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Notes

Indium-Bridged Chelating Diamide Group IV Metal Olefin Polymerization Catalysts

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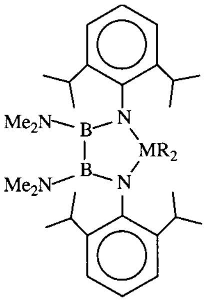
*Summary: The group IV metal chelating diamide complex **2** has been prepared and characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and single-crystal X-ray structure analysis. This complex is an active catalyst upon combining with the appropriate activator. The catalyst efficiencies, however, are considerably lower than those of Cp-based catalysts. The polydispersities of the polymers produced were found to be broader than those observed for Cp-based single-site catalytic systems.*

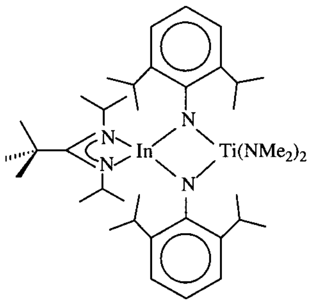
Introduction

The development of non-Cp-based early-transition-metal complexes that provide suitable precursors for the generation of homogeneous Ziegler−Natta olefin polymerization catalysts remains an active area of industrial and academic research.[1] One strategy which has met with considerable success involves the replacement of both cyclopentadienyl (Cp) ligands with an amido functionality. Of particular note are the recent reports of the preparation of a variety of four-, five-, and six-coordinate group 4 metal complexes that contain a chelating diamido ligand.[2] These compounds have been subsequently shown, upon activation, to afford catalysts capable of the living polymerization of 1-hexene and the copolymerization of ethylene and α-olefins. A recent extension of this work involved the incorporation of a bis(dimethylamido) diboron bridge into the ligand structure, resulting in complex **1**.[3] This class of complexes proved to be olefin polymerization catalysts upon activation, albeit demonstrating low activities and stability.

This paper describes our efforts into extending the class of Lewis acid bridged bis(amide) based complexes to include an indium bridge.[4] The research is driven to determine if the inclusion of the indium linkage for amide-based complexes results in improved catalytic properties relative to the previously described diboron analogues. We now report the synthesis, spectroscopic characterization, X-ray crystallographic analysis, and polymerization activity of the electrophilic indium-bridged titanium complex **2**.



1: M = Ti, Zr



2

Results and Discussion

Synthesis. The preparation of complex **2** is represented in Scheme 1. Initial attempts to synthesize the analogous complex starting with the simple $Et_2N-InCl_2$ reagent[5] as the potential bridging synthon were unsuccessful, due to the formation of multiple unidentified reaction products upon addition of 2 equiv of 2,6-diisopropylaniline lithium salt. An observed product in this reaction is metallic indium, characteristic of these reactions.[6] The *tert*-butyl-*N*,*N*′-diisopropylamidinate group was turned to as a stabilizing group to impart greater electronic as well as steric stabilization of the reactive indium center. This strategy resulted in the successful synthesis of **4** in good yield following recrystallization from toluene. Attempts to deprotonate **4** with

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[1] Britovsek, G. J. P.; Gibson, V. C.; Duncan, F. W. *Angew. Chem., Int. Ed.* **1999**, *38*, 428.

[2] (a) Scollard, J. D.; McConville, H. H.; Vittal, J. J.; Payne, N. C. *J. Mol. Catal.* **1998**, *128*, 201. (b) Schrock, R. R.; Bonitatebus, P. J., Jr.; Schrodi, Y. *Organometallics* **2001**, *20*, 1056. (c) Schrodi, Y.; Schrock, R. R.; Bonitatebus, P. J., Jr. *Organometallics* **2001**, *20*, 3560. (d) O'Connor, P. E.; Morrison, D. J.; Steeves, S.; Burrage, K.; Berg, D. J. *Organometallics* **2001**, *20*, 1153 and references therein.

[3] Patton, J. T.; Feng, S. G.; Abboud, K. A. *Organometallics* **2001**, *20*, 3399.

[4] Campbell, R. E., Jr.; Devore, D. D.; Feng, S.; Frazier, K. A.; Green, P. D.; Patton, J. T. Gallium or Indium Bridged Group IV Metal Complexes for Catalysts for Polymerization of Olefins, WO 01/46201.

[5] Prust, J.; Müller, P.; Rennekamp, C.; Roesky, H. W.; Usón, I. *J. Chem. Soc., Dalton Trans.* **2000**, 2265.

[6] Bradley, D. C.; Frigo, D. M.; Hursthouse, M. B.; Hussain, B. *Organometallics* **1988**, *7*, 1112.

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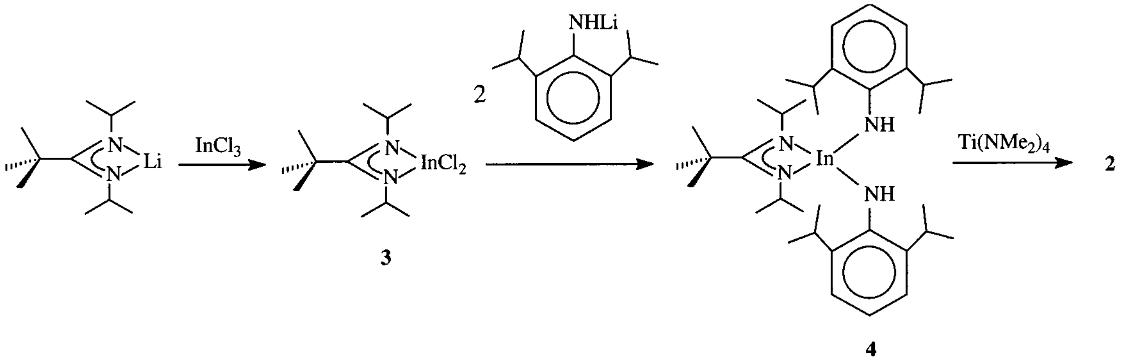
Scheme 1



reagents such as alkyllithiums were unsuccessful, leading to unidentified byproducts likely due to the high reactivity of the indium center. Successful metalation occurred when the ligand **4** was heated in a benzene solution of $Ti(NMe_2)_4$, resulting in the clean isolation of **2** following recrystallization. Attempts to exchange the dimethylamido groups from **2** with either chloride substituents using reagents such as TMS-Cl, BCl_3, and $HCl-NEt_3$ or direct conversion to the methyl substituents using $AlMe_3$ all met with failure: again, likely due to the reactive indium center. The ^1H NMR spectrum for compound **2** exhibits a sharp doublet and singlet for the isopropyl methyls and the *tert*-butyl group of the amidinate group, respectively. The isopropyl groups of the aniline substituents appear as a broad resonance at 1.36 ppm, indicating a hindered rotation about the isopropyl−aryl bond linkage. This broad resonance sharpens to a single doublet upon heating to 40 °C. The remainder of the room-temperature spectrum shows septets for the isopropyl methine groups of the amidinate and the aniline substituents at 3.80 and 3.93, respectively. The aromatic resonances exhibit the expected sharp triplet at 6.95 ppm and doublet at 7.17 ppm.

X-ray Crystal Structure Analysis. The molecular structures of **2**[7] and **4**[8] were confirmed by single-crystal X-ray structure analysis. The thermal ellipsoid drawings are shown in Figures 1 and 2. Selected bond distances and angles are included in Tables 1 and 2.[9] The X-ray single-crystal analyses reveal that compounds **2** and **4** exhibit symmetrically bound amidinate ligands to the indium moiety through the two nitrogen atoms, forming the expected planar four-membered rings. In the free ligand **4** the In−N1 and In−N4 bond lengths are virtually identical. The corresponding bond angles for **4**, In−N1−C11 and In−N4−C5 at 125.34(14) and 117.23(13)°, respectively, differ significantly, likely due to the distortion of these bonds, allowing for steric relief from the large isopropyl substituents. These same angles for **2** continue to exhibit asymmetry, but to a lesser degree at 117.89(16) and 120.17(16)° respectively. Again, this is likely attributed to the sterics of having six isopropyl groups on a single ligand fragment. This asymmetry in **2** can also be observed in the In−N1 and In−N4 bond lengths of 2.118(2) and 2.134(2) Å, respectively. One might speculate that, as the ligand is reorganized to accommodate the titanium chelation, one of the In−N(aniline) bonds is lengthened to decrease the isopropyl (aniline) and isopropyl (amidinate) steric congestion. In compound **2**, the N4−In−N1 bond angle is 85.14(8)°, relative to 107.61(7)° for **4**, due to the chelation of N1 and N4 to the titanium metal center again forming a planar four-membered metallacycle spirally linked to the other metallacycle through the indium center.

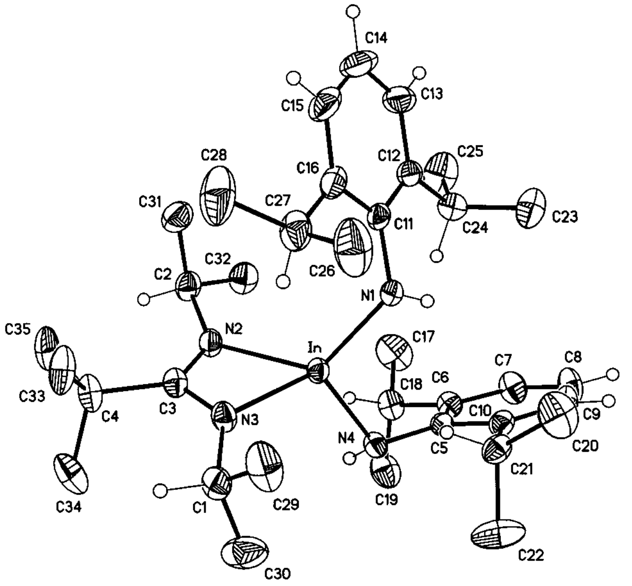


Figure 1. Molecular structure and numbering scheme for bis(2,6-diisopropylaniline)indium−*tert*-butyl-*N*,*N*′-diisopropylamidinate (**4**) with 40% probability thermal ellipsoids.

Polymerization Results. The complex **2** was an active polymerization catalyst upon combination with appropriate activators. Presumably, the activator package includes an alkylaluminum species to first exchange out the dimethylamido substituents on the titanium metal center followed by alkyl abstraction.[10] This method

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[7] Crystallographic data for **2**: formula $C_{39}H_{69}InN_6Ti$, fw = 784.72, monoclinic, space group $P2_1/n$ (No. 14), $a = 11.147(1)$ Å, $b = 20.878(2)$ Å, $c = 18.418(2)$ Å, $\beta = 102.158(2)°$, $V = 4190.2(7)$ Å^3, $Z = 4$, $d_{calcd} = 1.244$ g cm^{-3}, $T = 173(2)$ K, $\omega-2\theta$ scan, $6° < 2\theta < 55°$, λ(Mo Kα) = 0.710 73 Å, R (R_w) = 0.0359 (0.0728) for 444 parameters against 7143 reflections with $I > 2\sigma(I)$ out of 9621 unique reflections ($R_{int} = 0.0563$) by full-matrix least-squares methods, GOF = 0.937.

[8] Crystallographic data for **4**: formula $C_{35}H_{59}InN_4$, fw = 650.68, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.4828(6)$ Å, $b = 11.4576(7)$ Å, $c = 17.958(1)$ Å, $\beta = 99.087(1)°$, $V = 1780.2(2)$ Å^3, $Z = 2$, $d_{calcd} = 1.214$ g cm^{-3}, $T = 173(2)$ K, $\omega-2\theta$ scan, $6° < 2\theta < 55°$, λ(Mo Kα) = 0.710 73 Å, R (R_w) = 0.0296 (0.0752) for 384 parameters against 7252 reflections with $I > 2\sigma(I)$ out of 7941 unique reflections ($R_{int} = 0.0379$) by full-matrix least-squares methods, GOF = 1.029.

[9] See the Supporting Information for full crystallographic data and tables.

[10] Gibson, V. C.; Kimberley, B. S.; White, A. J. P.; Williams, D. J.; Howard, P. *Chem. Commun.* **1998**, 331.

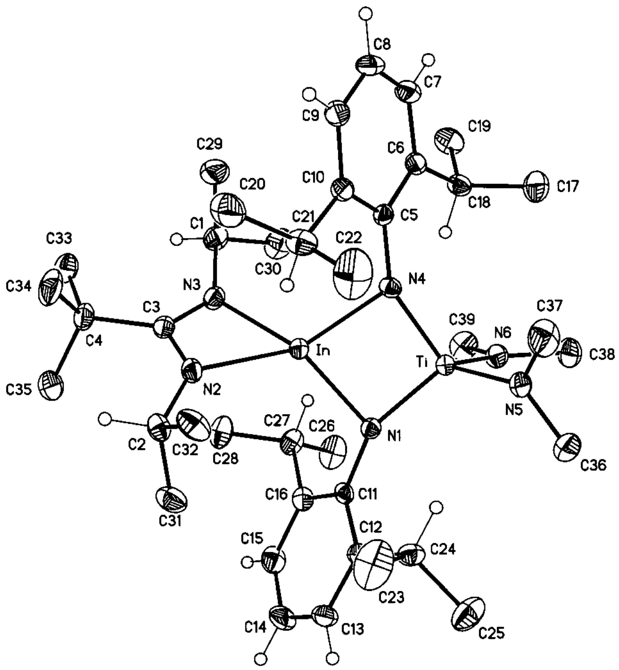

Figure 2. Molecular structure and numbering scheme for bis(dimethylamido)bis(2,6-diisopropylaniline)indium−(*tert*-butyl-*N*,*N*′-diisopropylamidinate)titanium (**2**) with 40% probability thermal ellipsoids.

Table 1. Selected Bond Lengths (Å) for 2 and 4

	2	4
In−N1	2.118(2)	2.072(2)
In−N2	2.162(2)	2.167(2)
In−N3	2.163(2)	2.160(2)
In−N4	2.134(2)	2.071(2)
In−Ti	2.8160(5)	
Ti−N1	1.910(2)	
Ti−N4	1.905(2)	
Ti−N5	1.901(2)	
Ti−N6	1.932(2)	

Table 2. Selected Angles (deg) for 2 and 4

	2	4
N4−In−N1	85.14(8)	107.61(7)
N4−In−N3	117.94(8)	113.88(7)
N1−In−N3	138.37(8)	125.83(8)
N4−In−N2	141.13(8)	120.83(7)
N1−In−N2	122.41(8)	121.82(7)
N3−In−N2	61.15(8)	60.91(7)
N3−C3−N2	110.3(2)	110.2(2)
In−N1−C11	117.9(2)	125.3(1)
In−N4−C5	120.2(2)	117.2(1)
N4−Ti−N1	97.91(9)	
N5−Ti−N6	101.4(1)	
N5−Ti−In	133.53(7)	
C11−N1−Ti	153.4(2)	
Ti−N1−In	88.56(8)	
C5−N4−Ti	150.9(2)	
Ti−N4−In	88.24(8)	

of activation has proven successful in related bis(cyclopentadienyl)-based systems.[11] The complex was activated in runs 1, 5, and 6 by injecting complex **4**, TIBA (triisobutylaluminum), and $[CPh_3][B(C_6F_5)_4]$ or MAO solutions independently into the reactor. Alternatively, **4** was activated by premixing the complex with TIBA and then injecting this mixture and $[CPh_3][B(C_6F_5)_4]$ or MAO solutions independently into the reactor in runs 2−4. In each case activation occurs in the presence of the olefin monomers. The polymerizations were conducted with ethylene on demand. The results for the ethylene/octene copolymerizations are summarized in Table 3. These results indicate that these catalysts exhibit low activity toward the polymerization of olefin monomers and, like the diborone bridged analogues, suffer from the formation of multiple catalyst sites.

Conclusions

A group IV metal complex comprised of an indium-bridged amido ligand has been synthesized. Complex **2** was prepared by reacting the neutral ligand with $Ti(NMe_2)_4$ via the elimination of $HNMe_2$. This complex has been shown to be an active olefin polymerization catalyst upon combination with the appropriate activator. Efforts to examine the structure−activity relationships of In-bridged amide-based complexes are currently underway.

Experimental Section

The ^1H (300 MHz) and $^{13}C\{^1H\}$ NMR (75 MHz) spectra were recorded on Varian Mercury Vx and Inova 300 spectrometers. The ^1H and ^{13}C NMR spectra are referenced to the residual solvent peaks and are reported in ppm relative to tetramethylsilane. All *J* values are given in Hz. Tetrahydrofuran (THF), diethyl ether, toluene, and hexane were used following passage through double columns charged with activated alumina and Q-5 catalyst. The compounds $Ti(NMe_2)_4$, 1,3-diisopropylcarbodiimide, *tert*-butyllithium, and 2,6-diisopropylaniline were all used as purchased from Aldrich. All syntheses were performed under dry nitrogen atmospheres using a combination of glovebox and high-vacuum techniques. High-resolution mass spectroscopy (HRMS) was performed by the University of Florida. Elemental analyses were performed by Oneida Research Services, Inc., Whitesboro, NY, and University of Michigan Thermal Analysis Group, Ann Arbor, MI.

Single-Crystal X-ray Analysis of Bis(2,6-diisopropylanilide)indium−*tert*-Butyl-*N*,*N*′-diisopropylamidinate (4) and Bis(dimethylamido)bis(2,6-diisopropylanilide)indium−(*tert*-Butyl-*N*,*N*′-diisopropylamidinate)titanium (2). Data were collected at 173 K on a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Cell parameters were refined using 8192 reflections. A hemisphere of data (1381 frames) was collected using the ω-scan method (0.3° frame width). The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was <1%). Absorption corrections by integration were applied on the basis of measured indexed crystal faces.

The structures were solved by direct methods in SHELXTL5 and refined using full-matrix least squares.[12] The non-H atoms were refined with anisotropic thermal parameters, and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms. In the final cycle of refinement of **2**, 7143 observed reflections with $I > 2\sigma(I)$ were used to refine 444 parameters and the resulting R1 and wR2 values were 3.59% and 7.28%, respectively. In the final cycle of refinement of **4**, 7252 observed reflections with $I > 2\sigma(I)$ were used to refine 384 parameters and the resulting R1 and wR2 values were 2.96% and 7.52%, respectively. Refinement was done using F^2.

Ethylene/Octene Copolymerizations. All feeds were passed though columns of activated alumina and Q-5 catalyst

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[11] Kim, I.; Jordan, R. F. *Macromolecules* **1996**, *29*, 489.

[12] Sheldrick, G. M. SHELXTL5; Bruker-AXS, Madison, WI, 1998.

Table 3. Ethylene/Octene Copolymerization Results

run	monomer	activator	T_p (°C)	exotherm (°C)	activity ((g of P)/(g of Ti))	M_w (PDI)
1	E/O	50 TIBA/1000 MAO	70	0.0	25 991	167 000 (9.54)
2	E/O	50 TIBA/1000 MAO	70	2.0	27 151	562 000 (9.95)
3	E/O	50 TIBA/[CPh$_3$][B(C$_6$F$_5$)$_4$]	70	4.0	34 113	598 000 (13.56)
4	E/O	50 TIBA/[CPh$_3$][B(C$_6$F$_5$)$_4$]	140	1.0	6 683	132 000 (17.4)
5	E/O	50 TIBA/1000 MAO	140	1.3	4 595	144 000 (12.8)

prior to introduction to the reactor. A stirred 2 L Parr reactor was charged with about 740 g of Isopar-E solvent and 118 g of 1-octene comonomer. Hydrogen was added as a molecular weight control agent by differential pressure expansion from a 75 mL addition tank at 25 psi (2070 kPa). The reactor contents were then heated to the polymerization temperature of 140 °C and saturated with ethylene at 500 psig (3.4 Mpa). The metal complex and activators were mixed as dilute toluene solutions, transferred to a catalyst addition tank, and injected into the reactor through a stainless steel transfer line. The polymerization conditions were maintained for 15 min with ethylene added on demand. Heat was continually removed from the reaction with an internal cooling coil. The resulting solution was removed from the reactor, quenched with isopropyl alcohol, and stabilized by the addition of 10 mL of a toluene solution containing approximately 67 mg of a hindered phenol antioxidant (Irganox 1010 from Ciba Geigy Corp.) and approximately 133 mg of a phosphorus stabilizer (Irgafos 168 from Ciba Geigy Corp.). Between polymerization runs a wash cycle was conducted in which 850 g of mixed alkanes were added to the reactor, which was then heated to 150 °C and then emptied of the heated solvent immediately prior to a new polymerization run.

Polymers were recovered by drying for about 20 h in a vacuum oven set at 140 °C. High-temperature gel permeation chromatography (GPC) analysis of polymer samples were carried out in 1,2,4-trichlorobenzene at 135 °C on a Waters 150C high-temperature instrument. A polystyrene/polyethylene universal calibration was carried out using narrow molecular weight distribution polystyrene standards from Polymer Laboratories with lonol as the flow meter.

Preparation of *tert*-Butyl-*N,N′*-diisopropylamidinate Lithium Salt. 1,3-Diisopropylcarbodiimide (7.000 g, 55.47 mmol) was stirred in hexane (50 mL) at 0 °C as *t*-BuLi (1.7 M solution in pentane) was added dropwise. This mixture was stirred overnight at room temperature, during which time a white precipitate formed. This mixture was then filtered and the white solid washed with hexane, dried under vacuum, and used without further purification or analysis (9.629 g, 91.2% yield).

Preparation of Dichloroindium−*tert*-Butyl-*N,N′*-diisopropylamidinate (3). *tert*-Butyl-*N,N′*-diisopropylamidinate lithium salt (9.629 g, 50.61 mmol) and indium trichloride (11.194 g, 50.61 mmol) were mixed together in diethyl ether (50 mL) at 0 °C and then stirred overnight at room temperature. After the reaction period the volatiles were removed and the residue extracted and filtered using hot toluene. The product was highly insoluble. Following extraction and filtration the residue was recrystallized from boiling toluene, resulting in the isolation of the desired product as a slightly pale yellow crystalline solid (8.990 g, 48.1% yield). ^{1}H NMR (CD$_2$Cl$_2$): δ 1.18 (d, $^3J_{HH}$ = 6.0 Hz, 12 H), 1.46 (s, 9 H), 4.38 (sept., $^3J_{HH}$ = 5.9 Hz, 2 H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 26.69, 29.79, 47.75. HRMS (EI): calcd for $C_{11}H_{23}N_2InCl_2$ *m/z* 368.0279, found 368.0280.

Preparation of 2,6-Diisopropylaniline Lithium Salt. *n*-BuLi (56.40 mmol, 35.25 mL of a 1.6 M solution in hexane) was added dropwise to a solution of 2,6-diisopropylaniline (10.00 g, 56.40 mmol) in hexane (100 mL). This mixture was stirred for 3 h, during which time a white precipitate formed. After the reaction period the mixture was filtered and the white salt washed with hexane, dried under vacuum, and used without further purification or analysis (9.988 g, 96.7% yield).

Preparation of Bis(2,6-diisopropylaniline)indium−*tert*-Butyl-*N,N′*-diisopropylamidinate (4). 2,6-Diisopropylaniline lithium salt (2.880 g, 15.72 mmol) in diethyl ether (10 mL) was added dropwise to a slurry of dichloroindium−*tert*-butyl-*N,N′*-diisopropylamidinate (2.900 g, 7.86 mmol) in diethyl ether (50 mL) at 0 °C. This mixture was then stirred overnight at room temperature. After the reaction period the volatiles were removed under vacuum and the residue extracted and filtered using hexane. Concentration of the filtrate and cooling to −10 °C overnight resulted in the isolation of the desired product as a pale yellow crystalline solid (2.982 g, 58.3% yield). ^{1}H NMR (C$_6$D$_6$): δ 0.86 (d, $^3J_{HH}$ = 6.0 Hz, 12 H), 1.06 (s, 9 H), 1.28 (d, $^3J_{HH}$ = 6.9 Hz, 24 H), 3.24 (sept, $^3J_{HH}$ = 6.6 Hz, 4 H), 3.48 (s, 2 H), 3.93 (sept, $^3J_{HH}$ = 6.3 Hz, 2 H), 6.90 (t, $^3J_{HH}$ = 7.5 Hz, 2 H), 7.13 (d, $^3J_{HH}$ = 2.4 Hz, 4 H). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 23.45, 26.59, 28.98, 29.80, 46.38, 118.83, 123.02, 137.46, 148.52. HRMS (EI): calcd for $C_{35}H_{59}N_4In$ *m/z* 650.3780, found 650.3752. Anal. Calcd for $C_{34}H_{59}N_4In$: C, 63.94; H, 9.31; N, 8.77. Found: C, 63.83; H, 9.81; N, 8.64.

Preparation of Bis(dimethylamido)bis(2,6-diisopropylanilide)indium−(*tert*-Butyl-*N,N′*-diisopropylamidinate)titanium (2). Bis(2,6-diisopropylanilide)indium−*tert*-butyl-*N,N′*-diisopropylamidinate (1.000 g, 1.54 mmol) and Ti(NMe$_2$)$_4$ were heated together in benzene (20 mL) at 60 °C for 8 h under a nitrogen bubbler. During this time the flask was occaissionally evacuated and then back-flushed with fresh nitrogen. The reaction mixture was then placed under full vacuum to remove all volatiles. The mixture was then extracted and filtered using toluene. The toluene solution was then concentrated and placed in a freezer (−10 °C) overnight, during which time the desired product precipitated as a yellow crystalline solid (0.394 g, 32.6% yield). ^{1}H NMR (C$_6$D$_6$): δ 0.67 (d, $^3J_{HH}$ = 6.0 Hz, 12 H), 0.90 (s, 9 H), 1.38 (br m, 24 H), 3.24 (s, 12 H), 3.82 (sept, $^3J_{HH}$ = 6.2 Hz, 2 H), 3.94 (sept, $^3J_{HH}$ = 6.9 Hz, 4 H), 6.96 (t, $^3J_{HH}$ = 7.6 Hz, 2 H), 7.18 (d, $^3J_{HH}$ = 7.8 Hz, 4 H). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 24.6 (br), 25.74, 28.38, 29.46, 31.92, 39.48, 46.56, 46.93, 120.09, 123.22, 138.59, 154.38, 174.86. HRMS (EI): calcd for $C_{39}H_{69}N_6InTi$ *m/z* 784.4103, found 784.4127. Attempts to obtain elemental analysis using highly purified crystals consistently gave low nitrogen analysis.

Acknowledgment. We are grateful to the polypropylene research group of The Dow Chemical Co. for general discussions. We also thank Judy Gunderson for the size exclusion chromatography analysis of the polymers.

Supporting Information Available: An ORTEP diagram and tables of crystal data, data collection, and refinement parameters, atomic coordinates, bond distances and angles, and isotropic displacement parameters for complexes **2** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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