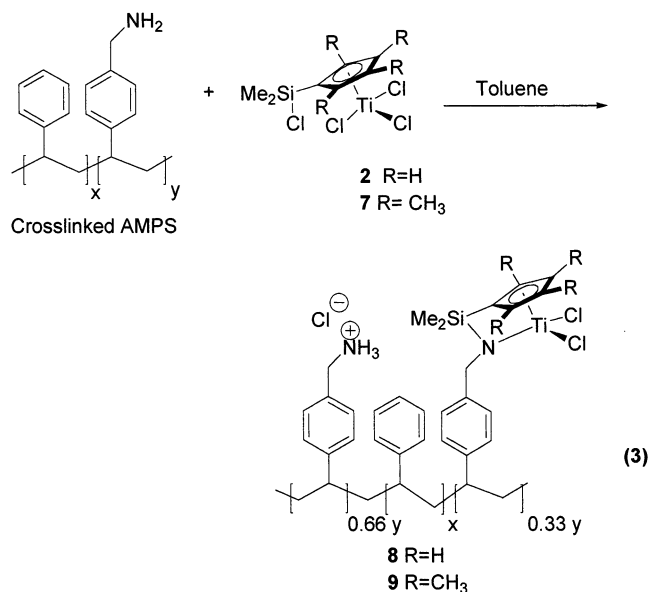
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singlet resonances for the methyl groups of $\text{Si}(\text{CH}_3)_2\text{Cl}$, $\text{CH}_3(\alpha)$, and $\text{CH}_3(\beta)$ were found in the ratio of 1:1:1 at δ 0.90, 2.38, and 2.59, respectively. A single silicon resonance is observed in the carbon-decoupled DEPT 45 ^{29}Si NMR at δ -5 that is attributed to $(\text{Si}(\text{CH}_3)_2\text{Cl})$. The high-resolution mass spectrum (HRMS) showed the presence of the molecular ion at m/z 367.9249. The purity of complex **7** was further confirmed by elemental analyses. In contrast, the reaction of **6** with ZrCl_4 in toluene at 100 °C over a period of 4 days affords a mixture of half-sandwich and zirconocene complexes which have been identified through ^1H and ^{13}C NMR. The silyl elimination of **6** with ZrCl_4 results in the chemoselective elimination of $(\text{CH}_3)_3\text{SiCl}$ but is not an efficient preparative route to the half-sandwich complex ((chlorodimethylsilyl)tetramethylcyclopentadienyl)zirconium trichloride.

The titanium precursor catalysts **2** and **7** have been treated with cross-linked (aminomethyl)polystyrene (AMPS, 1% cross-linking, 1.3 wt % N, 0.928 mmol of N/g of support). The mole ratio of amine content of the support to precursor catalysts was selected to be 3:1. The first amine equivalent of AMPS serves as the primary amine for the assembly of the CGC framework, and the other 2 equiv serves to scavenge the 2 equiv of HCl generated. The reaction of the precursor catalysts with swollen AMPS resin in hot toluene was allowed to proceed for 3 days, followed by numerous toluene washings to remove soluble byproducts and any residual precursor catalyst. The supports were then dried under vacuum at room temperature for a period of 12 h to afford CGC complexes **8** and **9**, respectively (eq 3).³³



The ^{29}Si NMR of complex **9** shows the presence of a single silicon resonance at δ -20.75, and this is attributed to the assembled CGC on the basis of literature precedence.³⁰ The elemental analyses showed the Ti:Si:Cl ratio to be 1:1:4, and the N:Ti ratio is 3:1. These data combined with the absence of NH and NH_2 bond stretches in the IR spectrum of **9** (KBr pellet) indicates that the efficiency of precursor loading is quantitative.

Moreover, the complete assembly of the CGC framework is indicated by the single ^{29}Si resonance.

The ^{29}Si NMR of **8** showed the presence of two silicon resonances. The resonance at δ -19.67 is attributed to the assembled CGC,³⁰ and the resonance at δ -10 can be attributed to a species bearing the chlorodimethylsilyl moiety, presumably not the precursor catalyst **2** given the number of toluene washings but rather a titanium amide complex. The elemental analyses showed the Ti:Si:Cl ratio to be 1:1:4, and the N:Ti ratio was found to be 3:1. The loading efficiency of the precursor is quantitative on the basis of both the results from elemental analysis and the infrared spectrum of **8** (KBr pellet), which shows the absence of NH and NH_2 stretches in the region of 3100–3500 cm^{-1} . However, the assembly of the CGC is incomplete, as seen from the ^{29}Si NMR results.

The supported catalyst systems **8** and **9** were tested for ethylene and ethylene/1-octene polymerizations. The cocatalyst used in these polymerization studies was MAO (30 wt % in toluene). An excess of cocatalyst was used to both activate the CGC and to scavenge the ammonium salts formed during the support protocol. Olefin polymerizations were conducted by charging a mixture of 10.0 mL of toluene and 1.0 mL of 30% MAO with a quantity of supported catalyst in a thick-walled glass reactor vessel. The system was pressurized with 60 psig of ethylene for a suitable time period with constant stirring. For 1-octene copolymerization studies the comonomer was added by means of an additional cylinder simultaneously with the ethylene. The ethylene overpressure was delivered into the reactor without the removal of the nitrogen atmosphere. At the end of the polymerization, the ethylene supply was stopped and the reactor was vented. The reaction mixture was quenched by the addition of 10% hydrochloric acid solution in methanol; the polymer was isolated by filtration and dried in a vacuum oven overnight. Experimental conditions, the yield of polymer, polymerization activity, molecular weights, and melting points of the polymers are shown in Table 1.

Using complex **9** in conjunction with MAO in a toluene slurry under 4 atm of ethylene pressure afforded polyethylene (Table 1, entry 1). Thermal analysis of the resulting polymer showed the presence of a unimodal melting peak for HDPE in both the first and second melt scans (DSC) with a final ΔH_f value of 56.9 J/g. The degree of crystallinity of this sample is substantially lower than that of corresponding HDPE samples prepared using soluble GCC. Presumably, the support is suppressing the crystallinity of the polymers as they are being synthesized. The extent to which a support may influence the degree of crystallinity for polyolefins prepared via heterogeneous SSC at this moment is not known. Molecular weight analysis using GPC of the polymer gives an M_w value of 529 000 and a PDI of 1.58. The response signals for both light scattering and refractive index detectors were unimodal. The physical characteristics of the polyethylene are fully consistent with the formation of HDPE from an SSC, presumably the heterogenized CGC complex **9**. However, it is possible that during polymerization processes using this supported catalyst in slurry mode, fragmentation of cyclopentadienyltitanium moieties may occur.^{20,25} The

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Table 1. Ethylene and Ethylene/1-Octene Copolymerization

entry	cat. (amt (mg))	Al:Ti	amt of comonomer added (mL)	yield (mg)	activity (kg/((mol of Ti) h (atm of C ₂)))	T _m ^c (°C)	ΔH (J/g)	comonomer incorpn (mol %) ^d	M _w (polymer)	PDI
1	9 (80.0) ^b	268	0	311	102.0	134.1	56.9	0	529 200	1.58
2	9 (110.0) ^a	195	5.0	329	8.0	119.5, 135.3	13.12	2.2	611 000	2.94
3	8 (25.3) ^a	422	0	900	38.7	135.5 (PE3a) 140.5 (PE3b)	76.5 128.4	0	200 220, 409 000	2.09, 1.95
4	8 (112.9) ^a	95.3	5.0	315	11.23	125.6	54.8	2.0	172 900	3.70
5	2 (2.25) ^a	659.3	0	277	4.9	133	125.0	0	447 550	2.67
6	2 (2.25) ^a	659.3	5.0	300	5.1	134.9	115.3	0	n.d.	n.d.

^a Ethylene pressure of 60 psig for 120 min. ^b Ethylene pressure of 60 psig for 45 min. ^c Second melt of DSC scan. ^d Monomer incorporation calculated according to ref 31.

resulting solubilized fragments would also polymerize ethylene to HDPE. It is thus difficult to ascertain conclusively the form of the active catalyst, or catalysts, when conducting ethylene polymerization beginning with a heterogeneous SSC.

The demonstrated ability of CGCs to incorporate α -olefins during copolymerization with ethylene provides a method for discerning between heterogenized CGCs and leached fragments.¹⁰ Ethylene/1-octene copolymerization was used to verify the presence of the assembled CGC complex **9** on the AMPS support (Table 1, entry 2) and to probe for the presence of leached Ti species. Thermal analysis of the resulting polymer reveals two melting endotherms. The lower melting peak occurs at 119.45 °C and has been attributed to the incorporation of 1-octene units. It is well-documented that a depression in melting point occurs with incorporation of α -olefins in a random fashion. The melting point has been correlated to the amount of comonomer incorporated into the HDPE, and this was determined to be 2.2 mol % of 1-octene, as determined by the depression in melting point of the copolymer through DSC³¹ and ¹³C NMR of the copolymer. A higher melting peak at 135.2 °C has been attributed to the formation of HDPE. This could be a consequence of an ethylene-only polymerization catalyst being formed by the abstraction of a titanium fragment by the action of MAO.

The observed multimodality of the DSC endotherms and broadening of GPC peaks that result from the copolymerization of ethylene and 1-octene is indicative of multiple catalysts being present during the reaction. To ascertain that the phenomena of leaching is the primary reason for the production of HDPE during copolymerization, the reactions were quenched with methanol at reaction times ranging from 20 min to 2 h (Supporting Information, Table 2 and Figures S3 and S4). The initial formation of LLDPE continues throughout the course of the reactions, and the formation of HDPE is observed only at longer reaction times. The action of MAO on the supported catalysts presumably leads to a leached Ti species that is selective for ethylene homopolymerization. On the other hand, precontacting **9** with MAO followed by filtration and use of the filtrate for ethylene homopolymerization and ethylene/octene copolymerization indicated a low activity of 10% relative to the activity for the supported catalysts in ethylene polymerization. Furthermore, the absence of 1-octene incorporation in the ethylene/octene copolymerization experiment using the filtrate is noted. Similar results

for ethylene polymerization have been reported for the attempted detection of leached species from support metallocene catalysts.²⁵ Another possible origin of the HDPE observed in the copolymerization experiments could be a result of diffusion limitation of 1-octene to a certain CGC site within the cross-linked polystyrene bead. However, diffusion limitations of the comonomer to catalyst sites dispersed throughout the AMPS was eliminated using a surplus of 1-octene in a well-stirred solvent-comonomer swollen bead.

The homopolymerization of ethylene using the mixed catalyst system **8** affords HDPE (Table 1, entry 3). Soxhlet extraction with refluxing toluene afforded two fractions, a lower molecular weight sample of lower crystallinity (PE3a) and a higher molecular weight sample with higher crystallinity (PE3b). This mixture of PE fractions correlates with the ²⁹Si NMR data, which showed the presence of two silicon moieties.

The copolymerization of ethylene and 1-octene using the mixed catalyst **8** was performed. Analysis of the resulting polymer by DSC reveals the presence of two melting endotherms during the first melt (Table 1, entry 5). These correspond to a mixture of LLDPE and HDPE fractions. Slow cooling of the melt to ambient temperature followed by a second melting revealed a single endotherm due to the cocrystallization of LLDPE and HDPE. The depression in melting point has been attributed to incorporation of 2.0 mol % of 1-octene. The polymer was extracted from the support using hot trichlorobenzene. Molecular weight analysis by GPC reveals a trace with an overall M_w value of 172 900 with a PDI of 3.70, and a slight shoulder of lower molecular weight is observed; this correlates well with the two melting endotherms observed in the first melt by DSC.

The polymerization of ethylene and the ethylene/1-octene copolymerization using the precursor catalyst **2** in conjunction with MAO both result in the formation of HDPE (Table 1, entries 5 and 6, respectively). This activated soluble catalyst presumably resembles that of a leached titanium species. The formation of LLDPE in entry 4 clearly is the consequence of the formation of a CGC architecture, as mono(cyclopentadienyl)titanium trichloride complexes did not incorporate α -olefins during copolymerization control experiments (entry 6).

Conclusions

Competitive silyl elimination for the mixed silyl complex **6** with both titanium and zirconium tetrachloride proceeds with chemoselective elimination of (CH₃)₃-SiCl. Silyl elimination from **6** with TiCl₄ proceeds cleanly for the exclusive formation of **7**. However, in the

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silyl elimination reaction of **6** with $ZrCl_4$ the rate of double insertion is comparable to that of half-sandwich formation, leading to the observed mixture of products. The reactivity differences between $TiCl_4$ and $ZrCl_4$ may be attributed to the differences in their size and in the Lewis acidities of the metal centers.

Protocols for supporting titanium complexes **2** and **7** on an AMPS matrix, affording catalysts **8** and **9**, respectively, have been established. The reaction chemistry of **2** with AMPS results in the formation of a mixture of CGC and a titanium amide. However, the reaction of **7** with AMPS exclusively affords the formation of CGC **9**, as confirmed by NMR and FT-IR analyses. Verification of the presence of the support CGC framework is evident by the formation of LLDPE from the copolymerization studies of ethylene and 1-octene. Characterizations of the molecular weight, molecular weight distributions, melting points, and enthalpies of fusion have been determined for these copolymers. The degrees of crystallinity of the polyolefins synthesized from these supported catalysts are substantially reduced relative to polymers produced using soluble CGCs. Copolymerization studies of ethylene and α -olefins provide an easy means for determining the efficiency of support of CGCs. The observation of LLDPE formation during ethylene/1-octene copolymerization using **9** is independent confirmation of the supported CGC form. However, an ethylene-only polymerization catalyst is apparently being formed by leaching of a titanium fragment from **9** at long reaction times. This is the first example of a supported catalyst system wherein the copolymerization ability of the supported and leached species differ such that by performing product analysis it is possible to differentiate the presence of a leached species from the starting supporting catalyst.

Experimental Section

Reagents and General Techniques. All reactions were performed under nitrogen in Schlenk glassware or in an inert-atmosphere drybox. All solvents used were obtained from a solvent manifold.³² The chlorosilanes such as $(CH_3)_3SiCl$ and $(CH_3)_2SiCl_2$ were distilled from calcium hydride. Tetramethylcyclopentadiene, CH_3Li (1.4 M in ether), $TiCl_4$, and presublimed $ZrCl_4$ were obtained from Aldrich and used as received. Complex **2** was synthesized following a literature procedure.¹⁹ Cross-linked (aminomethyl)polystyrene (AMPS, 1.29 wt % of N, 0.928 mmol of N/g of support, 1% cross-linking) beads were obtained from Polymer Laboratories Inc.

Instrumentation. 1H NMR spectra were obtained at 300 MHz using a Bruker DPX 300, ^{13}C NMR spectra were recorded at 75 MHz using Bruker DPX 300 in the continuously proton decoupled (CPD) mode, and ^{29}Si NMR spectra were recorded at 150 MHz on an Avance DPX 600 using the DEPT 45 pulse program for solution NMR. Solid-state ^{13}C and ^{29}Si NMR for the solid samples were recorded at 75 MHz on Bruker DSX 300 using the magic angle spinning–cross-polarization method in a 7 mm rotor at a spinning rate of 4500 Hz. Mass spectral analyses were performed using a JMS700 MStation (JEOL) high-resolution (HRMS) two-sector mass spectrometer in the

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(33) On treatment of AMPS with either **2** or **7** in a N:Ti mole ratio of 1:1 using 2 equiv of Et_3N as the acid scavenger, the ammonium salt formed during the support protocol could not be completely removed with toluene washings. The resulting polymerization activities were observed to be lower due to residual triethylamine.

EI (electron impact) mode. Elemental analysis was performed using three Exeter Analytical Inc. 240XA CHN analyzers, and a Leaman Labs Inc.-Dual View-DRE-Sequential-ICP was used to analyze the Ti and Si loadings in the samples. Gel permeation chromatography was performed with Polymer Laboratories PL-220 high-temperature GPC equipped with a Wyatt MiniDawn (620 nm diode laser) high-temperature light scattering detector and refractive index detector at 135 °C using 1,2,4-trichlorobenzene as solvent. The dn/dc value for polyethylene used was -0.11 . Thermal analysis was performed using a TA DSC 2910 instrument equipped with a liquid nitrogen cooling accessory unit under a continuous nitrogen purge (50 mL/min). Data reported were gathered for the first and second melt with a heating and cooling scan of 10 °C/min. Infrared analyses were performed using a Perkin-Elmer 2000 FTIR on samples prepared as KBr pellets.

Synthesis of 1-(Trimethylsilyl)-2,3,4,5-tetramethylcyclopentadiene (5). To a solution of 2,3,4,5-tetramethylcyclopentadiene (5.0 mL, 44 mmol) in a mixture of ether and toluene (1:4 v:v, 20 mL total) was added dropwise CH_3Li (44 mmol, 3.5 mL), and the resulting mixture was stirred overnight to ensure complete deprotonation. To this solution was added dropwise $(CH_3)_3SiCl$ (4.8 mL, 44 mmol), and the solution was stirred for 24 h at room temperature to ensure complete silylation. Lithium chloride was removed by filtering through Celite, and the volatiles were subsequently removed in vacuo; compound **5** was isolated as a pale yellow liquid (6.9 mL, 95% yield).

1H NMR ($CDCl_3$): δ 0.03 (s, 9 H, $Si(CH_3)_3$), 1.88 (s, 6 H, Cp $CH_3(\alpha)$), 1.97 (s, 6 H, Cp $CH_3(\beta)$), 2.75 (Cp H, attached to the ipso carbon). ^{13}C NMR ($CDCl_3$, CPD): δ 0.00 ($Si(CH_3)_3$), 12.90 (Cp $CH_3(\alpha)$), 16.20 (Cp $CH_3(\beta)$), 57.10 (ipso carbon C_1), 134.00, 137.00 (C_2 , C_3 Cp). Anal. Calcd for $C_{12}H_{22}Si$: C, 74.22; H, 11.34. Found: C, 74.18; H, 11.47.

Synthesis of 1-(Dimethylchlorosilyl)-1-(trimethylsilyl)-2,3,4,5-tetramethylcyclopentadiene (6). To a solution of **5** (5.79 mL, 30 mmol) in a mixture of ether and toluene (1:4 v:v, 20 mL total) was added CH_3Li (30 mmol, 2.15 mL), and the resulting solution was stirred overnight to ensure complete deprotonation. To the resulting solution was added dropwise $(CH_3)_2SiCl_2$ (3.87 mL, 30 mmol), and the mixture was stirred at room temperature for 3 days. Lithium chloride was removed by filtering through Celite, and the solvents were removed in vacuo. Compound **6** was isolated as a viscous yellow liquid (7.7 mL, 90% yield).

1H NMR ($CDCl_3$): δ 0.01 (s, 9 H, $Si(CH_3)_3$), 0.19 (s, 6 H, $Si(CH_3)_2Cl$), 1.82 (s, 6 H, Cp $CH_3(\alpha)$) and 2.03 (s, 6 H, Cp $CH_3(\beta)$). ^{13}C NMR ($CDCl_3$, CPD): δ -0.04 ($Si(CH_3)_3$), 2.65 ($Si(CH_3)_2Cl$), 11.75 (Cp $CH_3(\alpha)$), 15.44 (Cp $CH_3(\beta)$), 132.675 and 139.36 (C_2 , C_3 Cp), C_1 Cp not located. Anal. Calcd for $C_{14}H_{27}ClSi_2$: C, 58.64; H, 9.34. Found: C, 58.82; H, 9.75.

Synthesis of (1-(Chlorodimethylsilyl)-2,3,4,5-tetramethylcyclopentadienyl)titanium Trichloride (7). Compound **6** (3.0 mL, 9.45 mmol) was added dropwise to a solution of $TiCl_4$ (1.8 mL, 9.45 mmol) in 20 mL of dichloromethane, and the reaction mixture was stirred at room temperature for 3 days. Volatiles were then removed in vacuo; the residue was redissolved in 2 mL of dichloromethane to which 4 mL of hexane was added. Recrystallization at -30 °C over a period of 5 days afforded a dark red microcrystalline solid (2.83 g, 83% yield).

1H NMR (C_6D_6): δ 0.9 (s, 6 H, $Si(CH_3)_2Cl$), 2.38 (s, 6 H, Cp $CH_3(\alpha)$), 2.59 (s, 6 H, Cp $CH_3(\beta)$). ^{13}C NMR (C_6D_6 , CPD): δ 5.4 ($Si(CH_3)_2Cl$), 14.52 (Cp $CH_3(\alpha)$), 17.89 (Cp $CH_3(\beta)$), 143.00 and 145.00 (C_2 , C_3 Cp), C_1 Cp not located. ^{29}Si NMR (DEPT 45): δ -5 ($Si(CH_3)_2Cl$). HMRS: m/z 367.9385 (M^+ , calculated), 367.9249 (M^+ , observed). Anal. Calcd for $C_{11}H_{18}Cl_3SiTi$: C, 35.96; H, 4.89. Found: C, 35.83; H, 4.65.

Synthesis of Complex 8. To a slurry of AMPS copolymer (1 g of XL AMPS, 1.3 wt % of N, 0.928 mmol of N/g of support) in toluene was added 74 mg (0.247 mmol) of complex **2**, and

the solution was stirred at 80 °C for 3 days. The support was then washed with a dichloromethane/toluene mixture (1:4 v:v) numerous times, and the supported catalyst was recovered and vacuum-dried overnight at 60 °C, affording 0.8 g of yellow powder. Anal. Found: C, 80.10; H, 7.95; N, 1.79; Ti, 2.10; Cl, 6.29; Si, 1.4. ²⁹Si NMR (CP-MAS): δ -10.0, -19.67. IR (ν , cm⁻¹; KBr pellet): 3100 (s), 3028 (s), 2922 (s), 2849 (m), 1943 (m), 1872 (s), 1803 (m), 1601 (s), 1492 (s), 1452 (s), 1182 (m), 1155 (m, Si-N stretch), 1027 (m, Ti-N stretch), 907 (m), 840 (w), 697 (s), 467 (w, Ti-Cl stretch).

Synthesis of Complex 9. To a slurry of AMPS copolymer (1 g, 1.3 wt % of N, 0.928 mmol of N/g of support) in toluene was added 90.82 mg (0.23 mmol) of **7**, and the solution was stirred at 80 °C for 3 days. The supported catalyst was then washed with a dichloromethane/toluene mixture (1:4 v:v) numerous times, and the support was recovered and vacuum-dried at 50 °C overnight, affording 0.9 g of yellow-orange powder.

Anal. Found: C, 82.71; H, 7.38; N, 1.21; Ti, 1.5; Cl, 4.76; Si, 1.0. ²⁹Si NMR (CP-MAS): δ -20.75. IR (ν , cm⁻¹; KBr pellet): 3010 (s), 2979 (s), 2947 (s), 2882 (w), 2739 (m), 2623 (s), 2605 (s), 2532 (w), 2498 (s), 2359, 1445 (s), 1398 (s), 1365 (m), 1261 (m), 1173 (m, Si-N stretch), 1037 (s, Ti-N stretch), 851 (m), 807 (s), 697 (w), 462 (w, Ti-Cl stretch).

Representative Polymerization of Ethylene using Complex 8. To a mixture of 10 mL of toluene and 1.0 mL of 30% MAO placed in a polymerization reactor along with a stir bar was added 25.3 mg of complex **8**, and the reactor was pressurized with 60 psig of ethylene for 2 h at room temperature with constant stirring. After 2 h, the ethylene supply was stopped and the reactor was vented to remove excess ethylene, the reaction mixture was quenched with a 10% hydrochloric acid-90% methanol mixture, and the polyethyl-

ene was filtered out and dried in a vacuum oven overnight to afford 900 mg of polyethylene (Table 1, entry 5).

Representative Copolymerization of Ethylene and Octene using Complex 8. To a mixture of 10.0 mL of toluene and 1.0 mL of MAO in a polymerization reactor was added 112.9 mg of **8**. To this system was added 1-octene (5 mL), and ethylene at a pressure of 60 psig was supplied for 2 h at room temperature with constant stirring. The ethylene supply was stopped and the reactor was vented to remove excess ethylene, the reaction mixture was quenched with a 10% hydrochloric acid-90% methanol mixture, and the polymer was filtered out and dried in a vacuum oven overnight to afford 315 mg of product (Table 1, entry 6).

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Supporting Information Available: A table and figures giving additional data for the ethylene/1-octene copolymerization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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