Pendent Aminoalkyl-Substituted Monocyclopentadienyltitanium Compounds and Their Polymerization Behavior

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Received February 19, 1998

A series of new aminoalkyl-substituted monocyclopentadienyltitanium trichloride compounds have been prepared that contain pyridyl (2-picolyl), diisopropylaminoethyl, dimethylaminoethyl, and phenylethyl ligands. Incorporation of these pendent ligands to corresponding (cyclopentadienyl)triisopropoxytitanium and (indenyl)triisopropoxytitanium complexes are also described. The utility of these complexes for the polymerization of ethylene, propylene and styrene has been investigated.

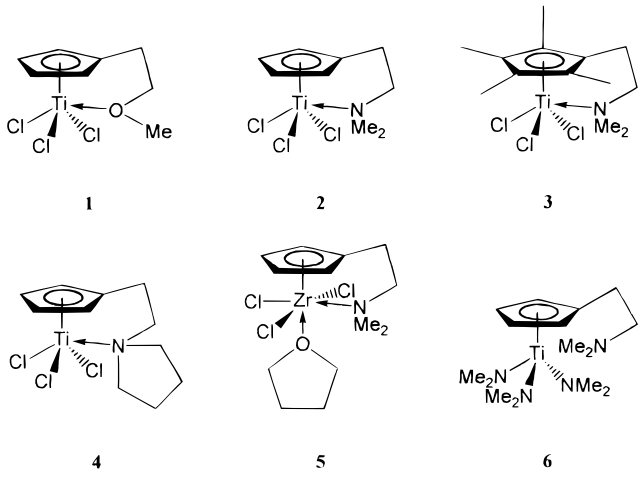
Introduction

With the discovery by Flores et al.[1] of the pendent aminoalkyl effect on organotitanium catalysts for the polymerization of ethylene, propylene, and styrene, considerable effort in our laboratory and elsewhere has been focused on the development of new, more active, and more stable catalyst systems of this type.

Qichen et al.[2] reported the first example of a chelated cyclopentadienyl ligand on a titanium half-sandwich complex. Their synthesis and X-ray structural determination of [η^5-(2-methoxyethyl)cyclopentadienyl]trichlorotitanium (**1**) demonstrated that the ether oxygen atom in the side chain attached to the cyclopentadienyl ring coordinates with the titanium atom to form a chelate ring (Chart 1). They also noted that **1** was considerably more sensitive to moisture and was thermally less stable than $CpTiCl_3$. Flores et al. developed the catalyst precursors [η^5-(2-dimethylaminoethyl)cyclopentadienyl]trichlorotitanium (**2**)[1] and [η^5-2,3,4,5-tetramethyl-1-(2-dimethylaminoethyl)cyclopentadienyl]-trichlorotitanium (**3**).[3] They demonstrated that **2** was approximately 100 times as active for the polymerization of ethylene as $CpTiCl_3$ and that both **2** and **3** were efficient catalyst precursors for the polymerization of propylene, giving atactic polymer of high molecular weight.

Recently, Herrmann et al.[4] reported the pyrrolidine and piperidine analogues of **1**, confirming Ti−N intramolecular coordination for the former (**4**) by an X-ray diffraction study. Jutzi and Kleimeier[5] also recently described the synthesis and molecular structure of the first zirconium analogue (**5**) containing a pendent aminoalkylcyclopentadienyl system. Their studies demonstrated direct coordination of the amino nitrogen to the zirconium center. They also prepared the tris(dimethylamido)titanium analogue (**6**).

Chart 1



In this paper, we report the synthesis of some analogues of **1** that contain bridged pyridyl (2-picolyl), diisopropylaminoethyl, and phenylethyl ligands. Extensions of these pendent ligands to corresponding (cyclopentadienyl)triisopropoxytitanium and (indenyl)triisopropoxytitanium complexes are described. The utility of these complexes for the polymerization of ethylene, propylene, and styrene is also discussed.

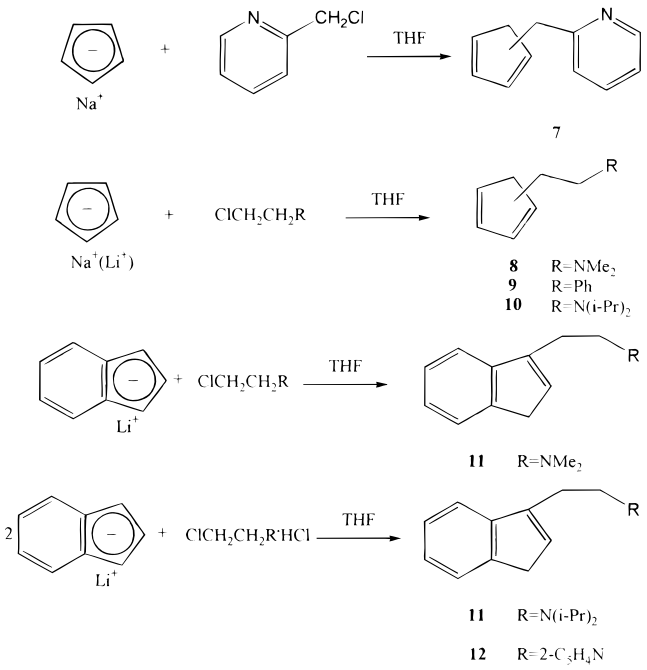
Results and Discussion

Synthesis of Pendent Ligands. All organic ligands used in the present study were prepared by modifications of the procedures described by Wang et al.[6] and Flores et al.[1] Reactions between cyclopentadienylsodium and 2-picolyl chloride, 2-dimethylaminoethyl chloride, and 2-bromoethylbenzene in THF solution produced (2-picolyl)cyclopentadiene (**7**), (2-dimethylaminoethyl)cyclopentadiene (**8**), and (2-phenylethyl)cyclopentadiene (**9**), respectively, in 67−78% yield. A similar

(1) Flores, J. C.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1994**, *13*, 4140.
(2) Qichen, H.; Yanlong, Q.; Guisheng, L. *Transition Met. Chem.* **1990**, *15*, 483.
(3) Flores, J. C.; Chien, J. C. W.; Rausch, M. D. *Macromolecules* **1996**, *29*, 8030.
(4) Herrmann, W. A.; Morawietz, M. J. A.; Priermeier, T. S.; Mashima, K. *J. Organomet. Chem.* **1995**, *486*, 291.
(5) Jutzi, P.; Kleimeier, J. *J. Organomet. Chem.* **1995**, *486*, 287.
(6) Wang, T.-F.; Lee, T.-Y.; Chou, J.-W.; Ong, C.-W. *J. Organomet. Chem.* **1992**, *423*, 31.

S0276-7333(98)00118-6 CCC: $15.00
Publication on Web 07/21/1998

Scheme 1



reaction in THF solution between 2-diisopropylaminoethyl chloride and cyclopentadienyllithium afforded (2-diisopropylaminoethyl)cyclopentadiene (**10**) in 46% yield. Analogous reactions between indenyllithium and 2-dimethylaminoethyl chloride, 2-diisopropylaminoethyl chloride, and 2-pyridylethyl chloride formed 3-(2-dimethylaminoethyl)indene (**11**), 3-(2-diisopropylaminoethyl)-indene (**12**), and 3-(2-pyridylethyl)indene (**13**) in yields of 50−95%, respectively. All pendent ligand compounds were purified by vacuum distillation and were characterized by elemental analyses as well as by their ^{1}H NMR spectra. Scheme 1 illustrates the syntheses of all the pendent ligands.

Two basic methods were used to generate the free chloroalkylamines from their respective hydrochlorides. In most cases, the amine was generated by reaction with an aqueous solution of potassium hydroxide, followed by extraction with hexane and benzene. Separation and drying of the organic layer over magnesium sulfate gave excellent results. In the case of several indenyllithium reactions, 2 equiv of the organolithium compound was used, and the amino reactant was added as the hydrochloride. The first equivalent was used as a base to convert the hydrochloride to the amine, and the second equivalent was used as a nucleophile, displacing the halide and generating the desired ligand.

All the aminoalkylcyclopentadienes generated in this study are thermally sensitive compounds. Vacuum distillation of the crude products in order to obtain pure ligands always gave red or dark orange tarlike residues. However, trapping the distilled product at dry ice temperatues allowed for long-term storage of the purified ligands without appreciable loss due to side reactions. Conversion to corresponding lithium cyclopentadienides and subsequent conversion to respective trimethylsilyl derivatives represents another means of trapping the distilled ligands.

Indenyllithium reacted with the chloroalkylamines to give the desired aminoalkylindenes in high yield (Scheme l). These ligands are stable at room temperature and can be readily distilled under vacuum to give elementally pure samples. The tarlike materials observed in the purification of the aminoalkylcyclopentadienes were not observed in distillations of the substituted indenes if the crude products were heated gently in an oil bath with good temperature control.

New Cyclopentadienylthallium Reagents Containing Pendent Ligands. During this study, three new substituted cyclopentadienylthallium reagents (**14**−**16**) were synthesized in excellent yield. Their utility as intermediates in reactions with both early and late organotransition metal halides was also demonstrated (Scheme 2).

Many mono- and persubstituted cyclopentadienylthallium compounds are reported in the literature, and their utility as synthetic intermediates makes them highly useful reagents.[7] Their relative stability and their ease of purification by vacuum sublimation are in contrast to analogous organosodium and organolithium reagents.

Reaction of **7** with 1 equiv of thallium ethoxide produced (2-picolyl)cyclopentadienylthallium (**14**) in 87% yield as a white solid that slowly darkened in the light at room temperature. Vacuum sublimation of the darkened material gave a white crystalline sublimate, which was used in a subsequent reaction with chlorodicarbonylrhodium dimer to form [η^5-(2-picolyl)cyclopentadienyl]dicarbonylrhodium (**17**) in 69% yield (Scheme 2). Vacuum distillation of **17** gave a sample of elemental purity but also resulted in some decomposition. Compound **17** is very hygroscopic and darkens on exposure to air.

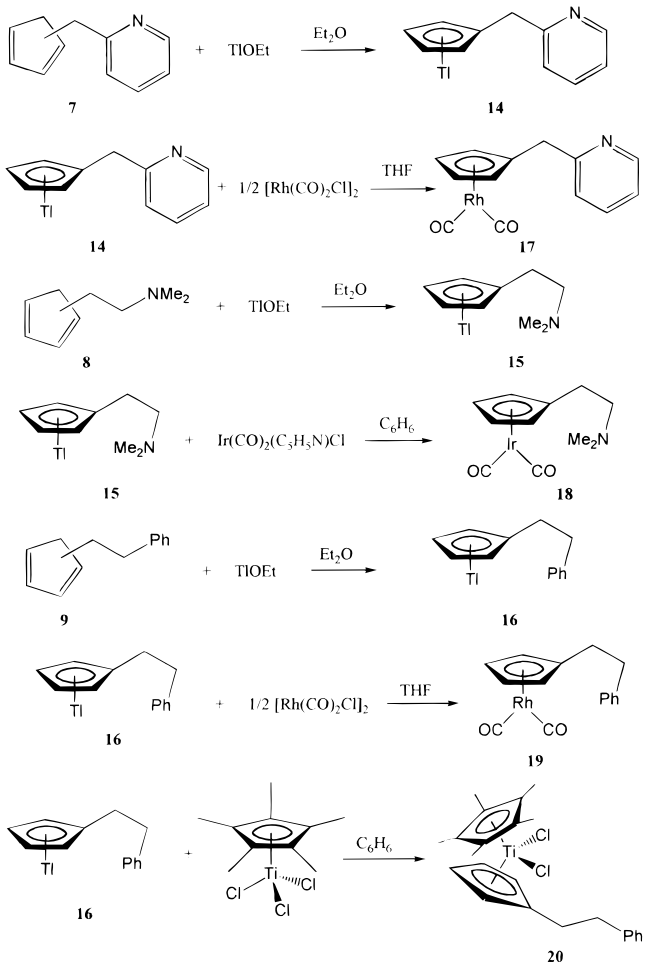
A reaction between **8** and thallium ethoxide produced (2-dimethylaminoethyl)cyclopentadienylthallium (**15**) in 97% yield. The product could be vacuum sublimed to afford **15** as a white crystalline solid that was of elemental purity but was best stored at −15 °C under argon and in the dark. Reaction of **15** with chlorodicarbonyl(pyridine)iridium gave [η^5-(2-dimethylaminoethyl)cyclopentadienyl]dicarbonyliridium (**18**) in higher yield (76%) than was obtained from the corresponding organolithium reagent (45%).[8]

(2-Phenylethyl)cyclopentadienylthallium (**16**) was obtained in 78% yield from a reaction between thallium ethoxide and **9**, followed by vacuum sublimation of the product. It was necessary to extract the crude product repeatedly with pentane before sublimation in order to remove a small amount of excess **9** which otherwise distilled with the desired product. Reactions of **16** with chlorodicarbonylrhodium dimer and with (η^5-penta-

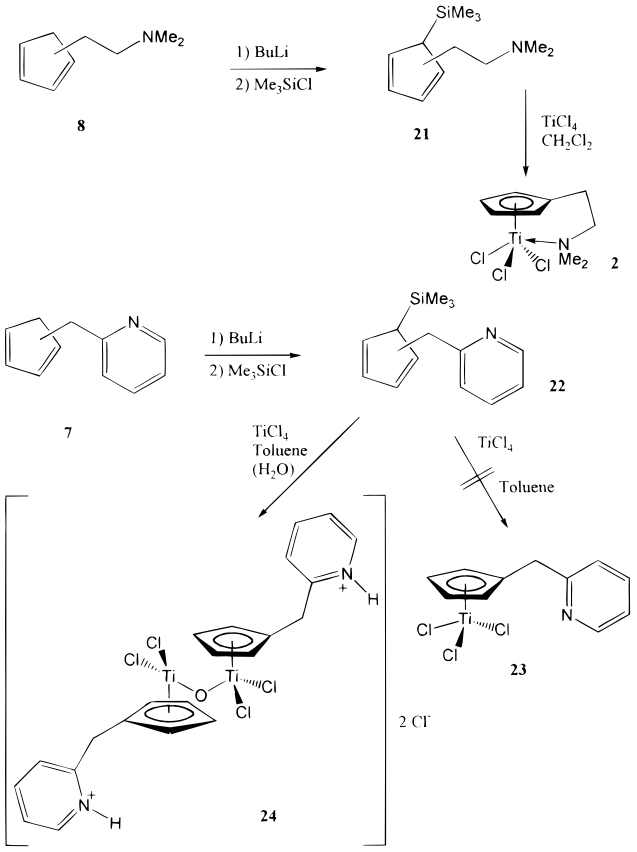
(7) See, for example: (a) Rausch, M. D.; Edwards, B. H.; Rogers, R, D.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 3882. (b) Conway, B. G.; Rausch, M. D. *Organometallics* **1985**, *4*, 688. (c) Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 4228. (d) Werner, H.; Otto, H.; Kraus, H. J. *J. Organomet. Chem.* **1986**, *315*, C57. (e) Spink, W. C.; Rausch, M. D. *J. Organomet. Chem.* **1986**, *308*, C1. (f) Schumann, H.; Janiak, C.; Khani, H. *J. Organomet. Chem.* **1987**, *330*, 347. (g) Arthurs, M.; Al-Daffaee, H. K.; Haslop, J.; Kubal, G.; Pearson, M. D.; Thatcher, P.; Curzon, E. *J. Chem. Soc., Dalton Trans.* **1987**, 2615. (h) Singh, P.; Rausch, M. D.; Bitterwolf, T. E. *J. Organomet. Chem.* **1988**, *352*, 273. (i) Rausch, M. D.; Lewison, J. F.; Hart, W. P. *J. Organomet. Chem.* **1988**, *358*, 161. (j) Rausch, M. D.; Spink, W. C.; Atwood, J. L.; Baskar, A. J.; Bott, S. G. *Organometallics* **1989**, *8*, 2627. (k) Jones, S. S.; Rausch, M. D.; Bitterwolf, T. E. *J. Organomet. Chem.* **1990**, *396*, 279. (l) Schumann, H.; Ghodsi, T.; Esser, L.; Hahn, E. *Chem. Ber.* **1993**, *126*, 591. (m) Jones, S. S.; Rausch, M. D.; Bitterwolf, T. E. *J. Organomet. Chem.* **1993**, *450*, 27.

(8) Blais, M. S.; Rausch, M. D. *J. Organomet. Chem.* **1995**, *502*, 1.

Scheme 2



Scheme 3



methylcyclopentadienyl)trichlorotitanium gave the desired products (**19**, **20**) in good yields.

Catalyst Precursor Synthesis. Initial studies were directed toward the synthesis and characterization of pendent [(aminoalkyl)cyclopentadienyl]trichlorotitanium compounds using the ligands described above. Compound **2** was prepared in high yield via the trimethylsilyl intermediate **21** by a modification of the original literature procedure (Scheme 3).[1] In the 2-picolyl system, ligand **7** was sucessfully converted into the corresponding trimethylsilyl intermediate **22** in 92% yield. However, in subsequent reactions of **22** with titanium tetrachloride under a variety of conditions, we were not able to isolate the desired trichloride **23** but obtained instead the μ-oxo dimer dihydrochloride **24** (Scheme 3). The extreme moisture sensitivity of **23** is derived from the fact that the pyridyl group in **23** can act as a driving force to facilitate its hydrolysis to form **24**, as has been observed previously for **2**. We were subsequently able to prepare **23** in 83% yield from a reaction between thallium reagent **14** and titanium tetrachloride in toluene; however, the compound could not be obtained in analytical purity due to its high sensitivity.

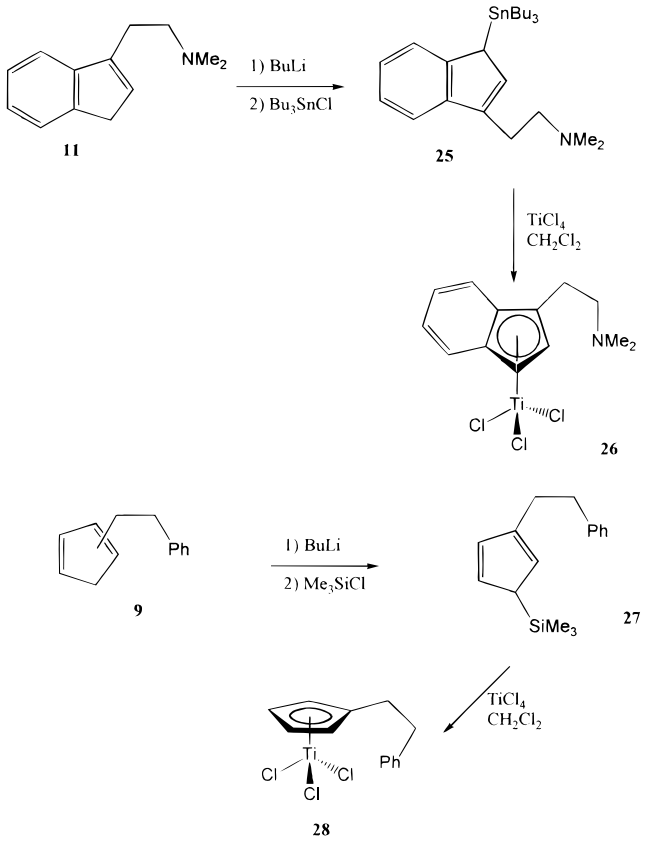
Several attempts to prepare [η^5-1-(2-dimethylaminoethyl)indenyl]trichlorotitanium (**26**) via a trimethylsilyl intermediate were unsuccessful. The reaction product appeared via NMR to be an amine coordination complex between the amino ligand of the silyl intermediate and titanium tetrachloride. However, using an approach employed by Shaw et al.[9] for monoindenyl trichloride derivatives of zirconium and hafnium, we were able to convert the indenyl ligand **11** to the tributyltin derivative **25** and subsequently into **26** (Scheme 4). The product was very air sensitive and could not be obtained in elemental purity. However, the reaction product was pure by NMR and proved to be an excellent catalyst for the polymerization of ethylene and propylene (see Polymerization Studies section).

In addition to pendent aminoalkyl-substituted systems, Flores et al.[10] synthesized [1-(2-phenylethyl)-2,3,4,5-tetramethylcyclopentadienyl]trichlorotitanium and determined that it was a good catalyst for the polymerization of both ethylene and styrene. For this reason, we also synthesized [η^5-(2-phenylethyl)cyclopentadienyl]-trichlorotitanium (**28**) from ligand **9** via the trimethylsilyl intermediate **27** (Scheme 4). The ligand **9** undergoes dimerization fairly rapidly, and an intractible tarry residue was formed during vacuum distillation. The ligand is best converted to either the trimethylsilyl derivative **27** or the thallium complex **16** for prolonged storage.

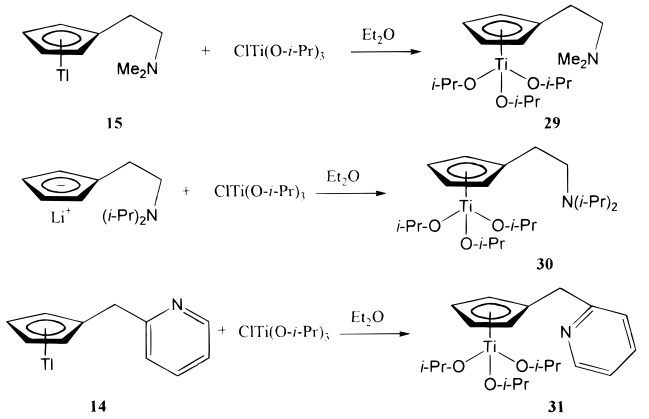
The extraordinarily high sensitivity of aminoalkyl-substituted cyclopentadienyltitanium trichlorides such as **23** and **26** prompted us to develop catalyst precursor systems that were more stable to hydrolysis. The use of chlorotitanium triisopropoxide to form analogous titanium triisopropoxide derivatives has several advantages.[11] First, the reaction products were much more

(9) Shaw, S. L.; Morris, R. J.; Huffman, J. C. *J. Organomet. Chem.* **1995**, *489*, C4.
(10) Flores, J. C.; Wood, J. S.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1996**, *15*, 4944.

Scheme 4



Scheme 5



stable to hydrolysis and could, therefore, be handled with greater ease. Second, the solubilities of the catalyst precursors were much greater due to the isopropoxide ligands. The synthesis of triisopropoxide derivatives was also more straightforward since there was no need to form trimethylsilyl analogues of the ligands. Both organolithium and -thallium intermediates proved to be useful as starting materials for a series of aminoalkyl-substituted cyclopentadienyltitanium triisopropoxides (**29**−**31**), as shown in Scheme 5.

The major drawback to these triisopropoxide catalyst precursors was the difficulty in purifying them, since they are thermally sensitive and have very high boiling points. Indeed, only [η^5-(2-dimethylaminoethyl)cyclopentadienyl]triisopropoxytitanium (**29**) could be vacuum distilled in elemental purity before thermal decomposition occurred. Compounds **30** and **31** decomposed before distillation; however, the crude products were pure enough for catalysis, and both gave polyethylene and polypropylene when used in olefin polymerizations (see Polymerization Studies).

(11) (a) Kucht, A.; Kucht, H.; Barry, S.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1993**, *12*, 3075. (b) Barry, S.; Kucht, A.; Kucht, H.; Rausch, M. D. *J. Organomet. Chem.* **1995**, *489*, 195.

Scheme 6

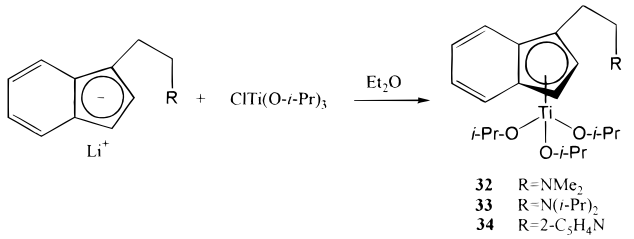


Table 1. Polymerization Data for Catalyst Precursors 26 and 32 (50 μM)

catalyst	monomer	T_p (°C)	time (h)	polymer yield (g)	activity (10^{-6})	M_w (10^{-5})	T_m (°C)
26	ethylene	21	0.167	1.41	9.1	0.72	135.5
26	propylene	21	1.0	1.21	0.12	1.8	
26	styrene	21	1.0	0.00367	0.017		
32	ethylene	22	0.5	1.986	4.1	3.7	133.9
32	propylene	22	6.0	3.20	0.32	4.3	

Three other catalyst precursors (**32**−**34**) were also prepared in the indenyl system using isopropoxide ancillary ligands. Scheme 6 illustrates the synthesis of these compounds. The isopropoxides **32**−**34** were all much more resistant to hydrolysis than any of the corresponding aminoalkyl-substituted cyclopentadienyltitanium trichlorides described above. They were obtained as orange-red high-boiling oils and were characterized by ^{1}H NMR spectra. All attempts at further purification were not successful.

Polymerization Studies. The pendent ligand catalyst precursors synthesized for this study were all activated using methylaluminoxane (MAO) as a cocatalyst. The individual catalysts were run under various polymerization conditions. Temperature, monomer, catalyst concentration, and cocatalyst concentration were varied in an attempt to optimize the polymerization results. Activity (A) was calculated as a function of grams of polymer produced per hour per mole of catalyst per concentration of monomer (moles for liquid monomers). Molecular weights (M_w) were determined by viscosity measurements, and melting temperatures (T_m) were determined by differential scanning calorimetry.

High ethylene polymerization activity was obtained for [(dimethylaminoethyl)indenyl]trichlorotitanium (**26**) ($A = 9 \times 10^6$). The polyethylene (PE) produced has low M_w (7.2×10^4) but good T_m (135.3 °C). Table 1 summarizes the polymerization data for catalyst **26**. It is extremely sensitive toward the environment, including moisture, oxygen, heat, and light. Precursor **26** was a relatively poor catalyst for propylene, with $A = 1.2 \times 10^5$ and $M_w = 1.8 \times 10^5$. It was even less active for styrene polymerization ($A = 1.7 \times 10^4$).

[(Dimethylaminoethyl)indenyl]triisopropoxytitanium (**32**) was also a good catalyst for ethylene polymerization, giving polymerization activity comparable to that reported for **2** by Flores et al.[1] to produce PE of

Table 2. Polymerization Data for Catalyst Precursors 33 and 34 (50 μM)

catalyst	monomer	T_p (°C)	time (h)	polymer yield (g)	activity (10^{-6})	M_w (10^{-5})	T_m (°C)
33	ethylene	21	3.5	0.72	0.22	0.88	134.8
33	propylene	21	3.5	0	0		
33	ethylene/hexene	21	3.5	0.44	0.43		
34	ethylene	21	6.0	0.31	0.056	3.5	135.2
34	propylene	21	6.0	trace	0		

Table 3. Polymerization Data for Catalyst Precursors 24, 29, 30, and 31 (50 μM)

catalyst	monomer	T_p (°C)	time (h)	polymer yield (g)	activity (10^{-6})	M_w (10^{-5})
24	ethylene	0	1.0	0.52	0.74	
24	ethylene	20	1.0	0.90	1.5	6.4
31	ethylene	75	4.0	3.02	2.9	6.8
31	styrene	75	12	0.068	0.0025	
29	ethylene	50	0.25	0.33	1.8	0.22
29	propylene	50	1.0	0.16	0.19	2.0
30	ethylene	25	1.0	0.89	0.96	0.81
30	propylene	25	5.0	0.22	0.027	

higher M_w but lower T_m. It has a slightly better activity for propylene than **26**, giving polymer of molecular weight similar to that of **2**. The glass transition temperature and ^{13}C NMR spectrum of the polypropylene are consistent with atactic polymer, as expected.

There was a long induction period for catalyst precursor **32** if it and the cocatalyst MAO were introduced separately. Apparently their reaction is slow in dilute concentration and in the presence of olefin. We found that the induction period could be eliminated and reasonable activities obtained with the isopropoxy-substituted catalyst precursor by preactivation of **32** with 2000 equiv of MAO. Typically, the catalyst precursor was dissolved in toluene, MAO was added, and the solution was stirred for 30 min. The major advantage of **32** was its enhanced stability and increased solubility.

Both [1-(2-diisopropylaminoethyl)indenyl]triisopropoxytitanium (**33**) and [1-(2-pyridylethyl)indenyl]triisopropoxytitanium (**34**) were an order of magnitude less reactive than **2** in the polymerization of ethylene. They were inactive toward propylene. Table 2 summarizes the polymerization data.

[(2-Picolyl)cyclopentadienyl]dichlorotitanium μ-oxo dimer dihydrochloride (**24**), [(2-picolyl)cyclopentadienyl]-triisopropoxytitanium (**31**), [(2-dimethylaminoethyl)-cyclopentadienyl]triisopropoxytitanium (**29**) and [(2-diisopropylaminoethyl)cyclopentadienyl]triisopropoxytitanium (**30**) were all preactivated with 2000 equiv of MAO for 30 min prior to injection. All of the catalyst precursors gave activities similar to that of **2** except for **30**, which was considerably lower. This is consistent with the data obtained for the indenyl systems (vide supra), where the diisopropylaminoethyl substituent gave very poor activities. Table 3 gives a summary of the polymerization data for these catalyst precursors.

Some definite trends were noted in the polymerization behavior of the pendent amino-substituted half-sandwich titanium catalyst precursors. The steric bulk of the diisopropylaminoethyl systems **30** and **33** definitely decreases the catalytic activity toward both ethylene and propylene compared to their dimethylaminoethyl counterparts **29** and **32**, respectively. There was also a significant reduction in polymer molecular weights. These two factors may indicate an interaction between the isopropyl groups on the nitrogen and the titanium center, partially blocking a coodination site on the titanium and inhibiting chain propagation.

Table 4. Polymerization Data for Catalyst Precursors 28 and 35

catalyst	catalyst concn (μM)	Al/Ti	monomer	T_p (°C)	time (h)	polymer yield (g)	activity (10^{-6})
28	50	4000/1	ethylene	20	1.0	0.0388	0.047
28	1	20000/1	ethylene	20	1.0	0.0066	0.41
28	1	20000/1	ethylene	50	1.0	0.0185	1.7
28	50	4000/1	styrene	20	0.67	0.2128	2.6
28	50	4000/1	styrene	50	1.0	1.541	12.8
35	50	4000/1	ethylene	20	0.08	0.290	3.75
35	50	4000/1	ethylene	50	0.08	0.147	2.56
35	50	4000/1	styrene	50	1.0	0.441	4.06

The even lower activity of **34** as a catalyst precursor was surprising. The reactivity of the other pendent pyridyl systems (**24** and **31**) would lead to the conclusion that **34** would be a good catalyst precursor. The difference between **34** and the other pyridyl systems is the length of the bridge between the nitrogen atom and the η^5-cyclopentadienyl ring. All of the highly active systems have two carbons between the nitrogen and the ring. In **34**, there are three carbons bridging the nitrogen and the ring. The extra torsional energy in the bridge and the changes in geometry of the nitrogen coordination to the titanium probably account for the decrease in catalytic activity of **34**.

The last catalyst precursor examined was [(2-phenylethyl)cyclopentadienyl]trichlorotitanium (**28**). Flores et al.[14] found that [1-(2-phenylethyl)-2,3,4,5-tetramethylcyclopentadienyl]trichlorotitanium (**35**) was an efficient catalyst for both ethylene and styrene. For this reason, we had high hopes for the catalytic activity of **28**. In a previous study, Flores et al.[3] had discovered that the pendent (2-dimethylaminoethyl)cyclopentadienyl system (**2**) was an order of magnitude better than the (2-dimethylaminoethyl)tetramethylcyclopentadienyl system (**3**). Table 4 shows a comparison of the catalytic properties of **28** and **35**.

The pendent ligand appears to have an effect on precursor **35**, as seen in the enhanced ethylene polymerization activity for **35**. This system also still shows an appreciable polymerization activity for styrene. The activities for styrene and ethylene are similar under the conditions of 50 °C and 4000/1 MAO-to-precursor ratio. This brings up the interesting possibility of copolymerization of ethylene and styrene using such a system. The poor polymerization activity of **28** relative to that of ethylene is surprising based on previous expectations. Precursor **28** behaves strictly like a nonpendent substituted cyclopentadienyltrichlorotitanium, giving excellent polymerization activity toward styrene, poor activity toward ethylene, and no activity toward propylene. This suggests the absence of bonding interaction between the pendent phenyl group and titanium.

(12) (a) Ready, T. E.; Day, R. O.; Chien, J. C. W.; Rausch, M. D. *Macromolecules* **1993**, *26*, 5822.

(13) (a) Llinas, G. H.; Dong, S.-H.; Mallin, D. T.; Rausch, M. D.; Lin, Y.-G.; Winter, H.H.; Chien, J. C. W. *Macromolecules* **1992**, *25*, 1242. (b) Tsai, W.-M.; Rausch, M. D.; Chien, J. C. W. *Appl. Organomet. Chem.* **1993**, *7*, 71.

(14) Flores, J. C.; Wood, J. S.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1996**, *15*, 4944.

Experimental Section

All operations were performed under an argon atmosphere using Schlenk and glovebox techniques. Argon was deoxygenated by BASF catalyst and dried with P_2O_5 and molecular sieves. Methylaluminoxane (MAO) was purchased from Akzo. All other chemicals were obtained from Aldrich unless otherwise stated. Reaction solvents were purified by distillation from sodium−potassium alloy under argon, except for dichloromethane which was distilled under argon from calcium hydride. Styrene was purified by distllation from calcium hydride under reduced pressure and stored at −25 °C under argon in the dark. Infrared spectra were recorded on a Perkin-Elmer 1600 FTIR in CH_2Cl_2 using subtraction techniques to remove solvent signals. GCMS were recorded on a Perkin-Elmer HP 5970A gas chromatograph−mass spectrometer. ^1H and ^{13}C NMR spectra were recorded on IBM NR-80 or Brucker AC200 spectrometers. Elemental analyses were performed by the University of Massachusetts Microanalytical Laboratory. ***Note:*** *Thallium and its compounds are extraordinarily toxic and must be handled with appropriate safety precautions. Suitable protective gloves should always be worn when handling these materials.*

(2-Picolyl)cyclopentadiene (7). An aqueous solution of 5.00 g (89.1 mmol) of KOH in 40 mL of H_2O was prepared and cooled to 0 °C in an ice bath. To the cooled solution was added 10.34 g (63.0 mmol) of 2-picolyl chloride hydrochloride, and the solution was extracted two times with 40 mL of benzene. The benzene layers were combined and dried over magnesium sulfate. The benzene solution was transferred via cannula to a solution of 66.7 mmol of cyclopentadienylsodium in 100 mL of THF (prepared by reacting 1.60 g (66.7 mmol) of NaH with 4.41 g (66.7 mmol) of freshly cracked cyclopentadiene in 100 mL of THF). The solution became warm during the addition, and a precipitate formed, giving a cloudy orange-brown appearance. After the solution was stirred overnight, 10 mL of H_2O was added, and the mixture was stirred for 10 min.

The layers were separated, and the organic layer was dried with magnesium sulfate. Removal of the volatiles gave an orange oil. The oil was vacuum distilled to give a light yellow oil, boiling from 62 to 68 °C at 0.1 mmHg (6.64 g, 67% yield). A second vacuum distillation gave a sample of elemental purity, bp 64−66 °C at 0.1 mmHg. Anal. Calcd for $C_{11}H_{11}N$: C, 84.04; H, 7.05; N, 8.91. Found: C, 83.83; H, 7.07; N, 8.85.

(2-Dimethylaminoethyl)cyclopentadiene (8). Compound **8** was prepared by a modification of the method developed by Wang et al.[6] Sodium hydride (1.69 g, 70.4 mmol) was placed in a 500-mL round-bottom Schlenk flask with 100 mL of THF and cooled to 0 °C, and 4.65 g (70.4 mmol) of freshly distilled cyclopentadiene was added dropwise. The mixture was allowed to stir until gas evolution ceased and all the sodium hydride was consumed. Free amine was generated via base extraction of (2-chloroethyl)dimethylamine hydrochloride. Potassium hydroxide (6.05 g) was dissolved in 75 mL of water, and 10.14 g of (2-chloroethyl)dimethylamine hydrochloride (70.4 mmol) was added. The solution was extracted with two 50-mL portions of hexane. The organic layers were combined and dried over magnesium sulfate. The cyclopentadienylsodium solution was placed in an ice bath, and the hexane solution of the free amine was added dropwise via a pressure-equalizing addition funnel. After the addition was complete, the reaction mixture was heated at reflux for 4 h and allowed to cool to room temperature. The cloudy yellow-brown suspension was hydrolyzed with 25 mL of water, and the layers were separated. The organic layer was rotary evaporated, and the resulting oil was vacuum distilled to give a colorless to light yellow oil (6.57 g, 68% yield) at 42 °C and 0.5 mmHg (it is necessary to cool the collection flask to −78 °C to prevent substantial loss of product). ^1H NMR ($CDCl_3$, 200 MHz): δ 6.47−6.06 (m, 3 H, vinylic C_5H_5), 2.96−2.90 (m, 2 H, sp^3 C_5H_5), 2.50 (m, 4 H, CH_2CH_2), 2.26 (bs, 6 H, NCH_3).

(2-Phenylethyl)cyclopentadiene (9). Cyclopentadienylsodium (55.63 mmol) was prepared by reacting 1.335 g (55.63 mmol) of NaH with 3.68 g (55.7 mmol) of freshly cracked cyclopentadiene in 100 mL of THF. The solution was allowed to stir until gas evolution ceased and the sodium hydride was consumed. To this solution, 10.295 g (55.63 mmol) of (2-bromoethyl)benzene was added dropwise. The addition must be done slowly because of the exothermic nature of the reaction. After the addition was complete, the reaction mixture was allowed to stir at room temperature for 1 h. The mixture was then hydrolyzed with aqueous ammonium chloride (50 mL), and the layers were separated. The aqueous layer was extracted with 50 mL of hexane, and the organic portions were combined and dried over magnesium sulfate. After filtration, the solvent was removed by rotary evaporation. The resulting oil was vacuum distilled, with the fraction boiling boiling between 91 and 93 °C collected as the main fraction (6.80 g, 71% yield). ^1H NMR ($CDCl_3$, 200 MHz): δ 7.33−7.18 (m, 5 H, aromatic), 6.45−6.04 (m, 3 H, vinylic), 2.96−2.64 (m, 6 H, CH_2CH_2 and sp^3 of C_5 ring). Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.65; H, 8.39.

(2-Diisopropylaminoethyl)cyclopentadiene (10). Cyclopentadienyllithium (75.2 mmol) was prepared from 5.04 g (76.6 mmol) of freshly cracked cyclopentadiene and 47.9 mL of 1.6 M *n*-BuLi (76.6 mmol) in 100 mL of THF at 0 °C, and the solution was allowed to warm to room temperature. (2-Chloroethyl)diisopropylamine hydrochloride (15.1 g, 75.2 mmol) was dissolved in 100 mL of 2 N aqueous NaOH and extracted with two 25-mL portions of hexane. The hexane fractions were combined and dried with magnesium sulfate. After filtration, this solution was added dropwise to the THF solution of cyclopentadienyllithium, and the resulting brown solution was refluxed for 4 h. After the brown suspension was allowed to cool to room temperature, 50 mL of H_2O was added, and after the solution was stirred for 5 min, the layers were separated. The solvent was removed under vacuum at room temperature, and the brown oil was vacuum distilled to give an orange oil (6.64 g, 45.7% yield) boiling at 64−68 °C and 0.5 mmHg. A second distillation produced an elementally pure sample. ^1H NMR ($CDCl_3$): δ (6.43−6.03 (m, 3 H, vinylic), 3.23−2.93 (m, 4 H, $NCH(CH_3)_2$ and sp^3 of C_5 ring), 2.56 (bs, 4 H, CH_2CH_2), 1.03 (d, 12 H, $CH(CH_3)_2$). Anal. Calcd for $C_{13}H_{23}N$: C, 80.76; H, 11.99; N, 7.24. Found: C, 80.47; H, 11.94, N, 7.02.

3-(2-Dimethylaminoethyl)indene (11). Into an argon-flushed round-bottom Schlenk flask were added 22.2 mL (0.190 mol) of indene, 150 mL of THF, and a magnetic stirring bar. The flask was cooled to 0 °C, and 118.5 mL of 1.6 M *n*-BuLi (0.190 mol) was added slowly via syringe. The reaction was allowed to warm to room temperature and stir for 2 h. (2-Chloroethyl)dimethylamine was generated via the solid-phase reaction of (2-chloroethyl)dimethylamine hydrochloride and powdered potassium hydroxide (1:2 molar ratio) and vacuum distillation of the amine using a dry ice−2-propanol cooled trap. The indenyllithium solution was cooled to 0 °C, and 20.4 g of the amine (0.190 mol) was added slowly via a pressure-equalizing addition funnel (considerable heat is generated if the addition is too fast). The solution turned cloudy upon warming to room temperature and was allowed to stir for an additional 2 h. The solution was hydrolyzed with 20 mL of H_2O, and the layers were separated. The organic layer was dried with magnesium sulfate, filtered, and rotary evaporated. The organic residue was vacuum distilled (112 °C at 0.01 mmHg) to give 33.5 g (94% yield) of a light yellow oil. The sample was distilled a second time to obtain a sample of elemental purity. ^1H NMR ($CDCl_3$): δ 7.47−7.20 (m, 4 H, C_6H_4), 6.25 (bs, 1 H, =CH), 3.32 (bs, 2 H, CH_2 of C_5 ring), 2.78−2.58 (m, 4 H, CH_2CH_2), 2.33 (s, 6 H, $N(CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ 145.3 (C3), 144.3 (C9), 142.5 (C8), 128.3, 126.0, 124.6, 123.7 (*C*4−7), 58.4 (CH_2CH_2N), 45.5 (NCH_3), (CH_2-

CH_2N), 26.2 (C1). Anal. Calcd for $C_{13}H_{17}N$: C, 83.37; H, 9.15; N, 7.48. Found: C, 83.15; H, 9.07; N, 7.27.

3-(2-Diisopropylaminoethyl)indene (12). Indene (9.31 g, 78.6 mmol) was placed in a Schlenk tube with 50 mL of THF and cooled to 0 °C, and 49.0 mL of 1.6 M *n*-BuLi (78.6 mmol) was added via syringe. After the solution was stirred for 2 h at room temperature, 7.80 g (39.3 mmol) of (2-chloroethyl)diisopropylamine hydrochloride was added as a solid. Heat was evolved, and the solution became lighter. The solution was allowed to stir overnight and was hydrolyzed with 20 mL of water. The layers were separated, and the organic layer was dried over magnesium sulfate. Filtration and removal of the solvent gave a red oil. The oil was vacuum distilled twice at 0.01 mmHg, and the fraction boiling at 126−127 °C was collected, giving 7.81 g (81.6% yield) of a yellow oil. ^{1}H NMR ($CDCl_3$) δ 7.47−7.19 (m, 4 H, C_6H_4), 6.23 (bs, 1 H, =CH), 3.33 (bs, 2 H, CH_2 of C_5 ring), 3.09 (h, 2 H, $NCH(CH_3)_2$, 2,72 (bs, 4 H, CH_2CH_2), 1.06 (d, 12 H, $NCH(CH_3)_2$. Anal. Calcd for $C_{17}H_{24}N$: C, 83.89; H, 10.35; N, 5.74. Found: C, 83.47; H, 10.28; N, 5.63.

3-(2-Pyridylethyl)indene (13). 2-Pyridylethanol was converted to (2-chloroethyl)pyridine hydrochloride by reaction with 1 equiv of thionyl chloride in methylene chloride. The resulting white solid was collected by suction filtration and used as a crude material in the next step of the reaction. Indene (7.8 g, 67.4 mmol) was dissolved in 50 mL of THF and cooled to 0 °C, and 42.1 mL of 1.6 M *n*-BuLi (67.4 mmol) was added by syringe. The solution was allowed to stir for 2 h, and 6.00 g (33.7 mmol) of 2-chloroethylpyridine hydrochloride was added as a solid. The solution became warm, and a solid precipitated. After the solution was stirred overnight, 50 mL of water was added, and the layers were separated. The organic layer was dried over magnesium sulfate and filtered, and the solvent was removed under vacuum. The resulting oil was vacuum distilled, and the fraction boiling at 126−128 °C and 0.1 mmHg was collected (3.75 g, 50.3% yield). ^{1}H NMR ($CDCl_3$): δ 8.58 (d, 1 H, pyr), 7.63−7.08 (m, 7 H, aromatic), 6.23 (bs, 1 H, =CH), 3.32 (bs, 2 H, CH_2 of C_5 ring), 3.21 (t, 2 H, CH_2CH_2), 3.02 (t, 2 H, CH_2CH_2). Anal. Calcd for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33. Found: C, 86.57; H, 6.77; N, 6.15.

(2-Picolyl)cyclopentadienylthallium (14). Freshly distilled (2-picolyl)cyclopentadiene (1.68 g, 10.7 mmol) was dissolved in 25 mL of diethyl ether, and 2.66 g (10.7 mmol) of thallium ethoxide was added dropwise. A white crystalline precipitate formed immediately. The solution was allowed to stir for 20 min and then collected on a Schlenk filter. The solid was washed twice with 30 mL of hexane. The white platelike crystals (3.36 g, 87%) were sublimed at 100 °C and 0.001 mmHg to obtain a sample of elemental purity. ^{1}H NMR (DMSO): δ 8.38−8.36 (m, 1 H, aromatic), 7.72−7.63 (d of t, 1 H, aromatic), 7.32−7.28 (d, 1 H, aromatic), 7.21−7.14 (t, 1 H, aromatic), 5.72−5.66 (m, 4 H, C_5H_4), 3.87 (s, 2 H, CH_2). Anal. Calcd for $C_{11}H_{10}NTl$: C, 36.64; H, 2.80; N, 3.88. Found: C, 36.99; H, 2.80, N, 3.85.

(2-Dimethylaminoethyl)cyclopentadienylthallium (15). Freshly distilled (2-dimethylaminoethyl)cyclopentadiene (0.64 g, 4.66 mmol) was dissolved in 25 mL of diethyl ether, and 1.16 g (4.66 mmol) of thallium ethoxide was added by syringe. After 1 min of stirring, a yellow precipitate formed. The solution was stirred for 2 h, and the solid was collected on a Schlenk filter (1.55 g, 97.9% yield). A sample was sublimed at 132 °C and 0.001 mmHg to give a white solid. ^{1}H NMR (DMSO) δ (5.79−5.75 (m, 4 H, C_5H_4), 2.50 (bs, 4 H, CH_2CH_2), 2.06 (s, 6 H, $N(CH_3)$. Anal. Calcd for $C_9H_{14}NTi$: C, 31.74; H, 4.14; N, 4.11. Found: C, 31.81; H, 4.12; N, 4.05.

(2-Phenylethyl)cyclopentadienylthallium (16). (2-Phenylethyl)cyclopentadiene (1.66 g, 9.67 mmol) was dissolved in 30 mL of diethyl ether, and 2.41 g (9.67 mmol) of thallium ethoxide was added. A white precipitate formed immediately, and the reaction mixture gelled. An additional 20 mL of ether was added, and the reaction was allowed to stir for 1 h. The white solid was collected on a Schlenk frit, washed several times with pentane, and dried under vacuum. The solid darkened during drying and was, therefore, placed in a sublimer and heated to 90 °C and 0.03 mmHg, giving 2.80 g (77.5% yield) of **16**. ^{1}H NMR (DMSO): δ 7.26−7.10 (m, 5 H, aromatic), 5.73 (t, 2 H, C_5H_4), 5.56 (t, 2 H, C_5H_4), 2.75 (m, 4 H, CH_2CH_2). Anal. Calcd for $C_{13}H_{13}Tl$: C, 41.79; H, 3.51. Found: C, 41.68; H, 3.54.

[η^5-(2-Picolyl)cyclopentadienyl]dicarbonylrhodium (17). (2-Picolyl)cyclopentadienylthallium (1.06 g, 2.77 mmol) was suspended in 25 mL of THF, 0.554 g (1.42 mmol) of chlorodicarbonylrhodium dimer was added, and the solution was allowed to stir overnight. The solvent was removed, and the residue was extracted with hexane. Silica (3 g, 100−200 mesh) was added, and the solvent was removed and placed on a 10- × 2-cm column packed dry with silica. Elution with hexane, hexane/dichloromethane (50/50), and dichloromethane gave no results. Elution with THF gave an orange band. Removal of the solvent produced 0.61 g of a red oil (69% yield). Vacuum distillation resulted in a single fraction as a red oil boling at 92 °C and 0.05 mmHg. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.56 (m, 1 H, aromatic), 7.65 (d of t, 1 H, aromatic), 7.26−7.13 (m, 2 H, aromatic), 5.51 (t, 2 H, C_5H_4), 5.34 (t, 2 H, C_5H_4), 3.82 (s, 2 H, CH_2). FTIR (CH_2Cl_2) ν(CO) 2042.8, 1976.3 cm^{-1}. Anal. Calcd for $C_{13}H_{10}NO_2Rh$: C, 49.55; H, 3.20; N, 4.44. Found: C, 49.82; H, 3.41; N, 4.41.

[η^5-(2-Dimethylaminoethyl)cyclopentadienyl]dicarbonyliridium (18). (2-Dimethylaminoethyl)cyclopentadienylthallium (2.40 g, 7.047 mmol) and 2.33 g (6.40 mmol) of chlorodicarbonyl(pyridine)iridium were allowed to react in 50 mL of benzene. The suspension was heated at reflux for 2 d and allowed to cool to room temperature. The solution was filtered and the solvent removed under vacuum, giving 2.46 g (76% yield) of a yellow oil. The oil was analyzed by ^{1}H NMR and FTIR and was found to be identical to **18** obtained previously.[8] The crude material was as pure as the distilled product obtained via the lithium salt.[8]

[η^5-(2-Phenylethyl)cyclopentadienyl]dicarbonylrhodium (19). (2-Phenylethyl)cyclopentadienylthallium (1.50 g, 4.014 mmol) was suspended in 25 mL of THF, and 0.780 g (2.007 mmol) of chlorodicarbonylrhodium dimer was added. The solution was stirred overnight and filtered. Silica gel (5 g, 100−200 mesh) was added, and the solvent was removed. The residue was added to a 10- × 2-cm dry packed column of silica. On elution with hexane, an orange band was obtained. Removal of the solvent gave 1.21 g of an orange oil (91.8% yield). Microdistillation of the product at 0.005 mmHg gave a single fraction boiling at a pot temperature of 110 °C. ^{1}H NMR ($CDCl_3$): δ 7.34−7.16 (m, 5 H, aromatic), 5.38 (t, 2 H, C_5H_4), 5.30 (t, 2 H, C_5H_4), 2.84 (m, 2 H, CH_2), 2.63 (m, 2 H, CH_2). Anal. Calcd for $C_{15}H_{13}O_2Rh$: C, 54.90; H, 3.99. Found: C, 54.81; H, 3.94.

[η^5-(2-Phenylethyl)cyclopentadienyl](η^5-pentamethylcyclopentadienyl)dichlorotitanium (20). (2-Phenylethyl)-cyclopentadienylthallium (1.30 g, 3.48 mmol) was suspended in 50 mL of benzene, and 1.46 g (5.04 mmol) of pentamethylcyclopentadienyltitanium trichloride was added. The solution turned yellow-orange after stirring overnight. Filtration and removal of the solvent gave a purple solid. The solid was dissolved in a minimum of toluene and cooled to −20 °C to give red crystals, which proved to be pentamethylcyclopentadienyltitanium trichloride. Removal of the solvent and extraction with hot hexane gave a small amount of crystals after cooling to room temperature. The solution was filtered and cooled to −20 °C to give 0.77 g (52% yield) of red crystals. ^{1}H NMR ($CDCl_3$): δ 7.26−7.12 (m, 5 H, aromatic), 5.99−5.95 (m, 4 H, C_5H_4), 3.01−2.94 (m, 4 H, CH_2), 2.03 (s, 15 H, CH_3). Anal. Calcd for $C_{23}H_{28}Cl_2Ti$: C, 65.26; H, 6.67. Found: C, 65.34; H, 6.66.

(2-Dimethylaminoethyl)trimethylsilylcyclopentadiene (21). Freshly distilled (2-dimethylaminoethyl)cyclo-

pentadiene (3.48 g, 21.9 mmol) was dissolved in 50 mL of diethyl ether and cooled to 0 °C, and 13.7 mL of 1.6 M *n*-BuLi in hexane (21.9 mmol) was added slowly via syringe. The solution was allowed to stir at room temperature for 4 h, and 3.04 g (21.9 mmol) of chlorotrimethylsilane was added. After the solution was stirred overnight and the solvent removed, the residue was extracted with 50 mL of pentane and filtered. Removal of the pentane gave 5.01 g of a yellow oil (87% yield). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.70−6.05 (m, 3 H, C_5H_4), 3.28−2.85 (m, 2 H, sp^3 ring), 2.65−2.37 (m, 4 H, CH_2CH_2N), 2.28 and 2.27 (s, 6 H, NCH_3), 0.14, 0.13, −0.04 (s, 9 H, $SiCH_3$).

[η^5-(2-Dimethylaminoethyl)cyclopentadienyl]trichlorotitanium (2). In a Schlenk tube were placed 100 mL of dichloromethane and 5.01 g (23.9 mmol) of (2-dimethylaminoethyl)trimethylsilylcyclopentadiene. The solution was cooled to −78 °C, and 2.63 mL of titanium tetrachloride was added via a syringe. A dark orange solution formed immediately. The solution was allowed to warm to room temperature, and the oily residue was triturated with 100 mL of pentane. The solid was collected on a Schlenk filter and dried under vacuum to give 6.10 g of a highly air- and moisture-sensitive yellow powder (88% yield). ^{1}H NMR (CD_2Cl_2, 80 MHz): δ 6.95 (t, 2 H, C_5H_4), 6.81 (t, 2 H, C_5H_4), 3.16 (m, 4 H, CH_2CH_2), 2.65 (s, 6 H, NCH_3).

[(2-Picolyl)cyclopentadienyl]trimethylsilane (22). (2-Picolyl)cyclopentadiene (7.09 g, 45.1 mmol) was dissolved in 50 mL of THF, and 30 mL of 1.6 M *n*-BuLi (45.1 mmol) was added dropwise. The solution turned dark red immediately but was allowed to stir at room temperature for 1 h. Chlorotrimethylsilane (4.9 g, 5.8 mL, 45 mmol) was added by syringe, and the solution was allowed to stir overnight. The THF was removed under vacuum, and the yellow oily solid was extracted with 50 mL of pentane. Filtration and removal of the pentane gave an orange oil (9.46 g, 91.5% yield). The oil was vacuum distilled at 96 °C and 0.1 mmHg to give a light yellow oil. ^{1}H NMR ($CDCl_3$): δ 8.49 (m, 1 H, aromatic), 7.57 (t, 1 H, aromatic), 7.24−7.07 (m, 2 H, aromatic), 6.41 and 6.16 (bs, 2 H, vinylic), 3.90 (bs, 2 H, CH_2), 3.26−2.93 (m, 1 H, CH sp^3). Anal. Calcd for $C_{14}H_{19}NSi$: C, 73.30; H, 8.35; N, 6.11. Found: C, 72.84; H, 8.73; N, 5.73.

[η^5-(2-Picolyl)cyclopentadienyl]dichlorotitanium μ-Oxo Dimer Dihydrochloride (24). [(2-Picolyl)cyclopentadienyl]-trimethylsilane (1.32 g, 5.36 mmol) was dissolved in 50 mL of toluene, and 1.01 g (5.36 mmol) of titanium tetrachloride was added slowly at room temperature. A bright orange precipitate formed immediately. The solution was filtered, and the solid was washed with hexane, dried under vacuum, analyzed by ^{1}H NMR, and determined to be the μ-oxo dimer. The solid was extracted with 50 mL of dichloromethane, and the solvent was removed after filtration to give 2.36 g of **24** as a bright orange solid. The solid was washed with pentane and toluene and placed under high vacuum overnight to give a sample of elemental purity. ^{1}H NMR ($CDCl_3$): δ 8.90 (m, 2 H, aromatic), 7.81 (t, 2 H, aromatic), 7.39 (m, 4 H, aromatic), 7.10−7.08 (m, 4 H, C_5H_4), 4.46 (s, 4 H, CH_2). Anal. Calcd for $C_{22}H_{22}Cl_6ON_2Ti_2$: C, 41.35; H, 3.47; N, 4.38. Found: C, 41.19; H, 3.03; N, 4.22.

[η^5-(2-Picolyl)cyclopentadienyl]trichlorotitanium (23). In a 100-mL Schlenk flask were added 0.69 g (1.90 mmol) of 2-picolylcyclopentadienylthallium, 0.360 g (2.00 mmol) of titanium tetrachloride, and 50 mL of toluene. The reaction mixture was stirred at room temperature for 24 h. The solution turned yellow immediately, and gradually a white precipitate formed. The solution was filtered, and the solvent was removed under vacuum. The yellow solid was trituated with hexane, and the solid was collected on a Schlenk filter. The solid was sublimed at 194 °C and 0.005 mmHg to give 0.49 g (83% yield) of an orange crystalline solid. ^{1}H NMR ($CDCl_3$): δ 8.93 (d, 1 H, aromatic), 7.85 (t, 1 H, aromatic), 7.40 (m, 2 H, aromatic), 7.14 (m, 4 H, C_5H_4), 4.47 (s, 2 H, CH_2), Anal. Calcd for $C_{11}H_{10}Cl_3NTi$: C, 42.56; H, 3.25; N, 4.51. Found: C, 43.02; H, 3.57; N, 4.61.

[3-(2-Dimethylaminoethyl)-1-indenyl]tributyltin (25). Into an argon-purged Schlenk tub were placed 4.59 g (24.5 mmol) of 3-(2-dimethylaminoethyl)indene and 100 mL of THF, and the solution was cooled in an ice bath. To the solution was added 15.3 mL of 1.6 M *n*-BuLi in hexane (24.5 mmol). The solution was allowed to warm to room temperature and stir for 4 h (note: this reaction takes all 4 h). To the bright red solution was added 7.977 g (24.5 mmol) of chlorotributyltin, and the reaction was allowed to stir for 2 d (this reaction is very slow). The solvent was removed under vacuum, and the orange residue was extracted with pentane. The extracts were combined and filtered to give an orange solution and a white solid. The solvent was removed to give an orange oil which turned slightly cloudy on standing. Repeated extraction with pentane and filtration gave a clear orange oil. ^{1}H NMR ($CDCl_3$): δ 7.50−7.13 (m, 4 H, C_6H_4), 6.46 (bs, 1 H, =CH), 4.01 (bs, 1 H, CH_2 of C_5 ring), 2.85 (m, 2 H, NCH_2), 2.65 (m, 2 H, ind-CH_2), 2.34 (s, 6 H, $N(CH_3)_2$), 1.36−0.69 (2 m, 27 H, $SnBu_3$).

[η^5-1-(2-Dimethylaminoethyl)indenyl]trichlorotitanium (26). In a Schlenk tube were placed 3.71 g (6.96 mmol) of [3-(2-dimethylaminoethyl)-1-indenyl]tributyltin and 50 mL of dichloromethane. The solution was cooled to −78 °C, and 1.32 g (6.96 mmol) of titanium tetrachloride was added via syringe. The solution turned dark green immediately. The solvent was removed, and the resulting oily green solid was washed two times with hexane and dried under vacuum. The green solid was highly air sensitive and turned red-brown with the slightest exposure to air. However, the crude material was of sufficient purity for polymerization studies. ^{1}H NMR ($CDCl_3$): δ 7.98−7.41 (m, 4 H, C_6H_4), 7.09 (d, 1 H, C_5H_2), 7.01 (d, 1 H, C_5H_2), 3.40 (m, 4 H, CH_2CH_2), 2.74 (s, 6 H, NCH_3).

(2-Phenylethyl)trimethylsilylcyclopentadiene (27). In a 100-mL Schlenk flask were placed 1.08 g (6.34 mmol) of 2-phenylethylcyclopentadiene and 20 mL of THF. The reaction mixture was cooled to 0 °C, and 4.0 mL of 1.6 M n-BuLi (6.4 mmol) was added, turning the solution a dark red. The solution was stirred overnight, and 1.5 mL (6.4 mmol) of chlorotrimethylsilane was added. The reaction was stirred for 8 h and turned a light yellow. The solvent was removed, and the residue was extracted with pentane. After filtration, the solvent was removed under vacuum, giving a light yellow oil. A ^{1}H NMR spectrum was taken and exhibited the expected values for the trimethylsilyl derivative. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.34−7.19 (m, 5 H, aromatic), 6.49−6.14 (m, 3 H, vinylic), 3.29 (bs, 1 H, sp^3 of C_5 ring), 2.94−2.66 (m, 4 H, CH_2-CH_2), 0.17, −0.06 (m, 9 H, $Si(CH_3)_3$).

[η^5-(2-Phenylethyl)cyclopentadienyl]trichlorotitanium (28). The yellow oil **27** (6.34 mmol) was placed in 40 mL of dichloromethane and cooled to −78 °C, and 1.2 g (6.4 mmol) of titanium tetrachloride was added. The reaction mixture was allowed to warm to room temperature and was stirred for 4 h. The solvent was removed under vacuum, giving an orange powder after two triturations with pentane. The powder was dried under vacuum to give 1.65 g (80.5% yield) of **28**. A sample was dissolved in a minimum amount of toluene, and hexane was layered on top of the toluene solution. After the solution was cooled for 3 d at −20 °C, orange crystals were obtained. ^{1}H NMR ($CDCl_3$): δ 7.34−7.12 (m, 5 H, aromatic), 6.92 (t, 2 H, C_5H_4), 6.76 (t, 2 H, C_5H_4), 3.19 (m, 2 H, CH_2), 2.98 (m, 2 H, CH_2). Anal. Calcd for $C_{13}H_{13}Cl_3Ti$: C, 48.27; H, 4.05. Found: C, 48.70; H, 3.92.

[η^5-(2-Dimethylaminoethyl)cyclopentadienyl]triisopropoxytitanium (29). To a hexane solution containing 0.920 g of chlorotitanium triisopropoxide (3.53 mmol) was added 1.23 g (3.61 mmol) of (2-dimethylaminoethyl)cyclopentadienylthallium. The solution changed color immediately but was stirred overnight. Filtration gave a gray solid and an orange solution. The hexane was removed under vacuum, and the resulting orange oil was vacuum distilled, giving a light

yellow oil of bp 112−113 °C at 0.001 mmHg. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.11(m, 2 H, C_5H_4), 6.07 (m, 2 H, C_5H_4), 4.54 (hept, 3 H, C*H*$(CH_3)_3$), 2.89 (t, 2 H, CH_2), 2.59 (t, 2 H, CH_2), 2.19 (s, 6 H, NCH_3), 1.20 (d, 18 H, CH(C*H*$_3)_2$, (80 MHz) (6.11 (m, 4 H, C_5H_4), 4.54 (hept, 3 H, C*H*$(CH_3)_2$, 2.66 (m, 4 H, CH_2-CH_2), 2.29 (s, 6 H, NCH_3), 1.20 (d, 18 H, CH(C*H*$_3)_2$). Anal. Calcd for $C_{18}H_{35}NO_3Ti$: C, 59.83; H, 9.76; N, 3.99. Found: C, 58.99; H, 9.99; N, 3.43.

[η^5-(2-Diisopropylaminoethyl)cyclopentadienyl]triisopropoxytitanium (30). To a solution of 2.42 g (12.5 mmol) of 2-diisopropylaminocyclopentadiene in 100 mL of THF was added 7.8 mL of 1.6 M *n*-BuLi (12.5 mmol) in hexane at 0 °C. The reaction mixture was stirred for 6 h at room temperature, and 3.25 g (12.5 mmol) of chlorotitanium triisopropoxide was added as a solid. After the solution was stirred overnight, the THF was removed under vacuum, and the residue was extracted 2 times with 50 mL of pentane. Filtration via cannula and removal of the solvent under vacuum gave a yellow oil. All attempts to vacuum distill the product led to decomposition. However, the product was determined by ^{1}H NMR to be pure enough for polymerization studies.^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.14 (m, 2 H, C_5H_4), 6.11 (m, 2 H, C_5H_4), 4.54 (hept, 3 H, OC*H*$(CH_3)_2$), 3.05 (hept, 3 H, NC*H*$(CH_3)_2$), 2.66 (bs, 4 H, CH_2CH_2), 1.20 (d, 18 H, OCH(C*H*$_3)_2$), 1.02 (d, 12 H, NCH(C*H*$_3)_2$).

[η^5-(2-Picolyl)cyclopentadienyl]triisopropoxytitanium (31). (2-Picolyl)cyclopentadienylthallium (2.80 g, 7.76 mmol) was placed in 50 mL of diethyl ether, and 2.02 g (7.76 mmol) of chlorotitanium triisopropoxide was added. The solution was stirred overnight, and the ether was removed under vacuum. The yellow cloudy residue was extracted with hexane and filtered, leaving a gray precipitate. Removal of the hexane under vacuum gave 2.91 g of a yellow oil (98% yield). A sample of the oil was vacuum distilled at 0.001 mmHg, but the sample decomposed on heating before distilling at approximately 95 °C. The original crude material was extracted with hexane and filtered, and the solvent was removed. After being placed on high vacuum and heating to 40 °C overnight, a sample was sent for elemental analysis. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.56 (m, 1 H, aromatic), 7.59 (t, 1 H, aromatic), 7.19 (m, 2 H, aromatic), 6.19 (t, 2 H, C_5H_4), 6.12 (t, 2 H, C_5H_4), 4.57 (hept, 3 H, C*H*$(CH_3)_2$), 4.11 (s, 2 H, CH_2), 1.12 (d, 18 H, CH(C*H*$_3)_2$). Anal. Calcd for $C_{20}H_{31}NO_3Ti$: C, 62.98; H, 8.19; N, 3.67. Found: C, 59.47; H, 7.93, N, 3.41.

[η^5-1-(2-Dimethylaminoethyl)indenyl]triisopropoxytitanium (32). In a Schlenk tube were placed 5.06 g (27.0 mmol) of 3-(2-dimethylaminoethyl)indene, 50 mL of THF, and 16.9 mL of 1.6 M *n*-BuLi (27.0 mmol). The solution was stirred overnight, and 7.04 g of chlorotitanium triisopropoxide was added. The solution turned very dark, and a precipitate formed. The THF was removed under vacuum, and the red tarry residue was extracted with hexane. Filtration gave a red-orange solution, and removal of the solvent resulted in a red oil (l0.74 g, 97.2% yield). ^{1}H NMR ($CDCl_3$): δ 7.44−7.15 (m, 4 H, C_6H_4), 6.80 (d, 1 H, C_5H_2), 6.53 (d, 1 H, C_5H_2), 4.49 (hept, 3 H, C*H*$(CH_3)_2$), 2.67 (m, 4 H, CH_2CH_2), 2.25 (s, 6 H, NCH_3), 1.25 (d, 18 H, C*H*$(CH_3)_2$).

[η^5-1-(2-Diisopropylaminoethyl)indenyl]triisopropoxytitanium (33). In a Schlenk tube were placed 1.13 g (4.6 mmol) of 3-(2-diisopropylaminoethyl)indene and 50 mL of hexane. The solution was cooled to 0 °C, and 2.9 mL of 1.6 M n-BuLi (4.6 mmol) was added via syringe. After the solution was stirred overnight at room temperature, 1.2 g (4.6 mmol) of chlorotitanium triisopropoxide was added, causing the solution to turn orange and a white precipitate to form. The reaction mixture was stirred overnight and filtered. Removal of the solvent gave an orange oil which was analyzed by ^{1}H NMR and found to be the desired product. All attempts at purification failed. ^{1}H NMR ($CDCl_3$): δ 7.43−7.17 (m, 4 H, C_6H_4), 6.81 (d, 1 H, C_5H_2), 6.58 (d, 1 H, C_5H_2), 4.48 (hept, 3 H, OC*H*$(CH_3)_2$), 3.99 (t, 2 H, CH_2), 3.55 (t, 2 H, CH_2), 3.01 (hept, 2 H, NC*H*$(CH_3)_2$), 1.23 (d, 18 H, OCH(C*H*$_3)_2$), 1.07 (m, 12 H, NCH(C*H*$_3)_2$).

[η^5-1-(2-Pyridylethyl)indenyl]triisopropoxytitanium (34). In a Schlenk tube were placed 2.76 g (12.4 mmol) of 3-(2-pyridylethyl)indene, 10 mL of THF, and 50 mL of hexane. The solution was cooled to 0 °C, and 7.8 mL of 1.6 M n-BuLi (12.4 mmol) was added by syringe. The solution was allowed to stir overnight, and 3.24 g (12.4 mmol) of chlorotitanium triisopropoxide was added as a solid. A white solid formed immediately, and the solution turned orange. The mixture was allowed to stir overnight, and the solvent was removed under vacuum. Extraction with hexane and filtration gave an orange solution. Removal of the solvent gave a red-orange oil. ^{1}H NMR ($CDCl_3$): δ 8.54 (m, 1 H, pyr), 7.58−7.07 (m, 7 H, pyr and aromatic), 6.83 (d, 1 H, C_5 ring), 6.57 (d, 1 H, C_5 ring), 4.51 (hept, 3 H, OC*H*$(CH_3)_2$), 3.22−2.77 (m, 4 H, CH_2CH_2), 1.24 (d, 18 H, OCH(C*H*$_3)_2$).

Polymerization and Polymer Characterization. Polymerization grade ethylene and propylene were dried and purified by passing them through Matheson gas purifiers (model 6436). Polymerizations were carried out in 250-mL crown-capped glass pressure reactors with magnetic stirring and thermostated to the desired temperature. The system was first evacuated and flushed with argon three times and then charged with 50 mL of toluene (freshly distilled from Na/K alloy). The system was evacuated again and charged with the appropriate gaseous monomer. In the case of liquid monomers, 5 mL of styrene was injected into the bottle.

The order of reagent addition was monomer, MAO, and catalyst. All of the triisopropoxytitanium catalysts were preactivated by addition of 2000 equiv of MAO to the catalyst solution and stirring for 30 min. The polymerization mixture was quenched with 2% HCl in methanol, filtered, and washed with methanol. The polymer samples were dried in a vacuum oven at 0.1 mmHg and 70 °C to a constant weight.

The activity values were calculated using the measured solubility of propylene and ethylene or the known number of moles of liquid monomer injected. DSC melting endotherms were obtained on either Perkin-Elmer DSC-4 or Du Pont TA 2000, SCD 10 instruments. Molecular weight determinations were made by viscosity measurements in Decalin at 135 °C.

The procedures used to polymerize styrene[12] and ethylene or propylene[13] have been given in detail previously.

Acknowledgment. The authors are grateful to Barrie Rhodes for technical assistance.

OM980118C