Selectivity in Propylene Polymerization with Group 4 Cp−Amido Catalysts

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Mono-Cp−amido complexes [η^5:η^1-Cp′SiMe$_2$(NR)]MCl$_2$ (M = Ti, Zr) have been synthesized by metathesis and amine elimination routes in low to moderate yields (5−50%). Two optically active examples based on (*S*)-(−)-(α)-methylbenzylamine are presented, and the molecular structure of (+)-(*R*)-[η^5: η^1-(Ind)SiMe$_2$-(S)-NCHMePh]TiCl$_2$ (**4**) has been determined by X-ray crystallography. These complexes are active in the presence of methylaluminoxane for propylene polymerization and yield high molecular weight atactic polymers with slight syndiotactic enrichment. Productivities, molecular weights, and tacticities are dependent on Cp′ and NR. Incorporation of a chiral amine into the ligand framework has little effect on stereospecificity. Polypropylenes derived from the titanium catalysts show significant amounts of 2,1-monomer insertion (2−5%).

The use of well-defined single-site metallocene catalysts in olefin polymerizations is well-established.[1] Isotactic, syndiotactic, and high molecular weight atactic polypropylenes can be produced through the appropriate choice of metallocene precursor.[1,2] Recently, a new class of homogeneous Ziegler−Natta catalysts were developed by researchers at Dow and Exxon.[3−5] These group 4 mono-cyclopentadienyl−amido (CpA) catalysts are based on the ligand system first prepared by Bercaw[6] for organoscandium complexes and are distinguished by a sterically accessible catalyst active site.[7,8] They differ from bis(cyclopentadienyl) metallocenes in their ability to readily incorporate α-olefins, notably styrene,[5,9,10] in copolymerizations with ethylene. These catalysts are remarkably stable up to polymerization temperatures of 160 °C, and the titanium derivatives are less easily reduced by methylaluminoxane (MAO) than the corresponding titanocenes.

Polypropylenes (PP) produced by CpA catalysts are generally atactic, with varying degrees of syndiotacticity.[5,10−13] However, one report in the patent literature[3] details several non-C_2 symmetric catalysts which yield isotactic-enriched polymers ([*mmmm*] > 75%) in the presence of MAO. Other reports indicate that propylene polymerization with cationic catalysts can yield either syndiotactic ([*r*] = 95%)[14] or isotactic ([*mmmm*] = 95%)[15] polymers depending on the nature of the initiating system. Additionally, little is known[13] about the regiospecificity of CpA catalysts in propylene polymerization.

In view of the extraordinary potential of these catalysts and the scattered and conflicting information in the patent literature regarding the mechanism of polymerization and origin of stereocontrol with CpA catalysts, we undertook a study of their propylene polymerization behavior. In particular, we sought to exploit chiral amino auxilliaries as either stereocontrol elements or resolving agents in the CpA ligand system. Herein, we report propylene polymerization results using several CpA catalysts of varying steric and electronic demands, including examples of optically active CpA catalysts.

Results

Preparation of Mono-Cp−Amido Complexes. Ligands were prepared according to published procedures. Treatment of (C$_p$′H)SiMe$_2$Cl (C$_p$′ = tetramethylcyclopentadienyl (Me$_4$C$_5$),[5] 1-indenyl (Ind),[5] and 9-fluorenyl (Flu)[16,17] with excess amine in THF yielded (Cp′H)SiMe$_2$NHR (R = ^{t}Bu, (*S*)-(−)-α-methylbenzyl, C$_6$H$_{11}$), which can be purified by distillation.[18] Scheme

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1997.

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(16) Okuda, J.; Schattenmann, F. J.; Wocadlo, S.; Massa, W. *Organometallics* **1995**, *14*, 789−795.
(17) We found, like Okuda, that FluSiMe$_2$Cl cannot be prepared without some contamination by Flu$_2$SiMe$_2$. However, sublimation at 60 mTorr/100 °C gave pure FluSiMe$_2$Cl.
(18) As Herrmann showed, Ind−amino ligands are isolated as mixtures of regioisomers.

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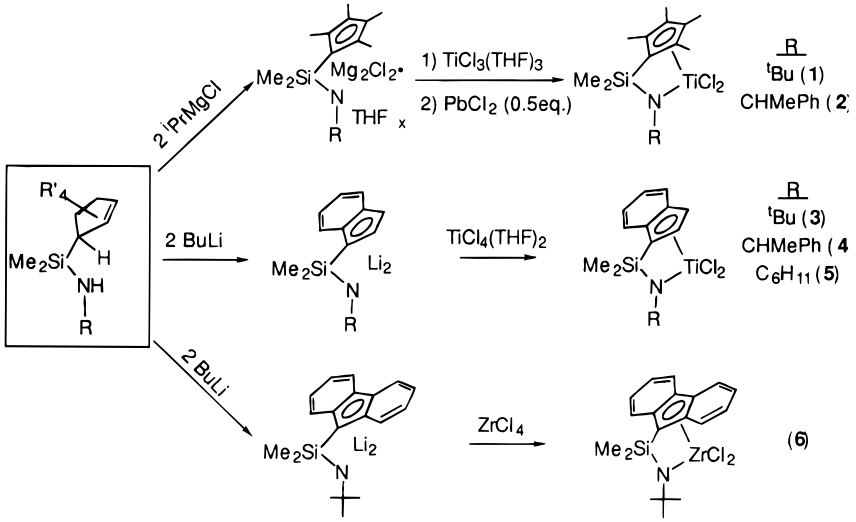
Scheme 1. Synthetic Approaches to Mono-Cp−Amido Complexes



1 summarizes the general synthetic routes. When Cp′ = Me_4C_5, double deprotonation with isopropylmagnesium chloride[5] in THF/toluene followed by reaction with $TiCl_3(THF)_3$ and $PbCl_2$ oxidation[19] gave [η^5:η^1-Me_4C_5-$SiMe_2NR$]$TiCl_2$ in yields of 52% (**1**) and 16% (**2**).

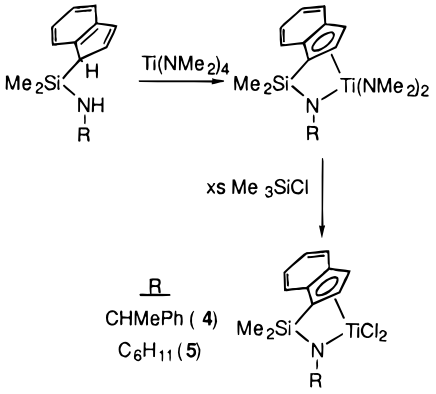
Several routes were explored to prepare the indenyl−amido complexes. Reaction of the indenyl dimagnesio dichloride salts with $TiCl_3(THF)_3$ followed by $PbCl_2$ oxidation or with $TiCl_4(THF)_2$ was unsuccessful, as was the reaction of the dilithio salts with $TiCl_4$. The only viable metathesis route toward preparation of indenyl−amido complexes proved to be reaction of the dilithio salts with $TiCl_4(THF)_2$. Yields for this route were quite low (<20%).

In the synthesis of [$FluSiMe_2N^tBu$]$ZrCl_2$, it was noted[16] that preparations in THF or Et_2O yielded the Lewis base adducts [$FluSiMe_2N^tBu$]$ZrCl_2$·L (L = THF, Et_2O). Earlier syntheses[3] of [η^5:η^1-$FluSiMe_2N^tBu$]$ZrCl_2$ utilized Et_2O as a reaction solvent but made no mention of base adducts. We therefore sought to prepare base-free [$FluSiMe_2N^tBu$]$ZrCl_2$ by treatment of the ligand dilithio salt with $ZrCl_4$ in toluene. The product is obtained as bright yellow, air- and moisture-sensitive crystals in 35% yield.

Optically active complexes **2**[20,21] and **4** based on the commercially available chiral (*S*)-(−)-(α)-methylbenzylamine were prepared by the methods mentioned above for Me_4C_5 and indene derivatives. In the case of **2**, only one isomer is possible and it gives a complex with an optical rotation of $[\alpha]_{589} = -190.5°$ (c = 1.3 mg/mL, CH_2Cl_2). On the other hand, two diastereomers are possible for **4** because of the two possible orientations of the indenyl ring. A single diastereomer was isolated by preferential crystallization from Et_2O/CH_2Cl_2 to give (+)-(*R*)-[η^5:η^1-(Ind)$SiMe_2$-(*S*)-NCHMePh]$TiCl_2$ (**4**), with an optical rotation of $[\alpha]_{589} = +402°$ (c = 0.95mg/mL, CH_2Cl_2).

Low yields for the metathesis routes, especially for the Ind complexes, prompted us to follow the recent route of Herrmann[22] for preparation of indenyl−amido complexes via amine elimination from $Ti(NR_2)_4$. Double protonation of $Ti(NMe_2)_4$ with (Ind−*H*)$SiMe_2NHR$ (R = (*S*)-(−)-α-methylbenzyl, C_6H_{11}) in refluxing toluene gave the expected diamide (Scheme 2). The (*S*)-(−)-α-methylbenzylamine derivative yields two diastereomers in a ratio of 1.33/1 by ^{1}H NMR. Subsequent treatment with excess Me_3SiCl[8,23] in CH_2Cl_2 cleanly gave the desired dichlorides in overall yields of 39% for the single diastereomer of **4** and 45% for **5**.

Scheme 2. Synthesis of Indenyl Complexes by Amine Elimination



Crystal Structure Data for 4. To gain information on the steric demands of the indenyl complexes and the potential influence of metal chirality on reaction stereospecificity, a single-crystal X-ray diffraction analysis of **4** was performed. The crystal structure is illustrated in Figure 1, and relevant bond distances and angles are listed in Table 1.

The structural features of **4** are similar to those for **1**.[5,8] In particular, the "bite angle" (θ) of the ligand, defined as Cp(cent)−Ti−N, is 106.3°. The metal to ligand bond distances are also similar to those for **1**, with Ti(1)−N(1) = 1.915 Å (vs 1.907 Å) and Ti(1)−Ind(cent) = 2.045 Å (vs 2.030 Å). The structure reveals a pseudo-C_2 symmetry when considering the aromatic rings of the indene and the phenyl group of methyl-

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(20) During the preparation of this manuscript, Okuda reported the synthesis of this complex by similar methods.

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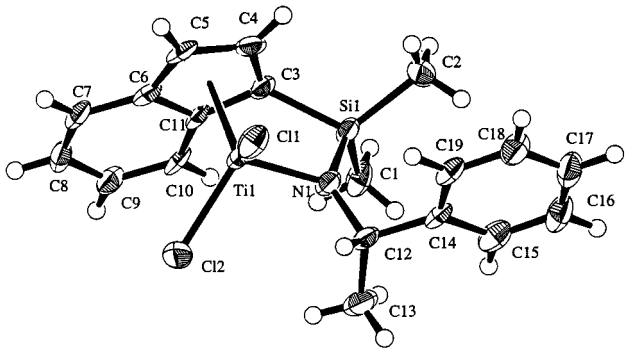

Figure 1. ORTEP diagram of (+)-(*R*)-[η^5:η^1-(Ind)$SiMe_2$-(*S*)-NCHMePh]$TiCl_2$ (**4**).

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

Ti(1)−Cl(1)	2.257(2)	Ti(1)−Cl(2)	2.258(2)
Ti(1)−N(1)	1.915(5)	Ti(1)−Ind(cent)	2.045
Si(1)−N(1)	1.739(6)	Si(1)−C(3)	1.876(6)
Cl(1)−Ti(1)−Cl(2)	102.54(8)	Ind−Ti(1)−N(1)	106.3
Ti(1)−N(1)−C(12)	120.4(4)	Ti(1)−N(1)−Si(1)	106.9(3)
Si(1)−N(1)−C(12)	132.7(4)	N(1)−Si(1)−C(3)	90.0(3)

benzylamine. The orientation of the phenyl group is such that it is pointed away from the underside of the indene ring, while the methyl group lies under the ring. This effectively directs the α-H toward the metal center. The lessened steric demands of this amino group relative to the more sterically demanding t-butylamine of **1** may explain the 6° smaller Ti(1)−N(1)−C(12) angle (120.4°) relative to that for **1** (Ti−N−C = 132.7°).

Propylene Polymerizations. Propylene polymerizations were conducted for catalysts **1**−**6** in toluene solution at 50 psig or in liquid propylene at 30 °C (±1 °C) for 1 h. Conditions for catalysts **5** and **6** were chosen to match those used by Canich;[3] similar conditions were used for catalysts **1**−**4**. The results are summarized in Table 2.

Productivities for entries 1−14 are low relative to most metallocene catalysts for propylene polymerization, but are similar to those reported by Canich.[3] The low productivities are likely a consequence of low Al/M, as indicated by the increased productivities for entries 13 and 14 relative to entries 5 and 6. The Me_4C_5-based catalysts (entries 1−4) are on average more active than the Ind (entries 5−10) and Flu (entries 11,12) analogues.

The appropriate choice of cyclopentadienyl ligand appears to have the most influence on the resultant polymer molecular weight. Me_4C_5-based catalysts **1** and **2** and Flu-based **6** give polymers with higher molecular weights (>250 000) than Ind-based catalysts. The amino group appears to have no clear effect on M_w (entries 1 and 2 vs 3 and 4, 5 and 6 vs 7 and 8).

Polymer microstructures for entries 1−14 were determined by ^{13}C NMR. In all cases, except for entries 5 and 6, the polymers were almost completely atactic, with a slight syndiotactic preference.[24] The similarity in tacticity for polymerizations at 50 psig vs those in the bulk monomer suggest that there is no strong tacticity dependence on monomer concentration.[25]

Incorporation of (S)-(−)-(α)-methylbenzylamine or cyclohexylamine into the ligand framework (catalysts **2**, **4**, and **5**) seems to have a slight effect in lowering the stereospecificity of polymerization (compare catalysts **3** vs **4**, entries 5−8).

Regioselectivity. All of the Me_4C_5- and Ind-based catalysts (**1**−**5**) give polymers with a significant amount of regioirregularities, while the fluorenylzirconium catalyst **6** gives no misinsertions. Figure 2 shows this difference between entries 8 and 12, respectively. Cheng and Ewen[26] have assigned the ^{13}C NMR chemical shifts for regioirregularities in atactic PP by comparison with calculated spectra. They observed peaks due to 2,1- and 1,3-misinsertions (Figure 3) which were sensitive to the overall tacticity of the polymer, as they were greatly broadened relative to those for isotactic PP.[25,27] ^{13}C NMR spectra of entries 2, 4, 6, and 8 were obtained to identify the type of misinsertions and to quantify the degree of regioirregularities. According to the method of Resconi[25] and Mizuno,[27] the percentages of 2,1- and 1,3-misinsertions can be calculated from the following equations

$$\%2,1 = C_3/(CH_2(\text{main}) + 3C_3 + C_{3'}) \quad (1)$$

$$\%1,3 = C_{3'}/(CH_2(\text{main}) + 3C_3 + C_{3'}) \quad (2)$$

where C_3 and $C_{3'}$ represent the intensities of carbons 3 and 3′ of the regioirregular units (Figure 3) and CH_2(main) is the intensity of all methylene units arising from 1,2-insertions. We were unable to identify resonances corresponding to 1,3-misinsertions ($C_{3'} = 0$) for these samples. However, using the the peak assignments shown in Figure 2, we calculate the amount of 2,1-insertion to be 2.2% for catalyst **1** (entry 2), 3.6% for catalyst **2** (entry 4), 2.8% for catalyst **3** (entry 6), and 4.7% for catalyst **4** (entry 8).

Discussion

The CpA catalyst has proven to be very useful due to its ability to copolymerize ethylene with α-olefins. These catalysts are especially attractive because they are able to operate at high temperatures without significant drops in productivity and molecular weight. For example, Stevens reports[5] that an ethylene/1-octene copolymer produced at 160 °C with [$(Me_4C_5)SiMe_2N^tBu$]-$TiCl_2$ and MAO had M_w = 53 000 and productivity = 27 000 kg/mol × Ti. One important commercial material made from these catalysts is a linear low-density polyethylene (LLDPE) with the processing characteristics of low-density polyethylene (LDPE).[28] The ease with which these catalysts incorporate α-olefins appears to be a consequence of the sterically accessible nature of the coordination site.

One might predict that the open nature of these catalysts would limit stereospecificity in α-olefin polymerization. We found that catalysts **5** and **6** (entries 11−14), reported to be isospecific[3] under these conditions, gave polymers which were almost completely atactic with a bias toward syndiotactic. C_s-symmetric

(24) In addition, DSC analysis showed a complete lack of crystallinity for entries 1−4, 11, and 12.

(25) Resconi, L.; Fait, A.; Piemontesi, F.; Colonnesi, M.; Rychlicki, H.; Zeigler, R. *Macromolecules* **1995**, *28*, 6667−6676.

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(28) Lai, S.; Yaw; Wilson, J. R.; Knight, G. W.; Stevens, J. C. (Dow Chemical) U.S. Patent 5,278,272, 1994.

Table 2. Propylene Polymerization using Catalysts 1−6[a]

entry	catalyst	[catalyst] (μM)	P (psig)	Al/M	yield (g)	productivity[b]	*mmmm*[c]	*rrrr*[c]	M_w ($\times 10^{-3}$)[d]	M_w/M_n[d]	% 2,1
1	1	38	50	289	3.10	820	2.7	17.7	583	2.01	
2	1	38	100[e]	289	2.89	380	1.0	23.3	400	1.68	2.2
3	2	34	50	350	1.11	325	2.8	7.9	820	1.77	
4	2	34	100[e]	350	1.28	188	4.3	10.4	269	3.55	3.6
5	3	39	50	350	0.22	56	16.3	5.0	118	1.83	
6	3	39	100[e]	350	0.15	19	14.5	7.4	37	2.29	2.8
7	4	34	50	350	0.25	72	6.2	11.2	130	2.80	
8	4	34	100[e]	350	1.33	196	5.5	12.9	111	2.04	4.7
9	5	36	50	400	0.23	63	5.7	11.9	130	3.55	
10	5	36	100[e]	400	1.72	239	4.6	7.5	165	2.20	
11	6	46	50	350	0.14	31	1.3	14.5	652	1.78	
12	6	46	120[f]	350	0.11	17	3.4	17.8	779	1.94	0
13	3	39	50	1000	0.79	203	12.1	6.1	130	1.96	
14	3	39	100[e]	1000	1.48	190	12.2	8.5	133	2.07	

[a] Polymerizations were carried out in toluene with MAO at 30 °C (±1 °C) for 1 h. [b] Productivity in kg PP/mol M × h. [c] Determined by ^{13}C NMR spectrum. [d] Determined by gel-permeation chromatography. [e] Pressure of a mixture of 100 mL of toluene and 100 mL of propylene. [f] Pressure of a mixture of 50 mL of toluene and 100 mL of propylene.

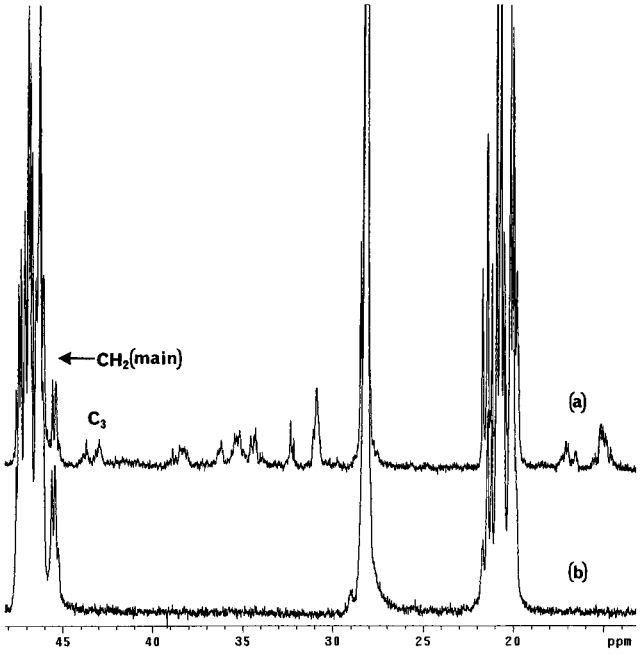

Figure 2. ^{13}C NMR spectra of polymer derived from (a) catalyst **4** (entry 12) and (b) catalyst **6** (entry 8).

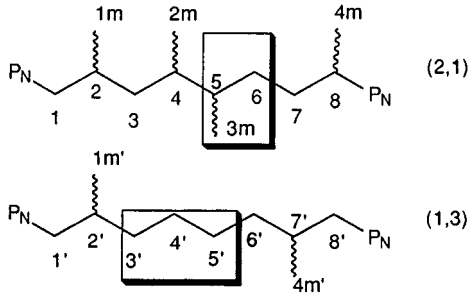

Figure 3. Representation of regioerrors.

1 and **6** could be expected on symmetry grounds to be syndiospecific much like $Me_2C(Flu)(Cp)ZrCl_2$.[29] Of the catalysts studied, **1** and **6** gave polymers with the highest [*rrrr*] values, which are nevertheless quite modest (14 < [*rrrr*] < 23, entries 1, 2, 11, 12). Ziegler[30] has studied simulated M−C_α rotation processes for Ziegler−Natta catalysts, and he found these rearrangements to be much less hindered for CpA complexes than for Cp_2M systems. The CpA complexes also have a higher calculated barrier to monomer insertion (ca. 5 kcal) than their metallocene counterparts. Polymer chain rotation about the metal center between insertions could lead to atactic polymerization in a Cossee−Arlman polymerization mechanism.[31]

Statistical analysis of these polymers revealed that the Bernoullian model for chain-end control is the dominant propagation mechanism for all catalysts except **3.** Polymers derived from Me_4C_5- and Flu-based catalysts have Bernoullian indices ($\beta = 4[mm][rr]/[mr]^2$) which are very close to 1.0, indicating chain-end control, while the indenyl analogues show slightly higher β values (see Supporting Information). Polymers from **3** have average β values equal to 2.32, indicating some small influence of this ligand on the stereospecificity of polymerization.

The accessible coordination site of these catalysts also leads to lower regiospecificity in propylene polymerization. A notable exception is the fluorenylzirconium catalyst **6**, which yields highly regioregular, atactic polypropylene. At this time, it is not clear if the higher regiospecificity of **6** is a consequence of the fluorenyl ligand or the nature of the metal atom. Attempts to compare metal effects were complicated by our inability to synthesize either indenylzirconium or fluorenyltitanium analogues. Also, it is known[5] that a zirconium analogue of **1** shows very low activity in propylene polymerization.

In Figure 4, the effects of the Cp and amido ligand on molecular weight, productivity, isospecificity, and regiospecificity are summarized. It is apparent that Me_4C_5-based catalysts (**1**, **2**) generally have higher molecular weights and productivities than their indenyl analogues (**3**, **4**) under these polymerization conditions. This is likely the effect of the increased electron-donating character of the Me_4C_5 ligand, which may lead to a decrease in chain termination (i.e., β-H elimination) and/or increased stabilization of the active species toward reduction. The effect of the amido ligand on M_w and productivity is inconclusive; however, in the indenyl series, where the electronic effect of the Cp ligand may be minimized, the less sterically encumbered secondary amides (**4**, **5**) tend to be more productive and give

(29) Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 6255.

(30) Fan, L.; Harrison, D.; Woo, T. K.; Ziegler, T. *Organometallics* **1995**, *14*, 2018−2026.

(31) Arlman, E. J.; Cossee, P. *J. Catal.* **1964**, *3*, 99.

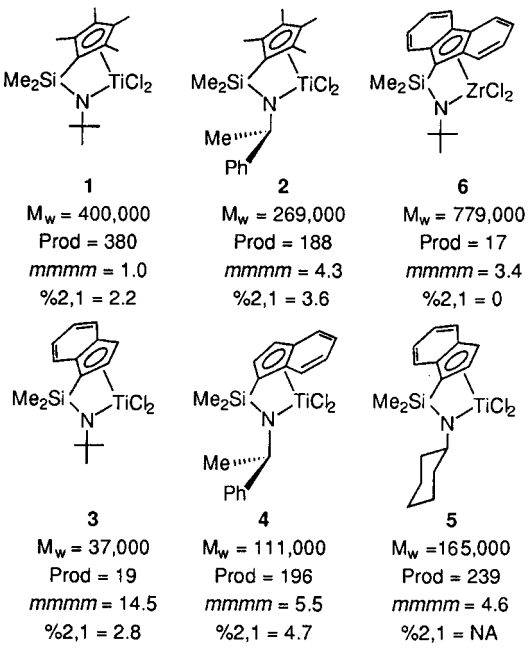

Figure 4. Summary of ligand effects on PP molecular weight, productivities, isospecificities, and regiospecificities of Cp−amido catalysts (Prod = productivity in kg PP/mol M × h).

slightly higher molecular weight PP than the tertiary amido catalyst (**3**).

At the same time, the overall trend toward atactic microstructures and the low *mmmm* values (< 6%) indicate that neither Cp nor amido ligands have a significant effect on the stereospecificity. While most of the catalysts studied tend toward a slight syndiotactic bias, only chiral indenyl complex **3** shows enhancements in *mm*. Perhaps in this case, the combination of sterics from a more encumbered amine and a less-demanding indenyl ring gives rise to a slight energy difference between the two sites available for monomer coordination or the polymer chain. Catalysts of a similar symmetry have been found to give hemiisotactic[32] or stereoblock[33−35] polypropylene.

Finally, while differences in the number of regioerrors are small, there does appear to be a noticeable influence of the ligand environment on the regiospecificity of these titanium catalysts. Quantitative ^{13}C NMR reveals that the more sterically hindered Me_4C_5-based catalysts (**1** and **2**) produce polymers with about 0.5−1.0% less 2,1-insertion than their indenyl analogues (**3** and **4**). The amino group has a slightly greater effect, with N^{t}Bu-based catalysts (**1** and **3**) leading to 1.5−2.0% less misinsertion than the NCHMePh analogues (**2** and **4**).

Experimental Section

General Conditions. All experiments involving air-sensitive compounds were performed under nitrogen in a Vacuum Atmospheres drybox or under argon using standard Schlenk line techniques. Hydrocarbon solvents, diethyl ether, tetrahydrofuran, benzene-d_6, tetrahydrofuran-d_8, and toluene-d_8 were distilled from sodium/benzophenone ketyl. Methylene chloride, chloroform, and chloroform-*d* were distilled from calcium hydride. Deuterated solvents were obtained from Cambridge Isotopes Labs.

Butyllithium, dimethyldichlorosilane, isopropylmagnesium chloride, fluorene, $PbCl_2$, and $TiCl_4(THF)_2$ were obtained from Aldrich and used as received. $ZrCl_4$ was obtained from Fluka and used as received. Indene (Wiley) was dried over 3 Å Molecular sieves and distilled. *tert*-Butylamine, (*S*)-(−)-α-methylbenzylamine, and cyclohexylamine were obtained from Aldrich and distilled from calcium hydride. $(Me_4C_5H)SiMe_2Cl$,[5] $[(Me_4C_5)SiMe_2N^tBu]Mg_2Cl_2(THF)_2$,[5] (Ind−*H*)$SiMe_2Cl$,[5] $[(Ind)SiMe_2N^tBu]Li_2$,[5] $[\eta^5:\eta^1\text{-}(Ind)SiMe_2N(C_6H_{11})]TiCl_2$ (**5**),[3] $[FluSiMe_2N^tBu]Li_2$,[16] $TiCl_3(THF)_3$,[36] and $Ti(NMe_2)_4$[37] were prepared according to literature procedures. $[\eta^5:\eta^1\text{-}(Ind)SiMe_2N(C_6H_{11})]TiCl_2$ (**5**) was also prepared by a modification of the procedure by Herrmann[22] (see below).

^1H NMR were recorded on Varian Gemini 200, Gemini 300, and XL-400 spectrometers and were referenced relative to TMS, while ^{13}C NMR were recorded at 100 MHz on a Varian XL-400 NMR spectrometer. Inverse-gated decoupled ^{13}C NMR spectra of PP samples 2, 4 , 6, and 8 were recorded on a Varian Unity Plus 500 spectrometer at 125.8 MHz. Optical rotations were measured on a JASCO DIP-360 digital polarimeter. Elemental Analyses were performed by Desert Analytics or E+R Microanalytics Laboratories.

Propylene Polymerizations. Polymerizations were carried out in a 450 mL stainless steel Parr reactor equipped with a magnetic stirrer. A cooling mixture (ethylene glycol/water) was passed through the reactor in conjunction with a heating mantle to maintain the temperature within ±1 °C.

Catalyst solutions were prepared by treating a toluene solution of the desired metal complex with solid MAO (Akzo, Type 4A), diluting to 25 mL with toluene, and stirring for 20 min. Meanwhile, toluene (75 mL) was injected into the reactor with a propylene back-pressure and then warmed to 30 °C. Propylene was then introduced as a gas for reactions at 50 psig or as a liquid (100 mL) for reactions at 100 psig. For entry 12, only 50 mL of toluene was used to give a final pressure of 120 psig. After equilibrating the reactor for 20 min, the catalyst solution was injected with either a propylene back-pressure (50 psig reactions) or an argon back-pressure (bulk reactions). The reactor was stirred for 1 h with the temperature maintained within ±1 °C. Polymerizations were terminated by injecting MeOH (20 mL) and venting for ca. 10 min. Polymers were precipitated by pouring the slurry into acidic MeOH (300 mL) and stirring overnight. Finally, the polymer was filtered, washed with MeOH, and then dried at 50−60 °C in a vacuum oven.

Polymer Characterizations. GPC measurements were carried out on 0.2% w/v filtered samples using Waters R401 with a Polymer Laboratories Mixed C (PLGel 5 μm) × 2 column set at 40 °C in THF. ^{13}C NMR spectra of polypropylene samples (100 mg) were obtained in $C_2D_2Cl_4$ (0.5 mL) at 100 °C. A spectral width of 80 ppm was used with a minimum of 6000 transients acquired for each spectrum. For the inverse-gated decoupled ^{13}C NMR spectra of PP 2 and 10, a minimum of 6400 transients were obtained with pulse width = 90° and relaxation delay. Chemical shifts were referenced to solvent (74.12 ppm).

$[\eta^5:\eta^1\text{-}(Me_4C_5)SiMe_2N^tBu]TiCl_2$ (1). A mixture of $[(Me_4C_5)SiMe_2N^tBu]Mg_2Cl_2(THF)_2$ (2.00 g, 3.90 mmol) and $TiCl_3(THF)_3$ (1.46 g, 3.94 mmol) were treated at −78 °C with THF (60 mL) with shaking. The light blue suspension was warmed to room temperature, darkening quickly to a deep red solution. After the mixture was stirred for 10 min, $PbCl_2$ (0.548 g, 1.97 mmol) was added as a solid and lead precipitated immediately. THF was removed in vacuo after 8 h and the

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residue was extracted with pentane (2 × 30 mL). Concentrating to 30 mL and cooling to −78 °C for 2 h gave a yellow microcrystalline solid (**4**). Yield: 0.767 g (53.4%). ^{1}H NMR (C_6D_6): δ 2.00 (s, 6H, CH_3), 1.99 (s, 6H, CH_3), 1.42 (s, 9 H, NC(CH_3)$_3$), 0.43 (s, 6H, Si(CH_3)$_2$). ^{13}C NMR (C_6D_6): δ 140.8, 138.1, 121.6, 62.4, 32.9, 16.4, 13.3, 5.6. Anal. Calcd for $C_{15}H_{27}Cl_2NSiTi$: C, 48.92; H, 7.39; N, 3.80. Found: C, 49.34; H, 7.57; N, 3.78.

(*S*)-(Me$_4$C$_5$H)SiMe$_2$NHCHMePh. A solution of (*S*)-(−)-α-methylbenzylamine (1.50 g, 12.4 mmol) in THF (10 mL) was added over 2 min to a solution of (Me$_4$C$_5$H)SiMe$_2$Cl (0.88 g, 4.11 mmol) in THF (20 mL) at room temperature. A dense white precipitate formed immediately. After the mixture was stirred for 24 h, THF was removed in vacuo and the resulting residue was extracted with pentane (3 × 10 mL). Removal of pentane in vacuo at 60 °C afforded **5**, a pale yellow oil (1.18 g, 96%). ^{1}H NMR ($CDCl_3$): δ 7.4−7.2 (m, 5H, Ar−*H*), 4.05 (m, 1H, NC*H*(CH$_3$), 2.00 (s, 3H, C$_5$CH_3), 1.94 (s, 3H, C$_5$CH_3), 1.83 (s, 3H, C$_5$CH_3), 1.82 (s, 3H, C$_5$CH_3), 1.36 (s, 3H, NCH(CH_3)), 0.80 (d, 1H, N*H*), −0.05 (s, 3H, SiCH_3), −0.06 (s, 3H, SiCH_3). ^{13}C NMR ($CDCl_3$): δ 151.0, 149.2, 135.5, 128.1, 126.2, 125.9, 56.6, 51.5, 28.0, 14.6, 11.2, −1.6, −1.7. Anal. Calcd for $C_{15}H_{27}Cl_2NSiTi$: C, 76.18; H, 9.76; N, 4.68. Found: C, 75.83; H, 9.59; N, 6.04.

[(*S*)-(Me$_4$C$_5$)SiMe$_2$NCHMePh]Mg$_2$Cl$_2$(THF). Isopropylmagnesium chloride (4.0 mL, 2.0 M in Et_2O) was dried in vacuo to remove Et_2O. The Grignard reagent was treated with a solution of (*S*)-(Me$_4$C$_5$H)SiMe$_2$NHCHMePh (1.18 g, 3.93 mmol) in THF (4 mL) and toluene (17 mL). The solution was refluxed for 36 h, during which some solids formed. Solvents were removed in vacuo to give a brittle glass, which was then slurried with pentane (20 mL) for 30 min. After the mixture was filtered, the white solid was dried under vacuum. Yield: 1.70 g (88%). THF coordination was confirmed by ^{1}H NMR in THF-d_8.

[η^5:η^1-(Me$_4$C$_5$)SiMe$_2$-(*S*)-NCHMePh]TiCl$_2$ (2). A suspension of $TiCl_3(THF)_3$ (1.13 g, 3.04 mmol) in THF (20 mL) was treated at −78 °C with a solution of [(*S*)-(Me$_4$C$_5$)SiMe$_2$-NCHMePh]Mg$_2$Cl$_2$(THF) (1.50 g, 3.07 mmol) in THF (20 mL) with shaking. The blue-green suspension was warmed to room temperature, darkening quickly to a deep yellow-red color. After the mixture was stirred for 15 min, $PbCl_2$ (0.427 g, 1.54 mmol) was added as a solid. The solution lightened slightly to yellow-brown, and lead precipitated over the course of 15 min. THF was removed in vacuo, and the brownish-yellow residue was exhaustively extracted with warm hexane (150 mL total). The extract was concentrated to 15 mL to give a yellow microcrystalline solid. Yield: 0.195 g (15%). ^{1}H NMR ($CDCl_3$): δ 7.4−7.3 (m, 2H, Ar−*H*), 7.2−7.1 (m, 3H, Ar−*H*), 6.22 (q, 1H, *J* = 7 Hz, NC*H*), 2.14 (s, 3H, CH_3C$_5$), 2.13 (s, 3H, CH_3C$_5$), 2.07 (s, 3H, CH_3C$_5$), 1.99 (s, 3H, CH_3C$_5$), 1.67 (d, 3H, CH_3), 0.45 (s, 3H, SiCH_3), −0.18 (s, 3H, SiCH_3). ^{13}C NMR ($CDCl_3$): δ 144.5, 140.8, 140.6, 136.1, 128.4, 128.2, 127.9, 127.5, 126.9, 103.5, 62.0, 19.5, 15.8, 12.9, 12.8, 4.5, 2.0. Anal. Calcd for $C_{19}H_{27}Cl_2NSiTi$: C, 54.81; H, 6.54; N, 3.37. Found: C, 53.99; H, 6.57; N, 2.86. $[\alpha]_{589}$ = −190.5° (*c* = 1.3 mg/mL, CH_2Cl_2).

[η^5:η^1-(Ind)SiMe$_2$N^{t}Bu]TiCl$_2$ (3).[38] A mixture of [(Ind)SiMe$_2$N^{t}Bu]Li$_2$ (0.462 g, 1.80 mmol) and $TiCl_4(THF)_2$ (0.603 g, 1.81 mmol) were treated at −78 °C with precooled −78 °C toluene (25 mL). After slowly warming the mixture to room temperature, the red suspension was stirred 24 h and then filtered. Removal of toluene from the supernatant in vacuo gave a sticky dark red solid. The solid was recrystallized from a mixture of hexane (10 mL) and toluene (5 mL) by slowly cooling to −50 °C overnight, followed by cooling to −78 °C for 2 days. The supernatant was decanted off at −78 °C, and the resulting red microcrystalline solid (**4**) was washed with −78 °C hexane and then dried in vacuo. Yield: 0.087 g (13%). ^{1}H NMR ($CDCl_3$): δ 7.76 (m, 2H, Ar−*H*), 7.44 (m, 1H, Ar−*H*), 7.34 (d, 1H, Ind−*H*) 7.32−7.28 (m, 2H, Ar−*H*), 6.58 (d, 1H, Ind−*H*), 1.39 (s, 9H, NC(CH_3)$_3$), 0.95 (s, 3H, SiCH_3), 0.69 (s, 3H, SiCH_3). ^{13}C NMR ($CDCl_3$): δ 135.9, 134.7, 129.1, 128.4, 128.3, 127.4, 126.3, 119.3, 98.4, 63.3, 32.2, 3.3, 0.9. Anal. Calcd for $C_{15}H_{21}Cl_2NSiTi$: C, 49.73; H, 5.84; N, 3.87. Found: C, 48.84; H, 5.99; N, 3.51.

(Ind−*H*)SiMe$_2$-(*S*)-NHCHMePh. A solution of (Ind−*H*)SiMe$_2$Cl (3.43 g, 16.4 mmol) in THF (50 mL) was treated at room temperature with (*S*)-(−)-α-methylbenzylamine (5.0 mL, 39 mmol) over a period of 1 min. A dense white precipitate formed immediately, and after adding additional THF (50 mL), the slurry was stirred overnight. Removal of THF in vacuo gave a white paste, which was extracted with hexane (3 × 25 mL). Concentrating the extract in vacuo and distillation (bp 130−140 °C/0.005 mmHg) gave a colorless oil, which was a mixture of three regioisomers. Yield: 4.24 g (88%). ^{1}H NMR ($CDCl_3$): δ 7.10−7.58 (m, 9H, Ar−*H*), 6.93 (d, 1H, Ind−*H*), 6.55−6.65 (m, 2H, Ind−*H*), 3.86, 3.94, 4.08 (m, 1H, NC*H*), 3.18, 3.49 (s, 1H, Ind−*H*), 1.20, 1.21, 1.29 (d, 3H, CH_3), 0.95, 0.68 (m, 1H, N*H*), 0.32, −0.09, −0.14 (d, 6H, Si(CH_3)). ^{13}C NMR ($CDCl_3$): δ 148.7, 145.5, 144.9, 144.3, 135.8, 128.9, 128.2, 128.1, 126.4, 126.3, 126.2, 126.0, 125.9, 125.7, 124.6, 124.2, 123.6, 123.5, 122.8, 122.3, 120.9, 51.7, 51.6, 48.3, 40.7, 27.9, −0.5, −2.5, −2.6, −2.9. Anal. Calcd for $C_{19}H_{23}NSi$: C, 77.76; H, 7.90; N, 4.77. Found: C, 78.02; H, 7.83; N, 5.77.

[(Ind)SiMe$_2$-(*S*)-NCHMePh]Li$_2$. A solution of (*S*)-(Ind−*H*)SiMe$_2$NHCHMePh (4.24 g, 14.4 mmol) in Et_2O (60 mL) was slowly treated with butyllithium (20 mL, 1.6 M in hexane) with stirring at room temperature. After the yellow-orange solution was stirred overnight, solvents were removed in vacuo to give a brittle glassy solid. Slurrying with hexane (50 mL) for 30 min and filtering gave an off-white solid, which was dried in vacuo. Yield: 4.08 g (93%).

(+)-(*R*)-[η^5:η^1-(Ind)SiMe$_2$-(*S*)-NCHMePh]TiCl$_2$ (4). A. Metathesis Route. A mixture of [(Ind)SiMe$_2$-(*S*)-NCHMePh]-Li$_2$ (0.935 g, 3.06 mmol) and $TiCl_4(THF)_2$ (1.022 g, 3.06 mmol) was treated at −78 °C with toluene (8 mL) precooled to −78 °C. The red suspension was slowly warmed to room temperature, stirred overnight, and filtered through Celite. Removing toluene in vacuo from the filtrate gave a red oil, which was subsequently treated with Et_2O (8 mL) at −20 °C. After the mixture was stirred at −20 °C for 10 min, a red-brown solid was isolated by decanting off the red supernatant and then drying in vacuo. This solid was recrystallized by treating with Et_2O (5 mL) and CH_2Cl_2 (5 mL), heating to dissolve the solid, and then slowly cooling to −40 °C overnight. This was further cooled to −78 °C for 2 h, and deep red block crystals (**4**) were isolated by decanting off the supernatant and drying in vacuo. Yield: 0.065 g (5.2%).

B. Amine Elimination/Me$_3$SiCl Chlorination. A solution of Ti(NMe$_2$)$_4$ (3.79 g, 16.9 mmol) in toluene (100 mL) was treated with a toluene solution (50 mL) of (*S*)-(Ind−*H*)SiMe$_2$-NHCHMePh (5.00g, 17.0 mmol) at −78 °C. The mixture was slowly warmed to room temperature and then brought to reflux with argon flow through an oil bubbler. The reaction was monitored by ^{1}H NMR and was completely converted after 3 days. Toluene was removed in vacuo to give a yellow-brown residue. ^{1}H NMR analysis revealed the presence of two diastereomers (**A, B**) in approximately 1.33/1 ratio. ^{1}H NMR (C_6D_6): δ 7.83 (d, 1H, Ar−*H*, **A**), 7.74 (d, 1H, Ar−*H*, **B**), 7.43 (d, 2H, Ar−*H*, **A**), 7.31 (d, 2H, Ar−*H*, **B**), 7.22−6.82 (m, 2H, Ar−*H*), 6.73 (d, 1H, Ind−*H*, **B**), 6.71 (d, 1H, Ind−*H*, **A**), 6.39 (d, 1H, Ind−*H*, **A**), 6.34 (d, 1H, Ind−*H*, **B**), 5.20 (q, 1H, NC*H*, **A**), 5.08 (q, 1H, NC*H*, **B**), 3.17 (s, 6H, N(CH_3)$_2$, **B**), 2.87 (s, 6H, N(CH_3)$_2$, **A**), 2.39 (s, 6H, N(CH_3)$_2$, **A**), 2.37 (s, 6H, N(CH_3)$_2$, **B**), 1.45 (d, 3H, CH_3, **A**), 1.41 (d, 3H, CH_3, **B**), 0.71 (s, 3H, SiCH_3, **A**), 0.45 (s, 3H, SiCH_3, **B**), 0.42 (s, 3H, SiCH_3, **A**), 0.30 (s, 3H, SiCH_3, **B**).

The yellow-brown residue was dissolved in CH_2Cl_2 (150 mL) and then treated with excess trimethylsilyl chloride (6.43 mL, 50.7 mmol) at room temperature. The color changed to dark red, and this was stirred overnight. All volatiles were then

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removed in vacuo to give a copious dark red powder, which was washed with Et_2O (75 mL, then 3 × 30 mL) and dried in vacuo. This powder was then stirred in CH_2Cl_2 (50 mL) for 30 min, and Et_2O (75 mL) was added. After the mixture was cooled at −20 °C overnight, deep red crystals (**4**) were isolated by decanting off the supernatant and drying in vacuo. Yield: 2.73 g (39.3% based on $Ti(NMe_2)_4$, 68.9% based on intermediate diastereomer **A**). ^{1}H NMR (C_6D_6): δ 7.53 (d, 1H, Ind−*H*), 7.4−6.7 (m, 9H, Ar−*H*), 6.31 (q, 1H, NC*H*), 6.18 (d, 1H, Ind−*H*), 1.41 (d, 3H, CH_3), 0.42 (s, 3H, SiCH_3), −0.36 (s, 3H, SiCH_3). ^{13}C NMR (C_6D_6): δ 144.3, 135.4, 134.7, 128.9, 128.8, 128.4, 127.3, 127.1, 126.6, 116.9, 98 (low intensity, tentative assignment), 64.0, 19.0, 2.4, −2.2. Anal. Calcd for $C_{19}H_{21}Cl_2NSiTi$: C, 55.62; H, 5.16; N, 3.41. Found: C, 55.11; H, 5.18; N, 3.29. $[\alpha]_{589} = +402°$ (c = 0.95 mg/mL, CH_2Cl_2).

[η^5:η^1-(Ind)SiMe$_2$N(C$_6$H$_{11}$)]TiCl$_2$ (5). Amine Elimination/Me$_3$SiCl Chlorination. A solution of $Ti(NMe_2)_4$ (0.41 g, 1.84 mmol) in toluene (15 mL) was treated with (Ind−*H*)-$SiMe_2NH(C_6H_{11})$ (0.50 g, 1.84 mmol) at −78 °C. The mixture was slowly warmed to room temperature and then brought to reflux. The reaction was monitored by ^{1}H NMR and was completely converted after 5 days. Toluene was removed in vacuo to give a red residue. ^{1}H NMR (C_6D_6): δ 7.82 (d, 1H, Ar−*H*), 7.43 (d, 1H, Ar−*H*), 6.98−6.85 (m, 2H, Ar−*H*), 6.71 (d, 1H, Ind−*H*), 6.33 (d, 1H, Ind−*H*), 3.80 (m, 1H, NC*H*), 3.17 (s, 6H, N(CH_3)$_2$), 2.41 (s, 6H, N(CH_3)$_2$), 1.85−1.00 (m, 11H, C_6H_{11}), 0.77 (s, 3H, SiCH_3), 0.52 (s, 3H, SiCH_3).

The red residue was dissolved in CH_2Cl_2 (10 mL) and then treated with excess trimethylsilyl chloride (0.51 mL, 4.0 mmol) at room temperature. After the mixture was stirred overnight, all volatiles were removed in vacuo to give an orange red powder, which was washed with pentane (30 mL) and dried in vacuo. Yield: 0.319 g (45% based on $Ti(NMe_2)_4$). ^{1}H NMR (C_6D_6): δ 7.53 (d, 1H, Ar−*H*), 7.27 (d, 1H, Ar−*H*), 7.01 (t, 1H, Ar−*H*), 6.93 (t, 1H, Ar−*H*), 6.82 (d, 1H, Ind−*H*), 6.35 (d, 1H, Ind−*H*), 4.97 (m, 1H, NC*H*), 2.00 (m, 1H, C_6H_{11}), 1.55 (m, 2H, C_6H_{11}), 1.36 (m, 2H, C_6H_{11}), 1.16 (m, 2H, C_6H_{11}), 0.90 (m, 2H, C_6H_{11}), 0.69 (m, 2H, C_6H_{11}), 0.47 (s, 3H, SiCH_3), 0.29 (s, 3H, SiCH_3). ^{13}C NMR ($CDCl_3$): δ 135.0, 134.1, 128.7, 128.6, 128.2, 127.1, 126.2, 116.7, 99 (low intensity, tentative assignment), 65.7, 34.3, 26.1, 25.6, 2.6, 0.4. Anal. Calcd for $C_{17}H_{23}Cl_2NSiTi$: C, 52.59; H, 5.97; N, 3.61. Found: C, 52.14; H, 5.84; N, 3.60.

[η^5:η^1-FluSiMe$_2$N^{t}Bu]ZrCl$_2$ (6). A suspension of [FluSiMe$_2$N^{t}Bu]Li_2 (1.00 g, 3.25 mmol) in toluene (100 mL) was treated with a slurry of $ZrCl_4$ (0.758 g, 3.25 mmol) in toluene (50 mL) at room temperature. The resulting bright yellow suspension darkened on stirring. After the mixture was stirred overnight, the suspension was filtered and the solids were washed with hot toluene (4 × 20 mL). The combined orange filtrates were concentrated in vacuo to 20 mL, and then hexane (75 mL) was added. Cooling to −20 °C overnight and then to −78 °C for 1 day yielded a crop of yellow microcrystalline solid. Yield: 0.275 g (18.6%). ^{1}H NMR (toluene-d_8): δ 7.82−7.69 (m, 4H, Ar−*H*), 7.18−7.10 (m, 2H, Ar−*H*), 7.00 (d, 2H, Ar−*H*), 1.27 (s, 9H, NC(CH_3)$_3$), 0.68 (s, 6H, Si(CH_3)$_2$). ^{13}C NMR: the poor solubility in deuterated hydrocarbons and decomposition in $CDCl_3$ led to characterization as the mono-THF adduct.[16] Anal. Calcd for $C_{19}H_{23}Cl_2NSiZr$: C, 50.09; H, 5.09; N, 3.07. Found: C, 50.09; H, 5.04; N, 2.83.

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Supporting Information Available: Text giving the experimental details associated with data collection and refinement and tables of crystal data, positional parameters, anisotropic thermal factors, bond distances, bond angles, and torsional angles for **4** and methyl pentad distributions for entries 1−14 (12 pages). Ordering information is given on any current masthead page.

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