Phenylene-Bridged Cp/Carboxamide Ligands for Titanium Complexes of Various Binding Modes and Their Ethylene/1-Octene Copolymerization

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o-Phenylene-bridged or substituted *o*-phenylene-bridged di- or trimethylcyclopentadienyl/carboxamide ligands 2-($RMe_2C_5H_2$)-4,6-$R'_2C_6H_2NHC(O)^tBu$ (R = Me or H; R′ = Me, H, or F) are prepared. When R′ is methyl or H, unbridged trichlorotitanium complexes containing a chloroimine unit as a pendant group, 2-[(η^5-RMe_2C_5H)$TiCl_3$]-4,6-$R'_2C_6H_2N{=}C(Cl)^tBu$ (**7**, R = H, R′ = H; **8**, R = Me, R′ = H; **9**, R = H, R′ = Me; **10**, R = Me, R′ = Me), are unexpectedly afforded through the successive addition of $Ti(NMe_2)_4$ and $SiCl_4$ to the ligands. The same treatment to the ligands where R′ = F affords oxygen-coordinated bridged complexes [2-(η^5-RMe_2C_5H)-4,6-$F_2C_6H_2N{=}C(O)^tBu$-κO]$TiCl_2$ (**11**, R = H; **12**, R = Me). The desired nitrogen-coordinated bridged complexes [2-(η^5-RMe_2C_5H)$C_6H_4NC(O)^tBu$-κ^2N,O]-$TiMe_2$ (**13**, R = H; **14**, R = Me) are obtained by reacting the corresponding dilithium compound with Me_2TiCl_2. The binding modes of **7**, **8**, **9**, **11**, and **14** are confirmed by X-ray crystallography. Trichlorotitanium complex **8** shows high activity in ethylene/1-octene copolymerization (activity, 100×10^6 g/molTi·h at 13 bar ethylene). Trimethylcyclopentadienyl complexes show higher activity than the dimethylcyclopentadienyl analogues, and the activities of **12** and **14** reach $\sim 65 \times 10^6$g/molTi·h. Complex **12** is excellent in incorporating 1-octene.

Introduction

The CGC (constrained-geometry catalyst) [$Me_2Si(\eta^5$-$Me_4C_5)(N^t$-Bu)]$TiCl_2$[1] is a typical representative among homogeneous Ziegler−Natta catalysts.[2,3] Its activated complex is thermally stable and provides a high molecular weight polymer with high content of α-olefin in ethylene/α-olefin copolymerizations, which enable its use in commercial processes. Various modifications have been successfully carried out either by the replacement of the Me_4C_5 unit with other π-donor ligands[4] or by the replacement of the N^tBu unit with other amides or phosphides,[5] but the modification of the bridge has not been so abundant and successful.[6] Recently, we disclosed a novel preparation route for the *o*-phenylene-bridged (dimethyl or trimethylcyclopentadienyl)/(amide or sulfonamide) ligand system.[7] The Suzuki coupling reaction of 2-bromoaniline compounds with 2-dihydroxyboryl-3,4-dimethyl-2-cyclopenten-1-one or 2-dihydroxyboryl-3-methyl-2-cyclopenten-1-one, which can be easily prepared on a 30 g scale in a laboratory, is a key step in the route (eq 1). The replacement of the silylene bridge with the *o*-phenylene group leads to a structural change in terms of a narrower Cp(cent)−Ti−N angle, which is indicative of a more "constrained feature" in the *o*-phenylene-bridged complexes. While the silicon atom in the CGC is severely deviated from the cyclopentadienyl plane,[8] the elements constituting the chelation in the *o*-phenylene-bridged complexes are not situated in a severely strained position. Some complexes are superior

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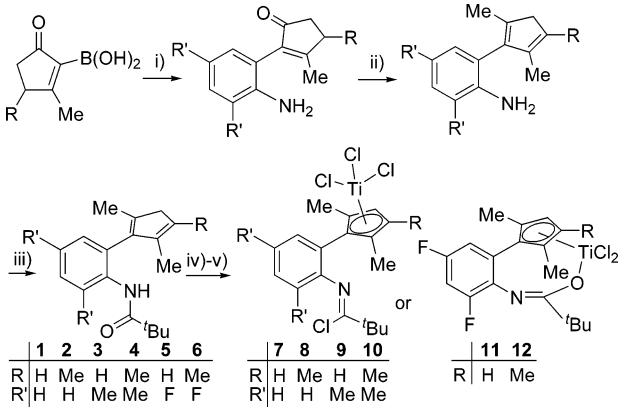
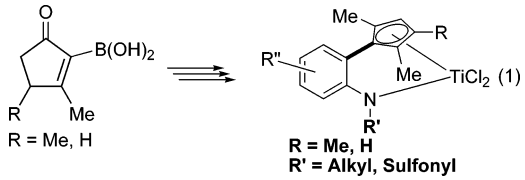
Scheme 1 [a]



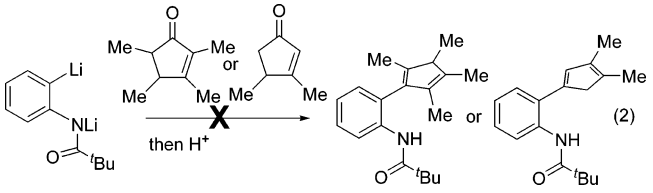
[a] Legend: (i) 2-$BrC_6H_2(R')_2NH_2$, Na_2CO_3, $Pd(PPh_3)_4$ (1 mol %); (ii) MeLi/$CeCl_3$, then HCl (2 N); (iii) pivaloyl chloride, Et_3N; (iv) $Ti(NMe_2)_4$; (v) $SiCl_4$.

to the CGC in ethylene/α-olefin copolymerization in terms of activity, α-olefin incorporation, and molecular weight of the obtained polymer. Herein, we report titanium complexes derived from *o*-phenylene-bridged di- or trimethylcyclopentadienyl/carboxamide ligands. By variation of the substituents on the ligand system or by changing the metalation method, titanium complexes of various coordination modes are provided and some interesting polymerization results are observed with the complexes in ethylene/1-octene copolymerization.

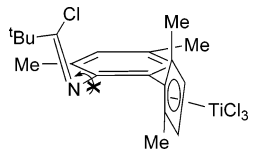


Results and Discussion

Synthesis and Characterization. Various aniline derivatives containing the $Me_2H_3C_5$ or $Me_3H_2C_5$ unit at the 2-position are prepared by the Suzuki coupling reaction of 2-bromoanilines with 2-dihydroxyboryl-3,4-dimethyl-2-cyclopenten-1-one or 2-dihydroxyboryl-3-methyl-2-cyclopenten-1-one.[7b] The addition of pivaloyl chloride (^{t}BuC(O)Cl) to the aniline derivatives in the presence of Et_3N affords **1**−**6** in 70−93% yields (Scheme 1). Usually, a mixture of isomers is obtained for substituted cyclopentadiene compounds by the facile 1,5-sigmatropic rearrangement,[9] but compounds **1**−**6** exist as a single isomer at room temperature, showing only one set of signals in the ^{1}H and ^{13}C NMR spectra. The isomer where two hydrogens are attached on the sp^3-carbon is thermodynamically more stable and is predominant at room temperature. The preparation of the *ortho*-lithiated compound of pivaloyl-protected aniline has already been reported,[10] but its reaction with 2,3,4,5-tetramethyl-2-cyclopenten-1-one or sterically less hindered 3,4-dimethyl-2-cyclopenten-1-one[11] does not provide the desired compound (eq 2). Probably, the strong basicity of the lithium carboxamide triggers the deprotonation of cyclopentenone, which blocks the desired nucleophilic attack of the carbanion on the carbonyl. Therefore, a synthetic route based on the Suzuki coupling reaction is unique for the preparation of this kind of ligand system.



Reaction of **1**−**6** with an equimolar amount of $Ti(NMe_2)_4$ at 80 °C for 1 day affords a bis(dimethylamido)titanium complex. A single Me_2N signal is observed as a singlet at 2.9 ppm in the ^{1}H NMR spectra of the symmetrically substituted $Me_2C_5H_2$ complexes, but two Me_2N signals are observed at 2.8 and 3.1 ppm for the Me_3C_5H complexes. When Me_2SiCl_2 is employed as a chlorinating agent, replacement of only one Me_2N ligand occurs.[12] The treatment of more powerful $SiCl_4$ in excess to the bis(dimethylamido)titanium complexes clearly provides one complex. The ^{1}H NMR spectra indicate that both Me_2N ligands are replaced with the chloride, but X-ray crystallographic studies reveal unexpected structures. For phenylene- and dimethylphenylene-bridged ligands, unbridged trichlorotitanium complexes are afforded (Scheme 1 and Figures 1−3).[13] The carboxamide unit is transformed to a chloroimine unit that is not coordinated with the titanium. A single Cp-H signal is observed at 6.03 in the ^{1}H NMR spectrum (C_6D_6) of the dimethylcyclopentadienyl complex **7**, but two abnormal Cp-H signals are observed at 5.90 and 6.18 ppm as doublets (J = 2.8 Hz) in 1:1 ratio for **9**. The only difference between **7** and **9** is the presence of methyl substituents on the phenylene bridge. This unexpected observation of the two Cp-H signals for **9** can be explained by the high rotation barrier around the N−C(phenylene) bond. The methyl group on the *ortho*-position of the phenylene bridge might block the rotation as shown below.[14] If the rotation is not allowed, the two Cp-H protons are considered diastereotoptic to each other, and two signals should be observed. For trimethyl complex **10**, the prohibited rotation gives rise to two isomers and actually two sets of signals are observed in 0.57:0.43 ratio in the ^{1}H NMR spectrum. The C═N carbon signals are observed at 156 ppm in the ^{13}C NMR spectra of **7**−**10**. In the case of ligands **1**−**6**, the carbonyl-carbon signals are observed at ∼176 ppm.



X-ray crystallographic studies reveal that an oxygen-coordinated dichlorotitanium complex is afforded when the same treatment is applied for the difluorophenylene-bridged ligand **5** (Scheme 1 and Figure 4). The ^{1}H and ^{13}C NMR spectra are in agreement with the structure. The N═*C*(^{t}Bu)-O carbon signal is observed at 168.3 ppm in the ^{13}C NMR spectrum of **11**. The analysis of the ^{1}H and ^{13}C NMR spectra of **12** suggests that a similar oxygen-coordinated complex is also afforded for the trimethylcyclopentadienyl ligand **6**. Especially, observation of a ^{13}C NMR signal at 168.7 strongly supports the −N═*C*(^{t}Bu)−O−Ti structure.

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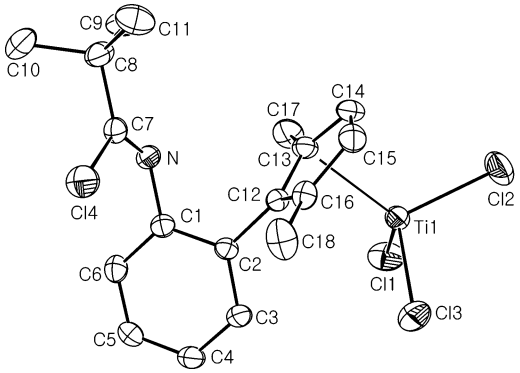
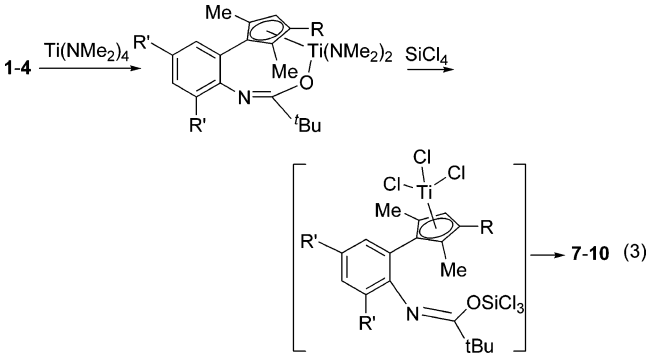
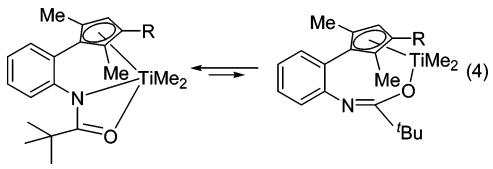


Figure 1. Thermal ellipsoid plot (30% probability level) of **7**. Selected bond distances (Å) and angles (deg): N−C(7), 1.240(4); C(7)−Cl(4), 1.785(3); Ti−Cp(c), 2.025; Ti(1)−Cl(1), 2.2352(11); Ti(1)−Cl(2), 2.2170(12); Ti(1)−Cl(3), 2.2276(11); N−C(7)−C(14), 120.6(3); N−C(7)−C(8), 124.7(3); C(8)−C(7)−Cl(4), 114.6(2); C(8)−C(7)−N−C(1), 0.8; Cl(4)−C(7)−N−C(1), 1.2; C(7)−N−C(1)−C(2), 100.3; C(13)−C(12)−C(2)−C(1), 67.9.

In the ^{13}C NMR spectra of all the intermediate $(NMe_2)_2Ti$ complexes, the most downfield shifted signals are observed at 168−171 ppm. Because the chemical shifts are very close to those observed for the oxygen-coordinated complexes **11** and **13** (168−171 ppm versus 168 ppm), it may be suggested that the structure of the intermediate $(NMe_2)_2Ti$ complexes is oxygen coordinated, as shown in eq 3. For carboxamide compounds **1**−**6**, the corresponding signals are observed at ∼176 ppm. The titanium atom is so oxophilic that the formation of the oxygen-coordinated complex may be more favorable than the formation of the nitrogen-coordinated one. A plausible pathway for the transformation of the $(NMe_2)_2Ti$ complexes to the chloroimine Cl_3Ti complexes **7**−**10** is proposed in eq 3. For $(NMe_2)_2Ti$ complexes derived from **1**−**4**, the oxygen ligand along with the two Me_2N ligands is replaced with chloride by the treatment of $SiCl_4$, affording the −N═C(^{t}Bu)OSiCl$_3$ unit as a pendant group, which is eventually transformed to −N═C(^{t}Bu)Cl.



The addition of the dilithium salt of **1** and **2** to in situ generated Me_2TiCl_2 in diethyl ether affords the desired chelated dimethyltitanium complexes **13** and **14** in 72% and 68% yields, respectively (Scheme 2).[15] The structure of **13** is confirmed by X-ray crystallography. In the ^{1}H NMR spectrum of **13** (C_6D_6), two sets of signals are observed in a 0.87:0.13 ratio. A signal set of the major isomer is composed of singlet signals at 6.46 (Cp-H), 1.62 (Cp-Me), 1.36 (^{t}Bu), and 1.09 (Ti-Me) in 2:6:9:6 integration ratios, which is in agreement with the structure drawn in Scheme 2. Meanwhile, the signal set of the minor isomer is also composed of singlet signals at 6.25 (Cp-H), 1.80 (Cp-Me), 1.46 (^{t}Bu), and 0.88 (Ti-Me) with the same integration ratio as observed for the major isomer. In the ^{1}H NMR spectrum of **14** (C_6D_6), two sets of signals are also observed in a 0.78:0.22 ratio. The purification of the complexes by multiple recrystallization does not eliminate the minor isomer, and even the ratio of the two isomers is not altered by the recrystallization, which implies that the two isomers are in equilibrium in solution. When the temperature is raised to 90 °C, the two signal sets are collapsed to a set of broad signals, strongly supporting the interconversion between the two isomers. In the ^{13}C NMR spectrum, the ^{t}Bu*C*(O)N-carbon signal is observed at 187−188 ppm for the major isomer, while the corresponding signal is observed dramatically upfield shifted at 165−166 ppm for the minor isomer. Since the chemical shift observed for the minor isomer is close to those observed for the oxygen-coordinated complexes **11** and **12** (165−166 ppm versus 168 ppm), we assume that the minor isomer is the oxygen-coordinated one, as drawn in eq 4.



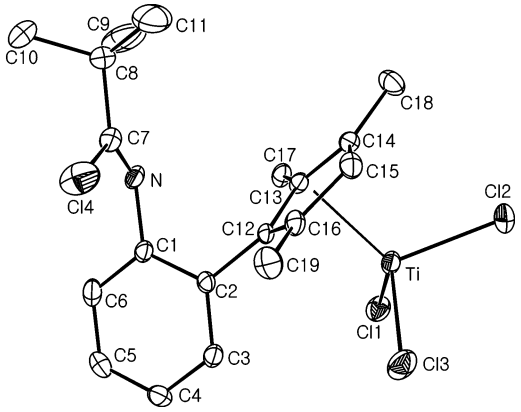


Figure 2. Thermal ellipsoid plot (30% probability level) of **8**. Selected bond distances (Å) and angles (deg): N−C(7), 1.234(7); C(7)−Cl(4), 1.770(6); Ti−Cp(c), 2.031; Ti−Cl(1), 2.2270(18); Ti−Cl(2), 2.2359(17); Ti−Cl(3), 2.2428(18); N−C(7)−C(14), 121.9-(5); N−C(7)−C(8), 124.0(6); C(8)−C(7)−Cl(4), 114.1(4); C(8)−C(7)−N−C(1), 1.9; Cl(4)−C(7)−N−C(1), 0.6; C(7)−N−C(1)−C(2), 86.6; C(13)−C(12)−C(2)−C(1), 61.9.

X-ray Crystallographic Studies. Figure 1 shows the structure of **7** with the selective bond distances and angles revealed by X-ray crystallography. The N−C(7) distance (1.240(4) Å) is indicative of a double bond and the measured C(7)−Cl(4) distance (1.785(3) Å) is in agreement with the tabulated carbon−chlorine bond distance.[16] The carbon (C(7)) attached to Cl and N is perfectly trigonal (the sum of the bond angles around the carbon, 360.0°). The double-bond character between the C(7) and N atoms is further supported by the dihedral angles of C(8)−C(7)−N−C(1) (0.8°) and Cl(4)−C(7)−N−C(1) (1.2°). These metrical parameters clearly indicate the chloroimine structure depicted in Scheme 1. The C(7), N, C(8), Cl(4), and C(1) atoms are situated in a plane, and the plane is almost perpendicular to the phenylene plane (the angle between the planes, 81.02(11)°). The cyclopentadienyl plane is skewed to the phenylene plane

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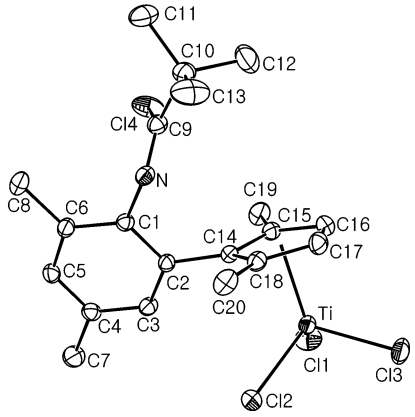


Figure 3. Thermal ellipsoid plot (30% probability level) of **9**. Selected bond distances (Å) and angles (deg): N−C(9), 1.241(3); Cl(4)−C(9), 1.790(2); Ti−Cp(c), 2.025; Ti(1)−Cl(1), 2.2329(7); Ti(1)−Cl(2), 2.2306(7); Ti(1)−Cl(3), 2.2338(7); N−C(9)−C(10), 124.9(2); C(10)−C(9)−Cl(4), 113.86(17); N−C(9)−Cl(4) 121.24(17); C(10)−C(9)−N−C(1), 4.8; Cl(4)−C(9)−N−C(1), 2.4; C(9)−N−C(1)−C(2), 98.6; C(15)−C(14)−C(2)−C(1), 103.4.

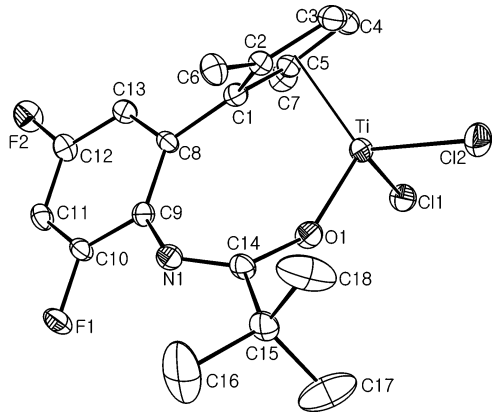
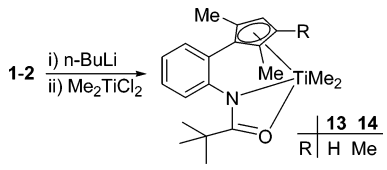


Figure 4. Thermal ellipsoid plot (30% probability level) of **11**. Selected bond distances (Å) and angles (deg): N(1)−C(14), 1.260(6); O(1)−C(14), 1.343(5); Ti−O(1), 1.802(3); Ti−Cl(1), 2.2434(15); Ti−Cl(2), 2.257(2); Ti−Cp(c), 2.016; Cl(1)−Ti−Cl(2), 103.98(7); Cp(c)−Ti−O(1), 112.66; O(1)−Ti−Cl(1), 102.89(11); O(1)−Ti−Cl(2), 102.03(11); C(14)−O(1)−Ti, 149.5(3); C(14)−N(1)−C(9), 128.9(4); N(1)−C(14)−O(1), 125.8(4); N(1)−C(14)−C(15), 120.6(4); O(1)−C(14)−C(15), 113.5(4); C(8)−C(9)−N(1), 129.7(4); C(9)−C(8)−C(1), 126.7(4); C(2)−C(1)−C(8)−C(9), 53.1.

Scheme 2



with an angle of 69.62(11)°. Figures 2 and 3 show the structure of **8** and **9**, respectively. The metrical parameters around the nitrogen atom are the same as those observed for **7**, confirming the chloroimine structure.

Figure 4 shows the structure of **11** with selected bond distances and angles. The N−C(O) distance (1.260(6) Å) is indicative of a double bond, while the NC−O distance (1.343(5) Å) is indicative of a shortened single bond. The Cp(cent)−Ti−O angle (112.66°) is bigger than those observed for Me_4Cp-phenoxy titanium complexes [2-(η^5-Me_4C_5)C_6H_4O-κ,O]$TiCl_2$ (∼107°)[17] and the Cp(cent)−Ti−N angle observed for the standard CGC (107.4°).[8] The C(1)−C(8)−C(9) angle (126.7(4)°) and the C(8)−C(9)−N(1) angle (129.7(4)°) are slightly increased from the ideal value of 120°. The wide Ti−O−C angle (149.53°) and relatively short Ti−O distance (1.802(3) Å) are indicative of some π-donation from the oxygen ligand to the titanium. The cyclopentadienyl plane and the phenylene plane are not situated perpendicularly but are tilted at 51.97(15)°.

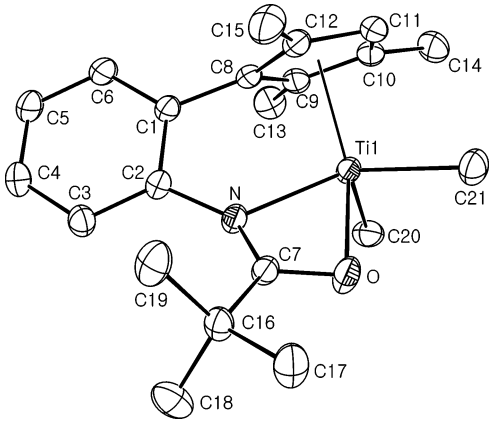


Figure 5. Thermal ellipsoid plot (30% probability level) of **14**. Selected bond distances (Å) and angles (deg): Ti−N, 2.1072(13); Ti−O, 2.1446(12); Ti−C(20), 2.0952(17); Ti−C(21), 2.1523(18); Ti−Cp(c), 2.056; N−C(7), 1.3262(19); O−C(7), 1.2822(18); Cp(c)−Ti−O, 151.00; C(20)−Ti−N, 100.86(6); N−Ti−C(21), 136.10(6); N−Ti−O, 60.78(5); C(20)−Ti−C(21), 99.45(8); O−C(7)−N, 111.11(13); O−C(7)−C(16), 118.80(13); N−C(7)−C(16), 130.05(14); C(2)−C(1)−C(8), 116.39(12); C(1)−C(2)−N, 111.90(13); C(7)−N−C(2), 136.91(13); C(7)−N−Ti, 93.27(9); C(2)−N−Ti, 126.61(10); C(7)−O−Ti, 92.85(9); Cp(c)−C(8)−C(1), 6.02; C(8)−Cp(c)−Ti, 87.92; C(9)−C(8)−C(1)−C(2), 99.1.

Figure 5 shows the structure of **14**. Even though the Ti−N and Ti−O distances (2.1072(13) and 2.1446(12) Å, respectively) are relatively long, when compared with the Ti−N distance observed for the standard CGC (1.907(4) Å)[8] and the Ti−O distances observed for **11** (1.802(3) Å) and the Me_4Cp-phenoxy complex (1.832(3) Å),[17] the measured Ti−N and Ti−O distances clearly indicate a chemical bonding between the Ti and N atoms and between the Ti and O atoms, respectively. Coordination geometry around the titanium center may be classified into a distorted trigonal bipyramidal with the oxygen and the cyclopentadienyl ligands situated at the axial positions. The C−O distance (1.2822(18) Å) is indicative of a double bond, while ^{t}BuC−N distance (1.3262(19) Å) is indicative of a shortened single bond. The Cp(cent)−Ti−N angle (101.36°) is close to that observed for the *o*-phenylene-bridged Cp/sulfon amido complex [2-(η^5-Me_3C_5H)$C_6H_4NSO_2C_6H_4CH_3$)]$TiCl_2$ (100.91°),[7b] but it is substantially smaller than those observed for the standard CGC (107.6°) and the *o*-phenylene-bridged Cp/amido complex [2-(η^5-Me_3C_5H)$C_6H_3NC_6H_{11}$]$TiCl_2$ (104.8°).[7a] The Cp(cent)−Ti−O angle is 151.00°. The Ti−Cp(cent)−C(bridgehead) angle (87.92°) and the Cp(cent)−C(bridgehead)−C(phenylene) angle (6.02°) are slightly deviated from the ideal values of 90° and 0°, respectively. The C(8)−C(1)−C(2) and C(1)−C(2)−N angles are also slightly contracted to 116.39(12)° and 111.90(13)° from the ideal 120°. The nitrogen atom is not perfectly trigonal (sum of the bond angles around nitrogen, 356.79°), but the sum of the angles is closer to the trigonal value (360°) rather than to the tetrahedral value (329.1°). The

(17) (a) Zhang, Y.; Mu, Y.; Lu, C.; Li, G.; Xu, J.; Zhang, Y.; Zhu, D.; Feng, S. *Organometallics* **2004**, *23*, 540. (b) Zhang, Y.; Wang, J.; Mu, Y.; Shi, Z.; Lu, C.; Zhang, Y.; Qiao, L.; Feng, S. *Organometallics* **2003**, *22*, 3877. (c) Chen, Y.-X.; Fu, P.-F.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 5958.

Table 1. Ethylene/1-Octene Copolymerization Results[a]

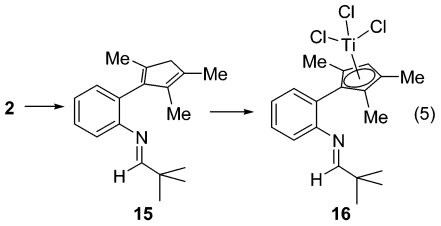
entry	catalyst	yield (g)	A[b]	T_m (°C)	density	[Oct][c]	MI[d]	M_w	M_w/M_n
1	**7**	64	76	62	0.863	22	1.6	114 000	2.8
2	**8**	85	100	60	0.860	23	6.3	73 000	2.9
3	**9**	8.2	9.9	111.8			0	124 000	4.6
4	**10**	10	12	111.0			0	155 000	5.3
5	**11**	17	20	62	0.861	23	0.26	186 000	4.0
6	**12**	54	63	broad	0.858	31	4.9	123 000	6.9
7	**13**	35	42	74	0.877	20	0.13	209 000	6.9
8	**14**	56	67	63	0.872	20	0.64	154 000	4.6
9	**16**	23	28	77	0.873		0.13	216 000	6.6
10	**19**	trace							
11	**CGC**	130	160	89	0.871	19	20	56 000	2.8

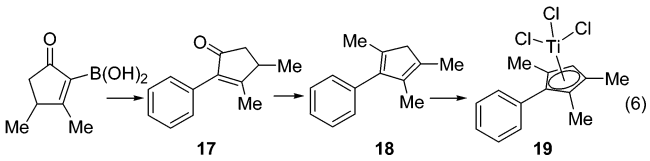
[a] Polymerization conditions: 1000 mL of a toluene solution of 1-octene (0.8 M), 5 μmol of complex, 15 μmol of $(Ph_3C)[B(C_6F_5)_4]$, 0.125 mmol of $^iBu_3Al$, 13 bar of ethylene, 10 min, temperature 90 °C. [b] Activity in units of 10^6 g/molTi·h. [c] 1-Octene content in the copolymer measured by the ^1H NMR. [d] Melt index, which is the melt flow rate (g/10 min) at 190 °C and using a load of 2160 g.

cyclopentadienyl plane and the phenylene plane are slightly tilted (the angle between the planes, 76.10(5)°).

Polymerization Studies. The newly prepared complexes are tested for ethylene/1-octene copolymerization after activation with $(Ph_3C)[B(C_6F_5)_4]$ and $^iBu_3Al$. The triisobutylaluminum is added both as a scavenger and as an alkylating agent. The polymerization conditions and the results are summarized in Table 1. Interestingly, the unbridged complexes **7** and **8** exhibit fairly good activity, and the activity of the Me_3C_5H complex **8** reaches 100×10^6 g/molTi·h. Under the same conditions, the standard CGC shows activity of 160×10^6 g/molTi·h. By replacing one methyl group on the cyclopentadienyl ligand with hydrogen, the activity is reduced to 76×10^6 g/molTi·h. The melting temperature of the polymer (T_m) and the density of the resin are mainly dependent on the 1-octene content in the copolymer. The lower the melting temperature or the lower the density, the higher the 1-octene content. A comparison of the densities (0.863, 0.860, 0.871 g/cm^3 for **7**, **8**, and the CGC, respectively) and the melting temperatures (62.2, 60.3, and 89.4 °C for **7**, **8**, and the CGC, respectively) of the polymers indicates that **7** and **8** are slightly superior to the CGC in incorporating 1-octene (entries 1, 2, and 11), which is also confirmed by the analysis of the ^1H NMR spectra of the polymers.[8b] The molecular weights of the polymers obtained by **7** and **8** (M_w, 114 000 and 73 000, respectively) are higher than that of the polymer obtained with the CGC (M_w, 56 000). The melt flow rate is mainly dependent on the molecular weight, and the molecular weight data obtained on the GPC are in agreement with the data of the melt flow rate (MI) of the resins (1.6, 6.3, and 20 g/10 min for **7**, **8**, and the CGC, respectively). Rather narrow molecular weight distributions (M_w/M_n, 2.8−2.9) are observed, indicating a single active species in the polymerization reaction.

Placing methyl groups on the phenylene bridge dramatically reduces the activity. The activity of **9** and **10** is almost 1/10 of those observed for **7** and **8** (entries 1/2 versus entries 3/4). Furthermore, the melting temperatures of the polymers (111.8 and 111.0 °C) indicate that complexes **9** and **10** are significantly inferior to **7**, **8**, and the CGC in incorporating 1-octene. We suspect that the fairly high activity and the excellent 1-octene incorporation ability of **7** and **8** might be attributed to the formation of nitrogen-coordinated active species during the activation process. For less active **9** and **10**, the rotation around the C(phenylene)−N bond is blocked by the presence of the methyl group on the phenylene bridge, possibly hampering the formation of the nitrogen-coordinated active species. To prove the critical role of the pendant chloroimine unit in affording the high activities, complex **16**, containing the aldimine group, and complex **19**, not containing any functional group on the same position, are prepared according to the route shown in eqs 5 and 6, respectively. As expected, complex **19** shows negligible activity, while the complex containing aldimine group **16** exhibits low activity (28×10^6 g/molTi·h).





The bridged complexes **11**−**14** exhibit moderate or good activity. The general trend observed in this work is that the activity of the trimethylcyclopentadienyl complex is higher than that of the corresponding dimethylcyclopentadienyl analogue. The activities of the trimethylcyclopentadienyl complexes **12** and **14** are 63×10^6 and 56×10^6 g/molTi·h, respectively. Interestingly, the oxygen-coordinated complex **12** is excellent in incorporating 1-octene, and the 1-octene content of the polymer (31 mol %) is significantly higher than that of the polymer obtained with the CGC (19 mol %). The bridged complexes **11**−**14** provide polymers of significantly higher molecular weight (Mw, 120 000−200 000) than the CGC (M_w, 56 000). Rather broad molecular weight distributions (M_w/M_n, 4−7) are observed even though the GPC traces are monomodal. The broadening of the molecular weight distribution might be ascribed to the binding mode change described in eq 3.

Summary. Phenylene-bridged or substituted phenylene-bridged di- or trimethylcyclopentadienyl/carboxamide ligands 2-$(RMe_2C_5H_2)$-4,6-$R'_2C_6H_2NHC(O)^tBu$ are prepared, from which titanium complexes of various binding modes are afforded. Unbridged trichlorotitanium complexes bearing a chloroimine unit as a pendant group, 2-$[(\eta^5\text{-}RMe_2C_5H)TiCl_3]$-4,6-$R'_2C_6H_2N{=}C(Cl)^tBu$ (**7**, R = H, R′ = H; **8**, R = Me, R′ = H; **9**, R = H, R′ = Me; **10**, R = Me, R′ = Me), are unexpectedly obtained by the successive treatment of $Ti(NMe_2)_4$ and $SiCl_4$ to the phenylene-bridged or dimethylphenylene-bridged ligands, but the same treatment on the difluorophenylene-bridged ligands provides oxygen-coordinated bridged complexes [2-$(\eta^5\text{-}RMe_2$-$C_5H)$-4,6-$F_2C_6H_2N{=}C(O)^tBu$-κO]$TiCl_2$ (**11**, R = H; **12**, R =

Me). The desired nitrogen-coordinated bridged complexes, [2-(η^5-RMe_2C_5H)$C_6H_4NC(O)^tBu$-κ^2N,O]$TiMe_2$ (**13**, R = H; **14**, R = Me), are obtained by reacting the dilithium compound with Me_2TiCl_2, but X-ray crystallographic studies show that both the nitrogen and the oxygen coordinate with the titanium. Connectivity and the binding modes of **7**, **8**, **9**, **11**, and **14** are confirmed by X-ray crystallography.

Interestingly, the unbridged complexes **7** and **8**, when activated with $(Ph_3C)[B(C_6F_5)_4]$ and $Al(^iBu)_3$, exhibit fairly good activity in ethylene/1-octene copolymerization, while the complexes **9** and **10**, which have dimethyl substituents on the phenylene bridge, are negligible. Complexes **7** and **8** are slightly superior to the CGC in incorporating 1-octene. The chloroimine unit (−N=C(Cl)^{t}Bu) plays a critical role in affording high activity. Very low activity is observed not only in the complex containing the aldimine group, 2-[(η^5-Me_3C_5H)$TiCl_3$]C_6H_4N=C(H)^{t}Bu (**16**), but also in the complex not having any pendant group, (η^5-Me_3PhC_5H)$TiCl_3$ (**19**). The bridged complexes **11**−**14** also exhibit moderate or good activity. The trimethylcyclopentadienyl complex shows higher activity than the corresponding dimethylcyclopentadienyl analogue, and the oxygen-coordinated complex **12** is excellent in incorporating 1-octene.

Experimental Section

General Remarks. All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk techniques. Toluene, pentane, THF, and C_6D_6 were distilled from benzophenone ketyl. Pyridine-d_5 and $SiCl_4$ were dried over CaH_2 and transferred under vacuum to reservoirs. NMR spectra were recorded on a Varian Mercury plus 400. Elemental analyses were carried out at the Inter-University Center Natural Science Facilities, Seoul National University. Gel permeation chromatograms (GPC) were obtained at 140 °C in trichlorobenzene using a Waters Model 150-C+ GPC, and the data were analyzed using a polystyrene analyzing curve. Differential scanning calorimetry (DSC) was performed on a Thermal Analysis 3100.

Compound 1. To a flask containing 2-($Me_2C_5H_3$)$C_6H_4NH_2$ (0.263 g, 1.42 mmol)[7b] in methylene chloride (10 mL) were added triethylamine (0.130 g, 1.29 mmol) and pivaloyl chloride (0.155 g, 1.29 mmol). After the solution was stirred for 1 h at room temperature, it was transferred to a separatory funnel containing aqueous HCl (2 N, 5 mL). After the mixture was vigorously shaken, the organic phase was collected and rapidly washed with aqueous saturated $NaHCO_3$ (5 mL). After the organic phase was dried over anhydrous $MgSO_4$, solvent was removed with a rotary evaporator to give a residue, which was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 10:1). A colorless oil was obtained (0.355 g, 93%). IR (neat): 3409 (N−H), 1681(C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.18 (s, 9H, $C(CH_3)_3$), 1.73 (q, J = 1.6 Hz, 3H, CH_3), 1.89 (s, 3H, CH_3), 3.06−3.11 (m, 2H, Cp-CH_2), 6.05 (d, J = 2.0 Hz, 1H, Cp-CH), 7.07 (dd, J = 7.6, 2.0 Hz, 1H, $H^{3\text{ or }6}$), 7.11 (td, J = 7.2, 1.2 Hz, 1H, $H^{4\text{ or }5}$), 7.33 (td, J = 8.4, 2.0 Hz, 1H, $H^{4\text{ or }5}$), 7.54 (s, 1H, NH), 8.44 (d, J = 8.0 Hz, 1H, $H^{3\text{ or }6}$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.47, 14.64, 27.42, 44.59, 119.15, 123.14, 125.27, 125.74, 128.07, 129.28, 136.02, 138.36, 142.64, 142.76, 175.93 ppm. Anal. Calc ($C_{18}H_{23}NO$): C, 80.26; H, 8.61; N, 5.20. Found: C, 80.41; H, 8.45; N, 5.24.

Compound 2. The compound was synthesized from 2-($Me_3C_5H_2$)$C_6H_4NH_2$ using the same conditions and procedures as for **1**. A light yellow oil was obtained (yield, 89%). IR (neat): 3409 (N−H), 1681 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.17 (s, 9H, $C(CH_3)_3$), 1.58 (s, 3H, CH_3), 1.83 (s, 3H, CH_3), 1.98 (s, 3H, CH_3), 3.01 (s, 2H, Cp-CH_2), 7.05 (dd, J = 7.6, 2.0 Hz, 1H, $H^{3\text{ or }6}$), 7.08 (td, J = 7.6, 1.2 Hz, 1H, $H^{4\text{ or }5}$), 7.30 (td, J = 7.6, 1.6 Hz, 1H, $H^{4\text{ or }5}$), 7.60 (s, 1H, NH), 8.44 (d, J = 8.4 Hz, 1H, $H^{3\text{ or }6}$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 11.46, 13.51, 14.17, 27.29, 39.71, 48.87, 118.94, 122.96, 126.21, 127.78, 129.13, 134.27, 134.63, 135.91, 137.91, 138.67, 175.75 ppm. Anal. Calc ($C_{19}H_{25}NO$): C, 80.52; H, 8.89; N, 4.94. Found: C, 80.41; H, 8.78; N, 4.64.

Compound 3. The compound was synthesized from 2-($Me_2C_5H_3$)-4,6-$Me_2C_6H_2NH_2$ using the same conditions and procedures as for **1**. A white solid was obtained (yield, 70%). Mp: 136 °C. IR (neat): 3317 (N-H), 1650 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.17 (s, 9H, $C(CH_3)_3$), 1.69 (s, 3H, CH_3), 1.85 (s, 3H, CH_3), 2.24 (s, 3H, Ph-CH_3), 2.34 (s, 3H, Ph-CH_3), 2.97 (br d, J = 1.2 Hz, 2H, Cp-CH_2), 5.94 (s, 1H, Cp-CH), 6.75 (s, 1H, NH), 6.78 (s, 1H, Ph-H), 7.03 (s, 1H, Ph-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.54, 14.58, 18.74, 21.08, 27.50, 44.19, 123.88, 127.76, 130.41, 130.53, 131.19, 132.90, 134.94, 135.59, 140.14, 143.35, 175.85 ppm. Anal. Calc ($C_{20}H_{27}NO$): C, 80.76; H, 9.15; N, 4.71. Found: C, 80.57; H, 8.92; N, 5.11.

Compound 4. The compound was synthesized from 2-($Me_3C_5H_2$)-4,6-$Me_2C_6H_2NH_2$ using the same conditions and procedures as for **1**. A white solid was obtained (yield, 89%). Mp: 134 °C. IR (neat): 3332 (N-H), 1650 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.16 (s, 9H, $C(CH_3)_3$), 1.54 (s, 3H, CH_3), 1.80 (s, 3H, CH_3), 1.94 (s, 3H, CH_3), 2.23 (s, 3H, Ph-CH_3), 2.33 (s, 3H, Ph-CH_3), 2.84−2.97 (m, 2H, Cp-CH_2), 6.76 (s, 2 H, Ph-H), 7.02 (s, 1 H, NH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 11.63, 13.50, 14.23, 18.79, 21.09, 27.46, 39.13, 48.64, 127.68, 130.28, 131.18, 132.85, 133.22, 134.79, 135.34, 135.47, 135.62, 140.51, 175.77 ppm. Anal. Calc ($C_{21}H_{29}$-NO): C, 80.98; H, 9.38; N, 4.50. Found: C, 80.72; H, 9.60; N, 4.90.

Compound 5. The compound was synthesized from 2-($Me_2C_5H_3$)-4,6-$F_2C_6H_2NH_2$ using the same conditions and procedures as for **1**. A white solid was obtained (yield, 76%). Mp: 144 °C. IR (neat): 3317 (N-H), 1666 (C=O) cm^{-1}. ^1H NMR (C_6D_6): δ 1.01 (s, 9H, $C(CH_3)_3$), 1.66 (s, 3H, CH_3), 1.72 (q, J = 2.0 Hz, 3H, CH_3), 2.66 (quintet, J = 1.6 Hz, 2H, Cp-CH_2), 5.79 (d, J = 2.0 Hz, 1H, Cp-CH), 6.36 (s, 1H, NH), 6.52 (s, IH, Ph-H), 6.54 (s, 1H, Ph-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.60 (CH_3), 14.63 (CH_3), 27.57 ($C(CH_3)_3$), 39.28 ($C(CH_3)_3$), 44.53 (Cp-CH_2), 103.58 (t, $^2J_{CF}$ = 25.1 Hz, CH), 112.41 (dd, $^2J_{CF}$ = 21.2, $^4J_{CF}$ = 3.8 Hz, CH), 120.89 (dd, J = 14, 6.0 Hz), 124.60 (=CH), 137.72 (dd, J = 11.0, 3.0 Hz), 138.56 (=C−C_6), 141.70 (=CCH_3), 142.95(=CCH_3), 158.48 (dd, $^1J_{CF}$ = 228, $^3J_{CF}$ = 12.9 Hz, CF), 161.00 (dd, $^1J_{CF}$ = 223, $^3J_{CF}$ = 12.2 Hz, CF), 175.52 (CO) ppm. Anal. Calc ($C_{18}H_{21}F_2NO$): C, 70.80; H, 6.93; N, 4.59. Found: C, 70.85; H, 7.10; N, 4.82.

Compound 6. The compound was synthesized from 2-($Me_3C_5H_2$)-4,6-$F_2C_6H_2NH_2$ using the same conditions and procedures as for **1**. A white solid was obtained (yield, 64%). Mp: 138 °C. IR (neat): 3301 (N-H), 1666 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.18 (s, 9H, $C(CH_3)_3$), 1.58 (s, 3H, CH_3), 1.82 (s, 3H, CH_3), 1.94 (s, 3H, CH_3), 2.92 (s, 2H, Cp-CH_2), 6.61 (s, 1H, NH), 6.67 (ddd, J = 8.4, 2.4, 1.2 Hz, 1H, H^5), 6.86 (ddd, J = 11.2, 9.2, 2.4 Hz, 1H, H^3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 11.57 (CH_3), 13.48 (CH_3), 14.28 (CH_3), 27.45 ($C(CH_3)_3$), 39.30 ($C(CH_3)_3$), 48.86 (Cp-CH_2), 103.26 (t, $^2J_{CF}$ = 25.0 Hz, CH), 112.00 (dd, $^2J_{CF}$ = 22.0, $^4J_{CF}$ = 3.1 Hz, CH), 119.61 (dd, J = 12.0, 3.0 Hz), 133.70, 134.31, 136.65 (d, J = 9.1 Hz), 137.47, 138.02, 157.50 (dd, $^1J_{CF}$ = 250, $^3J_{CF}$ = 12.9 Hz, CF), 160.55 (dd, $^1J_{CF}$ = 246, $^3J_{CF}$ = 12.9 Hz, CF), 176.00 (CO) ppm. Anal. Calc ($C_{19}H_{23}F_2NO$): C, 71.45; H, 7.26; N, 4.39. Found: C, 71.41; H, 7.38; N, 4.73.

Compound 7. Compound **1** (2.06 g, 7.65 mmol), $Ti(NMe_2)_4$ (1.72 g, 7.65 mmol), and toluene (20 mL) were added into a Schlenk flask. The solution was stirred for 1 day at 80 °C. Removal of solvent gave a red oil. ^1H NMR (C_6D_6): δ 1.43 (s, 9H, $C(CH_3)_3$), 1.94 (s, 6H, CH_3), 2.97 (s, 12H, NCH_3), 5.88 (s, 2H, Cp-H), 7.01 (td, J = 8.4, 1.2 Hz, 1H, $H^{4\text{ or }5}$), 7.26 (td, J = 8.4, 1.6 Hz, 1H, $H^{4\text{ or }5}$), 7.30 (d, J = 8.0 Hz, 1H, $H^{3\text{ or }6}$), 7.66 (d, J = 8.0 Hz, 1H, $H^{3\text{ or }6}$) ppm. $^{13}C\{^1H\}$ NMR(C_6D_6): δ 14.73 (Cp-CH_3), 29.14 ($C(CH_3)_3$), 39.77 ($C(CH_3)_3$), 48.35 (N-C), 112.35, 122.81, 123.10, 125.21, 125.55, 128.54, 131.55, 132.86, 144.65, 168.49 ppm. To a

flask containing the resulting bis(dimethylamido)titanium complex in toluene (20 mL) was added $SiCl_4$ (5.20 g, 30.6 mmol). After the solution was stirred 4 h at room temperature, all volatiles were removed under vacuum to give a yellow residue, which was triturated in pentane (30 mL) (1.77 g, 53%). Single crystals were obtained by vapor-phase addition of pentane to a benzene solution. ^{1}H NMR (C_6D_6): δ 0.93 (s, 9H, C(CH_3)$_3$), 2.21 (s, 6H, CH_3), 6.03 (s, 2H, Cp-H), 6.65 (d, J = 8.4 Hz, 1H, $H^{3\text{or }6}$), 6.89 (t, J = 7.6 Hz, 1H, $H^{4\text{ or }5}$), 7.03 (t, J = 8.0 Hz, 1H, H^4 ×c1→$^{r\,5}$), 7.67 (d, J = 7.6 Hz, 1H, $H^{3\text{ or }6}$) ppm. ^{13}C{^{1}H} NMR(C_6D_6): δ 17.19, 28.12, 43.89, 119.74, 123.05, 123.65, 125.28, 130.03, 131.89, 140.15, 140.79, 147.23, 155.97 ppm. Anal. Calc ($C_{18}H_{21}Cl_4NTi$): C, 49.02; H, 4.80; N, 3.18. Found: C, 49.18; H, 4.42; N, 3.24.

Compound 8. The complex was synthesized from **2** using the same conditions and procedures as for **7**. Overall yield from **2** was 73%. NMR data for the intermediate bis(dimethylamido)titanium complex: ^{1}H NMR (C_6D_6): δ 1.45 (s, 9H, C(CH_3)$_3$), 1.88 (s, 3H, CH_3), 1.94 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 2.81 (s, 6H, N-CH_3), 3.14 (s, 6H, N-CH_3), 5.86 (s, 1H, Cp-H), 7.03 (td, J = 7.2, 1.2 Hz, 1H, $H^{4\text{ or }5}$), 7.27 (dd, J = 7.6, 0.8 Hz, 1H, $H^{3\text{ or }6}$), 7.30 (td, J = 7.6, 1.2 Hz, 1H, $H^{4\text{ or }5}$), 7.70 (dd, J = 8.0, 0.8 Hz, 1H, $H^{3\text{ or }6}$) ppm. ^{13}C{^{1}H} NMR(C_6D_6): δ 12.79, 13.06, 14.13, 29.12, 39.76, 47.12, 49.85, 115.52, 120.22, 121.21, 121.31, 122.78, 125.59, 125.95, 128.48, 131.52, 132.95, 144.69, 168.90 ppm. Single crystals of **8** were obtained by vapor-phase addition of pentane to a benzene solution. Analytical data for **8**: ^{1}H NMR (C_6D_6): δ 0.91 (s, 9H, C(CH_3)$_3$), 2.00 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 5.99 (s, 1H, Cp-H), 6.66 (d, J = 8.0 Hz, 1H, $H^{3\text{ or }6}$), 6.91 (tt, J = 8.4, 1.2 Hz, 1H, $H^{4\text{ or }5}$), 7.04 (tt, J = 8.0, 1.2 Hz, 1H, $H^{4\text{ or }5}$), 7.73 (d, J = 8.0 Hz, 1H, $H^{3\text{ or }6}$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 15.19, 16.39, 17.49, 28.08, 43.85, 119.64, 123.63, 124.79, 125.22, 129.96, 132.13, 137.78, 138.85, 139.28, 141.78, 147.20, 155.74 ppm. Anal. Calc ($C_{19}H_{23}Cl_4NTi$): C, 50.15; H, 5.09; N, 3.08. Found: C, 50.24; H, 5.12; N, 3.24.

Compound 9. The complex was synthesized from **3** using the same conditions and procedures as for **7**. Overall yield from **3** was 55%. NMR data for the intermediate bis(dimethylamido)titanium complex: ^{1}H NMR (C_6D_6): δ 1.45 (s, 9H, C(CH_3)$_3$), 1.99 (s, 6H, N-CH_3), 2.26 (s, 3H, Ph-CH_3), 2.66 (s, 3H, Ph-CH_3), 2.99 (s, 12H, N-CH_3), 5.88 (s, 2H, Cp-H), 7.01 (s, 1H, Ph-H), 7.10 (s, 1H, Ph-H) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 14.95, 21.13, 21.62, 29.27, 40.31, 48.41, 112.42, 122.68, 124.75, 125.76, 130.97, 131.25, 131.40, 137.03, 140.39, 167.26 ppm. Single crystals of **9** were obtained in toluene solution at −30 °C. Analytical data for **9**: ^{1}H NMR (C_6D_6): δ 0.95 (s, 9H, C(CH_3)$_3$), 1.95 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 2.28 (s, 3H, Ph-CH_3), 2.30 (s, 3H, Ph-CH_3), 5.90 (d, J = 2.8 Hz, 1H, Cp-H), 6.18 (d, J = 2.8 Hz, 1H, Cp-H), 6.79 (s, 1H, Ph-H), 7.45 (s, 1H, Ph-H) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 17.09 (br), 17.69, 17.75, 21.04 (br), 28.19, 43.81, 121.94, 123.06 (d, J = 9.1 Hz), 124.39, 126.66, 129.88 (d, J = 9.1 Hz), 132.48 (d, J = 6.8 Hz), 134.36, 139.26, 140.70, 141.67, 143.93, 156.11 ppm. Anal. Calc ($C_{20}H_{25}Cl_4NTi$): C, 51.21; H, 5.37; N, 2.99. Found: C, 51.01; H, 5.25; N, 3.14.

Copmpound 10. The complex was synthesized from **4** using the same conditions and procedures as for **7**. Overall yield from **4** was 57%. The NMR data for the intermediate bis(dimethylamido)-titanium complex: ^{1}H NMR (C_6D_6): δ 1.45 (s, 9H, C(CH_3)$_3$), 1.92 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.27 (s, 3H, Ph-CH_3), 2.67 (s, 3H, Ph-CH_3), 2.83 (s, 6H, N-CH_3), 3.17 (s, 6H, N-CH_3), 5.89 (s, 1H, Cp-H), 7.00 (s, 1H, Ph-H), 7.11 (s, 1H, Ph-H) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 12.85, 13.30, 14.38, 21.18, 21.57, 29.26, 40.30, 47.22, 49.98, 115.62, 119.83, 120.80, 121.35, 125.15, 126.13, 130.91, 131.16, 131.47, 136.99, 140.40, 167.63 ppm. Two signal sets are observed for **10** in a 0.57:0.43 ratio in the NMR spectra. The minor signals are marked in italics. Analytical data for **10**: ^{1}H NMR (C_6D_6): δ *0.93* (s, 3.9H, C(CH_3)$_3$), 0.94 (s, 5.1H, C(CH_3)$_3$), *1.95* (s, 1.3H, CH_3), 1.96 (s, 1.7H, CH_3), 2.11 (s, 6H, Ph-CH_3), *2.25* (s, 1.3H, CH_3), 2.27 (s, 1.7H, CH_3), 2.32 (s, 1.7H, CH_3), *2.34* (s, 1.3H, CH_3), *5.85* (s, 0.43H, Cp-H), 6.12 (s, 0.57H, Cp-H), 6.81 (s, 1H, Ph-H), 7.51 (s, 0.57H, Ph-H), 7.55 (s, 0.43H, Ph-H) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 15.15, 15.80, 16.14, 16.81, 17.34, 17.70, 17.97, 21.07, 28.13, 43.76, 122.53, 122.60, 123.98, 124.03, 125.98, 126.57, 130.04, 130.20, 132.37, 134.28, 134.35, 136.96, 137.84, 138.59, 138.63, 139.38, 139.83, 142.27, 143.31, 143.80, 143.96, 155.80, 155.89 ppm. Anal. Calc ($C_{21}H_{27}Cl_4NTi$): C, 52.21; H, 5.63; N, 2.90. Found: C, 52.08; H, 5.35; N, 3.24.

Compound 11. The complex was synthesized from **5** using the same conditions and procedures as for **7**. Overall yield from **5** was 78%. The NMR data for the intermediate bis(dimethylamido)-titanium complex: ^{1}H NMR (C_6D_6): δ 1.40 (s, 9H, C(CH_3)$_3$), 1.81 (s, 6H, CH_3), 2.92 (s, 12H, NCH_3), 5.79 (s, 2H, Cp-H), 6.69−6.68 (m, 2H) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 14.51, 29.04, 48.29, 103.78 (t, $^2J_{CF}$ = 27.0 Hz, Ph-CH), 112.59, 113.69 (dd, $^2J_{CF}$ = 21.2, $^4J_{CF}$ = 3.8 Hz, CH), 122.86, 123.08, 128.14, 130.61 (dd, J = 9.0, 4.0 Hz), 157.49 (dd, $^1J_{CF}$ = 240, $^3J_{CF}$ = 12.8 Hz, CF), 159.31 (dd, $^1J_{CF}$ = 246, $^3J_{CF}$ = 12.1 Hz, CF), 170.32 (CO) ppm. Single crystals of **11** were obtained in toluene solution at −30 °C. Analytical data for **11**: ^{1}H NMR (C_6D_6): δ 1.33 (s, 9H, C(CH_3)$_3$), 1.81 (s, 6H, CH_3), 6.08 (s, 2H, Cp-H), 6.16 (ddd, J = 9.2, 6.4, 1.6 Hz, 1H, H^5), 6.54 (ddd, J = 9.6, 8.0, 3.6 Hz, 1H, H^3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 16.42 (CH_3), 28.64 (C(*C*H$_3$)$_3$), 42.10 (*C*(CH$_3$)$_3$), 105.47 (t, $^2J_{CF}$ = 25.8 Hz, Ph-CH), 113.85 (dd, $^2J_{CF}$ = 23.0, $^4J_{CF}$ = 3.8 Hz, Ph-CH), 122.46 (Cp-CH), 126.70 (d, J = 9.1 Hz), 127.05 (dd, J = 8.0, 4.0 Hz), 129.90, 132.43, 133.86, 158.99 (dd, $^1J_{CF}$ = 247, $^3J_{CF}$ = 13.7 Hz, CF), 159.91 (dd, $^1J_{CF}$ = 250, $^3J_{CF}$ = 12.9 Hz, CF), 168.29 (C═O) ppm. ^{19}F NMR (C_6D_6): δ −109.93 (q, J = 7.5 Hz), −118.22 (t, J = 7.5 Hz) ppm. Anal. Calc ($C_{18}H_{19}Cl_2F_2NOTi$): C, 51.22; H, 4.54; N, 3.32. Found: C, 51.41; H, 4.25; N, 3.24.

Compound 12. The complex was synthesized from **7** using the same conditions and procedures as for **7**. Overall yield from **6** was 89%. The NMR data for the intermediate bis(dimethylamido)-titanium complex: ^{1}H NMR (C_6D_6): δ 1.41 (s, 9H, C(CH_3)$_3$), 1.72 (s, 3H, CH_3), 1.84 (s, 3H, CH_3), 1.96 (s, 3H, CH_3), 2.77 (s, 6H, NCH_3), 3.09 (s, 6H, NCH_3), 5.80 (s, 1H, Cp-H), 6.70−6.82 (m, 2H, Ph-H) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 12.67 (CH_3), 12.80 (CH_3), 14.01 (CH_3), 29.04 (C(*C*H$_3$)$_3$), 40.28 (*C*(CH$_3$)$_3$), 47.11 (NC), 49.82 (NC), 103.67 (t, $^2J_{CF}$ = 25.7 Hz, Ph-CH), 112.75 (dd, $^2J_{CF}$ = 21.2, $^4J_{CF}$ = 3.8 Hz, CH), 115.74 (Cp-CH), 123.17 (br), 120.08 (Cp-*C*CH$_3$), 121.24 (Cp-*C*CH$_3$), 121.74 (Cp-*C*CH$_3$), 128.57 (d, J = 9.1 Hz), 130.64 (dd, J = 8.0, 4.1 Hz), 157.51 (dd, $^1J_{CF}$ = 261, $^3J_{CF}$ = 13.6 Hz, CF), 159.35 (dd, $^1J_{CF}$ = 246, $^3J_{CF}$ = 12.9 Hz, CF), 170.67 (CO) ppm. Analytically pure crystals of **12** were obtained in toluene solution at −30 °C. Analytical data for **12**: ^{1}H NMR (C_6D_6): δ 1.34 (s, 9H, C(CH_3)$_3$), 1.74 (s, 3H, CH_3), 1.89 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 5.91 (s, 1H, Cp-H), 6.24 (ddd, J = 11.6, 4.8, 2.4 Hz, 1H, H^5), 6.57 (ddd, J = 13.2, 8.8, 3.6 Hz, 1H, H^3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 14.12 (CH_3), 15.58 (CH_3), 16.69 (CH_3), 28.66 (C(*C*H$_3$)$_3$), 42.04 (*C*(CH$_3$)$_3$), 105.39 (t, $^2J_{CF}$ = 25.8 Hz, Ph-CH), 113.76 (dd, $^2J_{CF}$ = 22.0, $^4J_{CF}$ = 4.5 Hz, Ph-CH), 123.83 (Cp-CH), 128.57 (d, J = 9.1 Hz), 130.64 (dd, J = 8.0, 4.1 Hz), 130.39 (br), 130.68 (Cp-*C*CH$_3$), 131.35 (Cp-*C*CH$_3$), 135.90 (Cp-*C*CH$_3$), 158.96 (dd, $^1J_{CF}$ = 246, $^3J_{CF}$ = 13.7 Hz, CF), 159.98 (dd, $^1J_{CF}$ = 250, $^3J_{CF}$ = 12.9 Hz, CF), 168.68 ppm. ^{19}F NMR (C_6D_6): δ −108.11 (t, J = 7.9 Hz), −113.76 (q, J = 7.9 Hz) ppm. Anal. Calc ($C_{19}H_{21}Cl_2F_2NOTi$): C, 52.32; H, 4.85; N, 3.21. Found: C, 52.41; H, 4.75; N, 3.24.

Compound 13. To a stirred solution of **1** (1.31 g, 4.86 mmol) in cold diethyl ether (25 mL, −30 °C) was added *n*-BuLi (3.9 mL, 9.73 mmol, 2.5 M in hexane) dropwise. The solution was stirred for 6 h to give a light yellow solid, which was filtered and washed with diethyl ether (1.34 g, 89%). The ^{1}H and ^{13}C NMR spectra indicated that the dilithium salt was cleanly formed and 0.39 equiv of diethyl ether was incorporated. ^{1}H NMR (pyridine-d_5): δ 1.35 (s, 9H, C(CH_3)$_3$), 2.26 (s, 6H, CH_3), 6.28 (s, 2H, Cp-H), 6.90 (td,

J = 6.8, 1.6 Hz, 1H, $H^{4\text{ or }5}$), 7.01 (td, J = 7.2, 1.6 Hz, 1H, $H^{4\text{ or }5}$), 7.76 (dd, J = 7.6, 2.4 Hz, 1H, $H^{3\text{ or }6}$), 7.89 (d, J = 8.0 Hz, 1H, $H^{3\text{ or }6}$) ppm. $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 15.57, 29.86, 39.81, 103.50, 113.58, 115.13, 119.70, 123.99, 126.33, 131.13, 137.79, 153.18, 178.54 ppm. Diethyl ether (16 mL) and $TiCl_4$·DME (0.361 g, 1.29 mmol) were added into a flask. After the solution was cooled to −30 °C, MeLi (1.18 g, 2.58 mmol, 1.6 M in diethyl ether) was added dropwise and the mixture was stirred for 15 min. The dilithium salt (0.40 g, 1.29 mmol) was added as a solid, and the resulting solution was stirred for 3 h at room temperature. Solvent was removed under vacuum, and the product was extracted with pentane (15 mL). Removal of pentane gave a greenish-yellow solid (yield, 72%) that is pure by the analysis of the ^1H and ^{13}C NMR spectra. Analytically pure single crystals were obtained in pentane solution at −30 °C. Two signal sets are observed in the NMR spectra in a 0.87:0.13 ratio. The signals of the minor signals are marked in italics. ^1H NMR (C_6D_6, 25 °C): δ *0.89* (s, 0.78H, Ti-CH_3), 1.12 (s, 5.22H, Ti-CH_3), 1.36 (s, 7.83H, $C(CH_3)_3$), *1.47* (s, 1.17H, $C(CH_3)_3$), 1.62 (s, 5.22H, CH_3), *1.80* (s, 0.78H, CH_3), *6.23* (s, 0.26H, Cp-H), 6.46 (s, 1.74H, Cp-H), 6.85 (td, J = 7.2, 1.2 Hz, 1H, $H^{4\text{ or }5}$), 6.98 (td, J = 7.2, 1.6 Hz, 1H, $H^{4\text{ or }5}$), 7.01−7.05 (m, 2H, $H^{3\text{and}6}$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 13.59, *15.26*, 27.06, *29.04*, 39.53, *40.67*, *58.55*, 59.84, 115.27, *115.89*, 119.88, 123.23, *123.57*, *123.97*, *124.21*, 125.42, *127.85*, *127.97*, 128.21, *128.68*, 129.68, *129.96*, 131.56, 133.25, *142.18*, 149.63, *165.16*, 187.45 ppm. Anal. Calc ($C_{20}H_{27}NOTi$): C, 69.57; H, 7.88; N, 4.06. Found: C, 69.27; H, 7.81; N, 4.34.

Compound 14. The compound was synthesized from **2** using the same conditions and procedures as for **15** (overall yield, 68%). The ^1H and ^{13}C NMR spectra indicated that the dilithium salt was cleanly formed and 0.29 equiv of diethyl ether was incorporated. NMR data for the dilithium compound: ^1H NMR (pyridine-d_5): δ 1.35 (s, 9H, $C(CH_3)_3$), 2.12 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 6.11 (s, 1H, Cp-H), 6.90 (t, J = 6.8 Hz, 1H, $H^{4\text{ or }5}$), 7.02 (t, J = 7.2 Hz, 1H, $H^{4\text{ or }5}$), 7.76 (d, J = 7.6 Hz, 1H, $H^{3\text{ or }6}$), 7.89 (d, J = 7.6 Hz, 1H, $H^{3\text{ or }6}$) ppm. $^{13}C\{^1H\}$ NMR (pyridine-d_5): δ 12.90, 14.73, 15.38, 29.86, 39.77, 104.54, 110.31, 110.73, 111.16, 114.19, 119.61, 123.79, 126.32, 131.23, 138.08, 153.28, 178.48 ppm. Analytically pure crystals were obtained in pentane solution at −30 °C. Two signal sets are observed in the NMR spectra in a 0.78:0.22 ratio. Signals for the minor isomer are marked in italics. Analytical data for **14**: ^1H NMR (C_6D_6, 25 °C): δ *0.75* (s, 0.66H, Ti-CH_3), 0.88 (s, 0.66H, Ti-CH_3), 0.89 (s, 2.34H, Ti-CH_3), 1.23 (s, 2.34H, Ti-CH_3), 1.36 (s, 7.02H, $C(CH_3)_3$), *1.48* (s, 1.98H, $C(CH_3)_3$), 1.51 (s, 2.34H, CH_3), 1.66 (s, 2.34H, CH_3), *1.76* (s, 0.66H, CH_3), *1.79* (s, 0.66H, CH_3), *2.00* (s, 0.66H, CH_3), 2.16 (s, 2.34H, CH_3), *6.00* (s, 0.22H, Cp-H), 6.25 (s, 0.78H, Cp-H), 6.87 (t, J = 7.2, 0.78H, $H^{4\text{ or }5}$), *6.92* (t, J = 7.2, 0.22H, $H^{4\text{ or }5}$), 6.99 (t, J = 8.4 Hz, 1H, $H^{4\text{ or }5}$), 7.04 (d, J = 8.0 Hz, 0.78H, $H^{3\text{ or }6}$), 7.08 (d, J = 0.78 Hz, 2H, $H^{3\text{ or }6}$), *7.12* (d, J = 6.4 Hz, 0.22H, $H^{3\text{ or }6}$), *7.48* (d, J = 8.0 Hz, 0.22H, $H^{3\text{ or }6}$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 11.85, 13.19, *13.54*, 14.12, *14.56*, *14.89*, 27.16, *29.10*, 39.66, *40.64*, *55.87*, 57.57, *60.29*, 62.66, *116.87*, 117.05, 120.10, *121.11*, *122.48*, 123.06, 123.25, *123.98*, 124.18, 124.38, *124.66*, *125.80*, *126.75*, *128.02*, 128.63, 129.84, 130.32, *130.54*, 131.69, 133.26, *142.49*, 149.83, *165.50*, 187.89 ppm. Anal. Calc ($C_{21}H_{29}NOTi$): C, 70.19; H, 8.13; N, 3.90. Found: C, 70.41; H, 8.25; N, 3.84.

Complex 15. Molecular sieves (1.60 g), **2** (1.05 g, 5.27 mmol), pivaldehyde (0.68 g, 7.90 mmol), and toluene (10 mL) were added into a Schlenk flask. The solution was stirred for 32 h at room temperature. The volatiles were removed by vacuum to give a residue, which was extracted with pentane (15 mL). Removal of solvent gave a light yellow oil (1.39 g, 98%): ^1H NMR (C_6D_6): δ 0.92 (s, 9H, $C(CH_3)_3$), 1.73 (s, 3H, CH_3), 1.77 (s, 3H, CH_3), 1.80 (s, 3H, CH_3), 2.62 (dd, J = 7.2, 1.6 Hz, 2H, Cp-CH_2), 6.96 (td, J = 7.6, 1.6 Hz, 1H, $Ph^{4\text{ or }5}$), 7.00 (dd, J = 7.6, 0.8 Hz, 1H, $Ph^{3\text{ or }6}$), 7.09 (td, J = 7.6, 1.2 Hz, 1H, $Ph^{4\text{ or }5}$), 7.13 (dd, J = 7.2, 1.6 Hz, 1H, $Ph^{3\text{ or }6}$), 7.27 (s, 1H, N═C-H) ppm. $^{13}C\{^1H\}$ NMR(C_6D_6): δ 12.37, 13.72, 14.78, 26.66, 36.83, 48.85, 120.62, 124.32, 127.81, 129.24, 131.00, 131.71, 135.18, 136.50, 141.77, 152.31, 172.69 ppm.

Complex 16. The imine compound (0.600 g, 2.17 mmol), Ti-$(NMe_2)_4$ (0.487 g, 2.17 mmol), and toluene (12 mL) were added into a Schlenk flask. The solution was stirred for 12 h at 100 °C. Removal of solvent gave a red oil, which was extracted with pentane (10 mL). Removal of solvent gave the desired tris(dimethylamido)-titanium complex (0.783 g, 81%). ^1H NMR (C_6D_6): δ 0.96 (s, 9H, $C(CH_3)_3$), 1.89 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 3.13 (s, 18H, N-CH_3), 5.56 (s, 1H, Cp-CH), 7.01 (dd, J = 7.2, 1.6 Hz, 1H, $Ph^{3\text{ or }6}$), 7.10 (s, 1H, N═C-H), 7.12−7.19 (m, 2H, $Ph^{4\text{ and }5}$), 7.44 (dd, J = 6.0, 1.2 Hz, 1H, $Ph^{3\text{ or }6}$) ppm. $^{13}C\{^1H\}$ NMR(C_6D_6): δ 13.04, 13.27, 15.10, 26.75, 44.25, 49.63, 110.30, 119.16, 120.91, 121.05, 122.20, 124.08, 124.26, 127.77, 128.71, 134.04, 154.02, 172.66 ppm. To a flask containing the resulting tris(dimethylamido)-titanium complex (0.783 g, 1.75 mmol) in toluene (10 mL) was added Me_2SiCl_2 (0.679 g, 5.261 mmol). After the solution was stirred for 1 h at 50 °C, all volatiles were removed under vacuum to give a red residue, which was extracted with toluene (10 mL). Removal of solvent gave the desired trichloride complex (0.691 g, 94%). Analytical data for **16**: ^1H NMR (C_6D_6): δ 0.79 (s, 9H, $C(CH_3)_3$), 2.02 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 6.10 (s, 1H, Cp-CH), 6.67 (d, J = 8.0 Hz, 1H, $Ph^{3\text{ or }6}$), 6.97 (td, J = 7.2, 1.2 Hz, 1H, $Ph^{4\text{ or }5}$), 7.09 (td, J = 7.6, 1.2 Hz, 1H, $Ph^{4\text{ or }5}$), 7.11 (s, 1H, N═C−H), 7.70 (dd, J = 8.0, 1.2 Hz, 1H, $Ph^{3\text{ or }6}$) ppm. $^{13}C\{^1H\}$ NMR(C_6D_6): δ 15.27, 16.53, 17.71, 26.55, 36.99, 118.85, 124.97, 125.38, 125.69, 130.26, 132.00, 137.97, 139.19, 139.51, 143.15, 152.03, 172.69 ppm. Anal. Calc ($C_{19}H_{24}Cl_3NTi$): C, 54.25; H, 5.75; N, 3.33. Found: C, 54.41; H, 5.65; N, 3.24.

Compound 17. 2-(Dihydroxyboryl)-3-methyl-2-cyclopenten-1-one (1.00 g, 6.49 mmol), Na_2CO_3 (0.98 g, 9.3 mmol), and Pd-$(PPh_3)_4$ (0.215 g, 0.186 mmol) were added into a Schlenk flask inside a glovebox. The flask was brought out, and deoxygenated DME (21 mL), deoxygenated water (7 mL), and bromobenzene (0.971 g, 6.19 mmol) were added successively with a syringe. The mixture was stirred for 12 h at 95 °C. After the solution was cooled to room temperature, it was transferred to a separatory funnel containing ethyl acetate (30 mL). Water (30 mL) was added, and the organic phase was collected. The water phase was extracted with additional ethyl acetate (20 mL × 2). The organic phase was combined and dried over anhydrous $MgSO_4$. The solvent was removed with a rotary evaporator to give a residue, which was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 3:1) (1.07 g, 93%). IR (neat): 1695 (C═O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.18 (d, J = 7.6 Hz, 3H, CH_3), 2.02 (s, 3H, CH_3), 2.07 (d, J = 2.0 Hz, 1H, Cp-CH_2), 2.68 (dd, J = 18.0, 7.2 Hz, 1H, Cp-CH_2), 2.73−2.79 (m, 1H, Cp-CH), 7.18 (d, J = 8.0 Hz, 2H, $H^{2\text{ and }6}$), 7.19 (t, J = 6.0 Hz, 1H, H^4), 7.28 (t, J = 8.0 Hz, 2H, $H^{3\text{ and }5}$) ppm. $^{13}C\{^1H\}$ NMR($CDCl_3$): δ 15.94, 19.08, 37.26, 43.40, 127.27, 127.91, 128.84, 131.51, 139.45, 175.42, 206.24 ppm.

Compound 18. Compound **17** (1.05 g, 5.64 mmol) was dissolved in THF (51 mL). The solution was cooled to −78 °C, and MeLi (3.87 g, 8.46 mmol, 1.6 M solution in diethyl ether) was added with a syringe. After the mixture was stirred for 2 h at −78 °C, it was transferred to a separatory funnel containing H_2O (100 mL) and ethyl acetate (50 mL). The organic phase was collected, and the water phase was extracted further with additional ethyl acetate (20 mL × 2). The combined organic phase was shaken vigorously with aqueous HCl (2 N, 40 mL) for 2 min. The organic phase was collected and washed with saturated aqueous $NaHCO_3$ solution. After the organic phase was dried over anhydrous $MgSO_4$, the solvent was removed with a rotary evaporator to give a residue, which was purified by column chromatography on silica gel eluting

Table 2. Crystallographic Parameters of 7, 8, 9, 11, and 14

	7	8	9	11	14
formula	$C_{18}H_{21}Cl_4NTi$	$C_{19}H_{23}Cl_4NTi$	$C_{26}H_{25}Cl_4NTi$	$C_{18}H_{19}Cl_2F_2NOTi$	$C_{21}H_{29}NOTi$
fw	441.06	455.08	541.17	422.13	359.35
size, mm^3	0.33 × 0.14 × 0.13	0.28 × 0.12 × 0.10	0.37 × 0.21 × 0.14	0.45 × 0.35 × 0.29	0.47 × 0.32 × 0.18
a, Å	16.3487(9)	7.0671(17)	10.4334(5)	9.538(5)	9.0860(4)
b, Å	7.8575(4)	18.778(5)	12.0665(6)	13.643(3)	10.0478(5)
c, Å	17.2294(9)	16.371(4)	12.1840(6)	15.072(13)	11.6051(5)
α, deg	90	90	69.9080(10)	90	77.7360(10)
β, deg	108.4470(10)	95.393(5)	71.3620(10)	106.0120(10)	80.2020(10)
γ, deg	90	90	83.7550(10)	90	70.4210(10)
V, $Å^3$	2099.56(19)	2162.9(9)	1365.00(12)	1885.2(19)	969.79(8)
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	triclinic
space group	*P*2(1)/*n*	*P*2(1)/*c*	$P\bar{1}$	*P*2(1)/*n*	$P\bar{1}$
D(calc), g cm^{-1}	1.395	1.398	1.317	1.487	1.231
Z	4	4	2	4	2
μ, mm^{-1}	0.917	0.892	0.719	0.762	0.448
no. of data collected	21 020	19 639	18 860	14 384	13 357
no. of unique data	5213	5331	6761	3946	4793
no. of variables	222	233	296	226	225
R(%)	0.0463	0.0684	0.0400	0.0801	0.0367
R_w(%)	0.1128	0.1459	0.1091	0.1673	0.1021
goodness of fit	1.093	0.886	1.031	1.079	1.055

[a] Data collected at 233(2) K with Mo Kα radiation (λ(Kα) = 0.7107 Å), $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ with $F_o > 2.0\sigma(I)$, $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o)^2]^2]^{1/2}$ with $F_o > 2.0\sigma(I)$.

with hexane and ethyl acetate (v/v, 10:1). A colorless oil was obtained (0.644 g, 62%). ^{1}H NMR ($CDCl_3$): δ 1.66 (s, 3H, CH_3), 1.86 (s, 3H, CH_3), 1.88 (s, 3H, CH_3), 2.82 (s, 2H, Cp-CH_2), 7.11 (dd, J = 6.8, 1.6 Hz, 2H, $H^{3\text{ and }5}$), 7.17 (t, J = 7.2 Hz, 1H, H^4), 7.28 (t, J = 7.6 Hz, 2H, $H^{2\text{ and }6}$) ppm. $^{13}C\{^1H\}$ NMR($CDCl_3$): δ 12.31, 13.62, 14.39, 48.96, 125.61, 126.08, 127.79, 128.39, 129.10, 133.47, 135.08, 135.48, 137.04, 142.37 ppm. Anal. Calc ($C_{14}H_{16}$): C, 91.25; H, 8.75. Found: C, 91.41; H, 8.55.

Complex 19. The complex was synthesized from **18** using the same conditions and procedures as for **16**. Overall yield for the trichloride complex from **18** was 81% (red solid). The NMR data for the intermediate tris(dimethylamido)titanium complex: ^{1}H NMR (C_6D_6): δ 2.02 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 3.08 (s, 18H, N-CH_3), 5.68 (s, 1H, Cp-H), 7.11 (tt, J = 7.2, 1.6 Hz, 1H, H^4) 7.29 (tt, J = 7.2, 1.6 Hz, 2H, $H^{3\text{ or }5}$), 7.36 (dt, J = 6.8, 1.6 Hz, 2H, $H^{2\text{ or }6}$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 12.97, 13.16, 14.10, 49.40, 111.35, 119.49, 120.18, 120.85, 124.45, 126.06, 128.40, 131.01, 137.38 ppm. Analytical data for **19**: ^{1}H NMR (C_6D_6): δ 1.95 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 6.02 (s, 1H, Cp-H), 7.06 (t, J = 7.2 Hz, 1H, H^4), 7.12 (t, J = 7.2 Hz, 2H, $H^{3\text{ and }5}$), 7.25 (d, J = 6.8 Hz, 2H, $H^{2\text{ and }6}$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 14.97, 16.41, 17.46, 125.22, 128.55, 128.85, 130.48, 132.92, 136.49, 137.49, 139.29, 141.91 ppm. Anal. Calc ($C_{14}H_{15}Cl_3Ti$): C, 49.82; H, 4.48. Found: C, 49.79; H, 4.41.

Polymerization. To a 2.0 L Büchi reactor were added 1.0 L of toluene solution of 1-octene (0.80 M) and ^{i}Bu$_3$Al (0.5 mmol). After the solution was heated to 90 °C, it was saturated with ethylene gas (13 bar). An activated catalyst, which was prepared by mixing the complex (5.0 μmol Ti), [CPh_3][$B(C_6F_5)_4$] (15 μmol), and (^{i}Bu)$_3$Al (0.125 mmol) for 2 min, was charged by pressurizing the catalyst-feeding tank with N_2 pressure. After the ethylene (13 bar) was fed continuously for 10 min, the reaction mixture was drained into a flask containing ethanol to give white precipitates, which were collected by filtration and dried under vacuum.

X-ray Crystallography. Crystals of **7**−**9**, **11**, and **14** were mounted in thin-walled glass capillaries and sealed under argon. The data sets were collected on a Bruker Smart CCD detector single diffractometer. Mo Kα radiation (λ = 0.7107 Å) was used for all structures. The structures were solved by the direct methods using the SHELX-96 program and least-squares refinement using the SHELXL-Plus (5.1) software package. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the calculated positions. The crystal data and refinement results are summarized in Table 2.

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Supporting Information Available: Data in cif format for **7**, **8**, **9**, **11**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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