Synthesis of Half-Titanocenes Containing Phenoxy-imine Ligands and Their Use as Catalysts for Olefin Polymerization

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Various half-titanocenes containing phenoxy-imine ligands of the type Cp′$TiCl_2$[O-2-R^1-6-(R^2N═CH)-C_6H_3] [Cp′ = Cp* (C_5Me_5) and R^1, R^2 = Me, 2,6-^{i}Pr$_2C_6H_3$ (**1**); ^{t}Bu, 2,6-^{i}Pr$_2C_6H_3$ (**2**); Me, ^{t}Bu (**3**); ^{t}Bu, ^{t}Bu (**4**); Cp′ = 1,2,4-$Me_3C_5H_2$ and R^1, R^2 = Me, 2,6-^{i}Pr$_2C_6H_3$ (**5**); Cp′ = Cp and R^1, R^2 = Me, 2,6-^{i}Pr$_2C_6H_3$ (**6**); Me, ^{t}Bu (**7**)] were prepared by reaction of Cp′$TiCl_3$ with LiO-2-R^1-6-(R^2N═CH)C_6H_3 that were prepared *in situ* by treating the corresponding phenol with *n*-BuLi. Cp*$TiMe_2$[O-2-Me-6-{(2,6-^{i}Pr$_2C_6H_3$)N═CH}C_6H_3] (**8**) was prepared from Cp*$TiMe_3$ by treating with 2-Me-6-{(2,6-^{i}Pr$_2C_6H_3$)N═CH}C_6H_3-OH in *n*-hexane, and the reaction with [PhN(H)Me_2][B(C_6F_5)$_4$] was also explored. Structures for **1**−**3** and **5**−**8** were determined by X-ray crystallography, and the imino nitrogen in the phenoxy-imine ligand was not coordinated to Ti in all cases; the bond angles for Ti−O−C(Ph) were affected by substituents in both cyclopentadienyl and phenoxy-imine ligands. The catalytic activities for ethylene polymerization and syndiospecific styrene polymerization using **1**−**7**−MAO catalyst systems were highly affected by the substituents in both cyclopentadienyl and phenoxy-imine ligands; the Cp* analogues (**3**, **4**) exhibited notable activities for ethylene polymerization, whereas the Cp analogues (**6**, **7**) showed significant activities for syndiospecific styrene polymerization. The Cp analogue **6** was also an effective catalyst precursor for copolymerization of ethylene with norbornene.

Introduction

Design and synthesis of efficient transition metal complex catalysts toward precise, controlled olefin polymerization has attracted considerable attention,[1−8] and *nonbridged* half-metallocene-type group 4 transition metal complexes of the type Cp′M(L)X_2 (Cp′ = cyclopentadienyl group; M = Ti, Zr, Hf; L = anionic ligand such as OAr, NR_2, N═CR_2, N═PR_3, etc.; X = halogen, alkyl) have been considered as one of the promising candidates for new efficient catalysts.[8b,9−18] This is because these complex catalysts exhibit unique characteristics for production of new polymers that are not prepared by conventional Ziegler−Natta catalysts, as well as by ordinary metallocene type[1−4] and/or "constrained geometry" (linked Cp-amide) type catalysts.[4,5] Moreover, the synthesis is not very complicated, and the ligand modifications sterically and/or electronically should be easier especially than those in the ordinary linked half-metallocene-type complexes. We reported that the half-titanocenes containing

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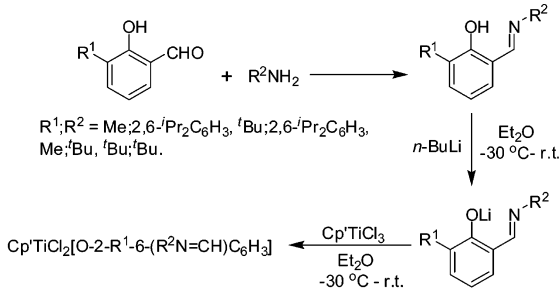
an aryloxo ligand of the type Cp′$TiCl_2$(OAr) (Cp′ = substituted cyclopentadienyl; OAr = aryloxo) exhibited notable catalytic activities for olefin polymerization,[18a,b] and we demonstrated later that a series of these complexes (containing aryloxo, amide, ketimide ligands) displayed unique characteristics especially for copolymerization of ethylene with α-olefin,[18b,d,19,20] styrene,[21] and norbornene.[22a,b] It was revealed that an efficient catalyst for desired polymerization can be simply modified by replacement of both the cyclopentadienyl fragment and anionic ancillary ligands.[8b] More recently, we had shown that efficient copolymerizations of ethylene with cyclohexene (CHE),[22c] 2-methyl-1-pentene (2M1P),[23] and vinylcyclohexane[24] had been achieved by using these complex catalysts.

Recently, we (group of Qian and Huang)[25] and Bochmann[26] reported synthesis of half-titanocenes containing phenoxy-imine ligands (e.g., $CpTiCl_2$[O-2-^{t}Bu-6-(RN=CH)C_6H_3], R = 2,4,6-$Me_3C_6H_2$, C_6F_5, C_6H_{11},[26] etc.) and their use as the catalyst precursors for olefin polymerization. Since studies concerning synthesis of various titanium/zirconium complexes containing bis(phenoxy-imine) ligands for olefin polymerization were made known by Fujita et al.,[27,28] we prepared a series of half-titanocenes containing substituted cyclopentadienyl and phenoxy-imine ligands and tested them as catalyst precursors for homo- and copolymerization of ethylene with various comonomers.

Scheme 1



Cp′ = Cp*, R^1;R^2 = Me;2,6-^{i}Pr$_2$C$_6$H$_3$ (**1**), ^{t}Bu;2,6-^{i}Pr$_2$C$_6$H$_3$ (**2**), Me;^{t}Bu (**3**), ^{t}Bu;^{t}Bu,(**4**),
Cp′ = 1,2,4-$Me_3C_5H_2$, R^1;R^2 = Me;2,6-^{i}Pr$_2$C$_6$H$_3$ (**5**),
Cp′ = Cp, R^1;R^2 = Me;2,6-^{i}Pr$_2$C$_6$H$_3$ (**6**), Me;^{t}Bu, (**7**).

Results and Discussion

1. Synthesis of Various (Cyclopentadienyl)(phenoxy-imine)titanium Complexes of the Type Cp′TiX_2[O-2-R^1-6-(R^2N=CH)C_6H_3] (X = Cl, Me). A series of substituted salicylaldimines (imino-phenols), 2-R^1-6-(R^2N=CH)C_6H_3OH [R^1, R^2 = Me, 2,6-^{i}Pr$_2$C$_6$H$_3$; ^{t}Bu, 2,6-^{i}Pr$_2$C$_6$H$_3$; Me, ^{t}Bu; ^{t}Bu, $_t$Bu], were prepared according to the reported procedures, by reaction of alkyl-substituted salicylaldehyde with 2,6-diisopropylaniline or *tert*-butylamine, respectively (Scheme 1).[27a] Various half-titanocenes containing phenoxy-imine ligands of the type Cp′$TiCl_2$[O-2-R^1-6-(R^2N=CH)C_6H_3] [Cp′ = Cp* (C_5Me_5) and R^1, R^2 = Me, 2,6-^{i}Pr$_2$C$_6$H$_3$ (**1**); ^{t}Bu, 2,6-^{i}Pr$_2$C$_6$H$_3$ (**2**); Me, ^{t}Bu (**3**); ^{t}Bu, ^{t}Bu (**4**); Cp′ = 1,2,4-$Me_3C_5H_2$ and R^1, R^2 = Me, 2,6-^{i}Pr$_2$C$_6$H$_3$ (**5**); Cp′ = Cp and R^1, R^2 = Me, 2,6-^{i}Pr$_2$C$_6$H$_3$ (**6**); Me, ^{t}Bu (**7**)] were prepared in Et_2O by reaction of Cp′$TiCl_3$ with LiO-2-R^1-6-(R^2N=CH)C_6H_3, which were prepared *in situ* by treating the corresponding phenol with 1.0 equiv of *n*-BuLi in Et_2O (Scheme 1). Analytically pure samples were collected as red microcrystals in moderate yields (50.6−72.5%) from a concentrated dichloromethane solution layered with *n*-hexane at −30 °C. The resultant dichloro complexes (**1**−**7**) were identified by ^{1}H and ^{13}C NMR spectra and elemental analyses, and the structures (for **1**−**3**, **5**−**7**) were determined by X-ray crystallography as described below (Figures 1 and 2).

The ^{1}H and ^{13}C NMR spectra for **1**−**7** were analogous to those reported previously.[25−27] For instance, a resonance ascribed to the imino protons in **1** was observed at 8.54 ppm, which is slightly downfield from that in the corresponding free imino phenol (8.28 ppm); a resonance ascribed to the imino carbon in **1** was observed at 156.9 ppm, whereas the resonance in the free ligand was observed at 159.2 ppm.

The dimethyl analogue Cp*$TiMe_2$[O-2-Me-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH}C_6H_3] (**8**) was prepared in high yield (92%) from Cp*$TiMe_3$ by treating with 1.0 equiv of 2-Me-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH}C_6H_3-OH in *n*-hexane (Scheme 2). The complex **8** was also identified by ^{1}H and ^{13}C NMR spectra and elemental analysis, and the structure was determined by X-ray crystallography (Figure 3). A resonance corresponding to protons for Ti−Me was observed as one singlet at 0.73 ppm (in C_6D_6), although the *ortho*-substituents in the phenoxy ligand in **8** were different (Me and the substituted imino), and no significant changes in the resonance in the ^{1}H NMR spectra (in $C_6D_5CD_3$) were observed even at various temperatures (−60 to 60 °C); this was somewhat different from that in, for example, $CpTiMe_2$(O-2-Np-4,6-^{t}-$Bu_2C_6H_2$) (Np = 1-naphthyl),[29] where two resonances ascribed to Ti−Me were observed. These results suggest that the imino nitrogen was not coordinated to Ti as described below.

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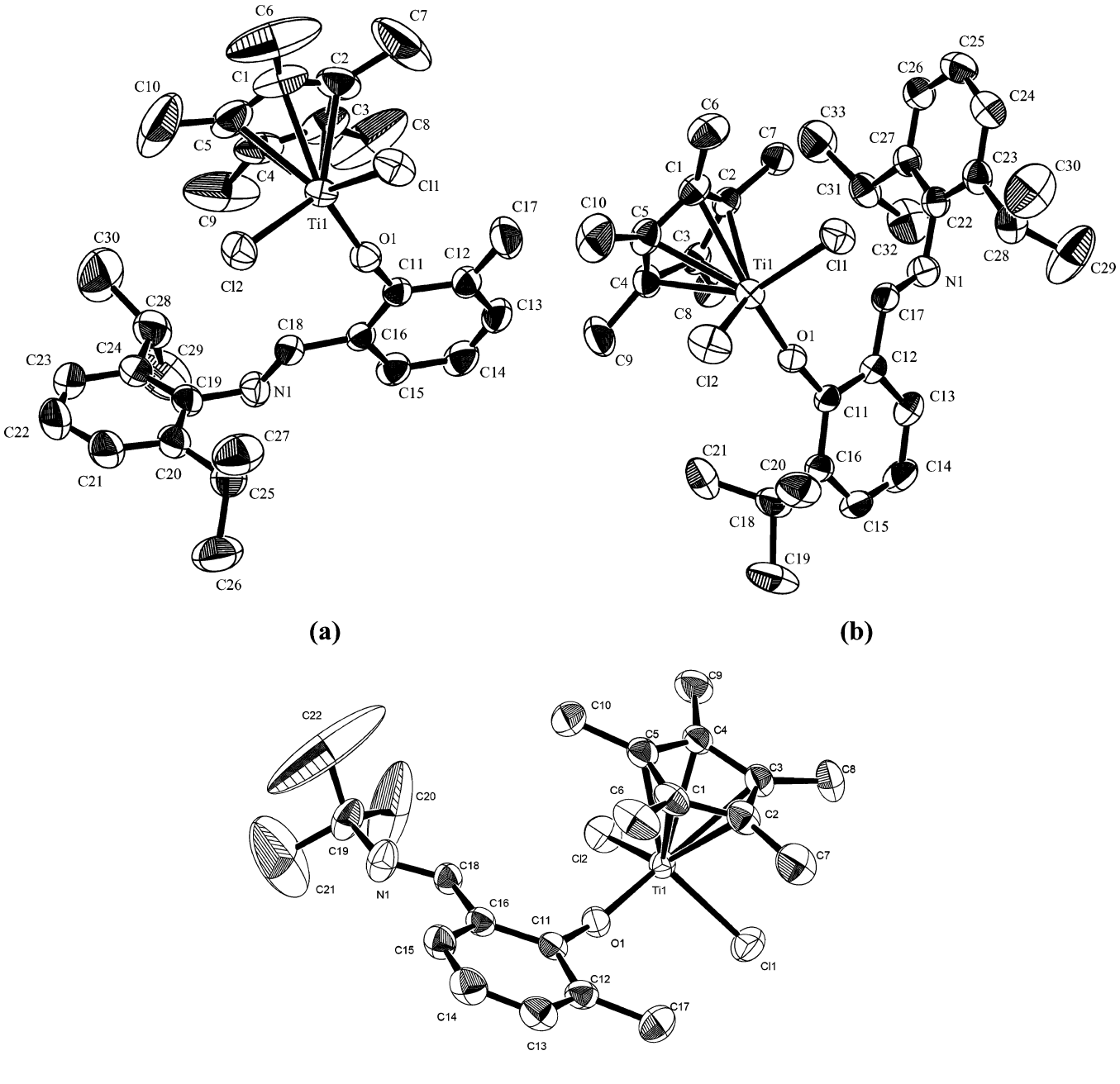

Figure 1. ORTEP drawings for $Cp^*TiCl_2[O\text{-}2\text{-}R^1\text{-}6\text{-}(R^2N{=}CH)C_6H_3]$. R^1, R^2 = (a) Me, 2,6-^{i}Pr$_2$C$_6$H$_3$ (**1**), (b) ^{t}Bu, 2,6-^{i}Pr$_2$C$_6$H$_3$ (**2**), (c) Me, ^{t}Bu (**3**). Thermal ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

Reaction of the dimethyl analogue (**8**) with $[PhN(H)Me_2][B(C_6F_5)_4]$ was explored in C_6D_5Br, and the protons corresponding to the Me group in the 2,6-^{i}Pr$_2$C$_6$H$_3$ group showed two doublets in the ^{1}H NMR spectrum. Only one resonance corresponding to the Me group was seen at 0.93 ppm, which is different from that in **8** (0.74 ppm). Moreover the ^{19}F NMR showed three resonances ascribed to F atoms in the *ortho*-, *meta*-, and *para*-positions. Although no significant changes were seen in the resonances ascribed to protons in the phenyl groups in addition to protons ascribed to $PhNMe_2$, these results presume the formation of the cationic complex $\{Cp^*TiMe[O\text{-}2\text{-}Me\text{-}6\text{-}\{(2,6\text{-}^i Pr_2C_6H_3)N{=}CH\}C_6H_3]\}^+[B(C_6F_5)_4]^-$ *in situ*, although we could not isolate the complex in a pure form.[30]

2. Crystal Structure Analysis for $Cp'TiX_2[O\text{-}2\text{-}R^1\text{-}6\text{-}(R^2N{=}CH)C_6H_3]$. The structure for **1** was determined by X-ray crystallography as shown in Figure 1a, and selected bond distances and angles are summarized in Table 1. The structure showed that **1** has a distorted tetrahedral geometry around the titanium metal center. The Ti−O bond distance in **1** [1.7968(16) Å] is slightly longer than those in $Cp'TiCl_2(O\text{-}2,6\text{-}^i Pr_2C_6H_3)$ [1.760(4)−1.773(2) Å, Cp′ = Cp, ^{t}BuC$_5$H$_4$, Cp*][18a,b] and $Cp^*TiCl_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ [1.785(2) Å],[31] but are close to those in $Cp^*TiCl_2(O\text{-}2,6\text{-}^t Bu_2C_6H_3)$ [1.804(2) Å][32] and $Cp^*TiCl_2(O$-

(30) A reviewer commented on the possibility of coordination of nitrogen in the imino group in the proposed cationic complex $\{Cp^*TiMe[O\text{-}2\text{-}Me\text{-}6\text{-}\{(2,6\text{-}^i Pr_2C_6H_3)N{=}CH\}C_6H_3]\}^+[B(C_6F_5)_4]^-$ and the complex was stabilized by C_6D_5Br, since there are two isopropyl doublets in the ^{1}H NMR spectra. However, we could not completely dismiss another possibility, coordination of $PhNMe_2$, although no significant changes in the resonances ascribed to the protons were seen. Therefore, K.N. did not describe this point, although the above assumption would be more likely.

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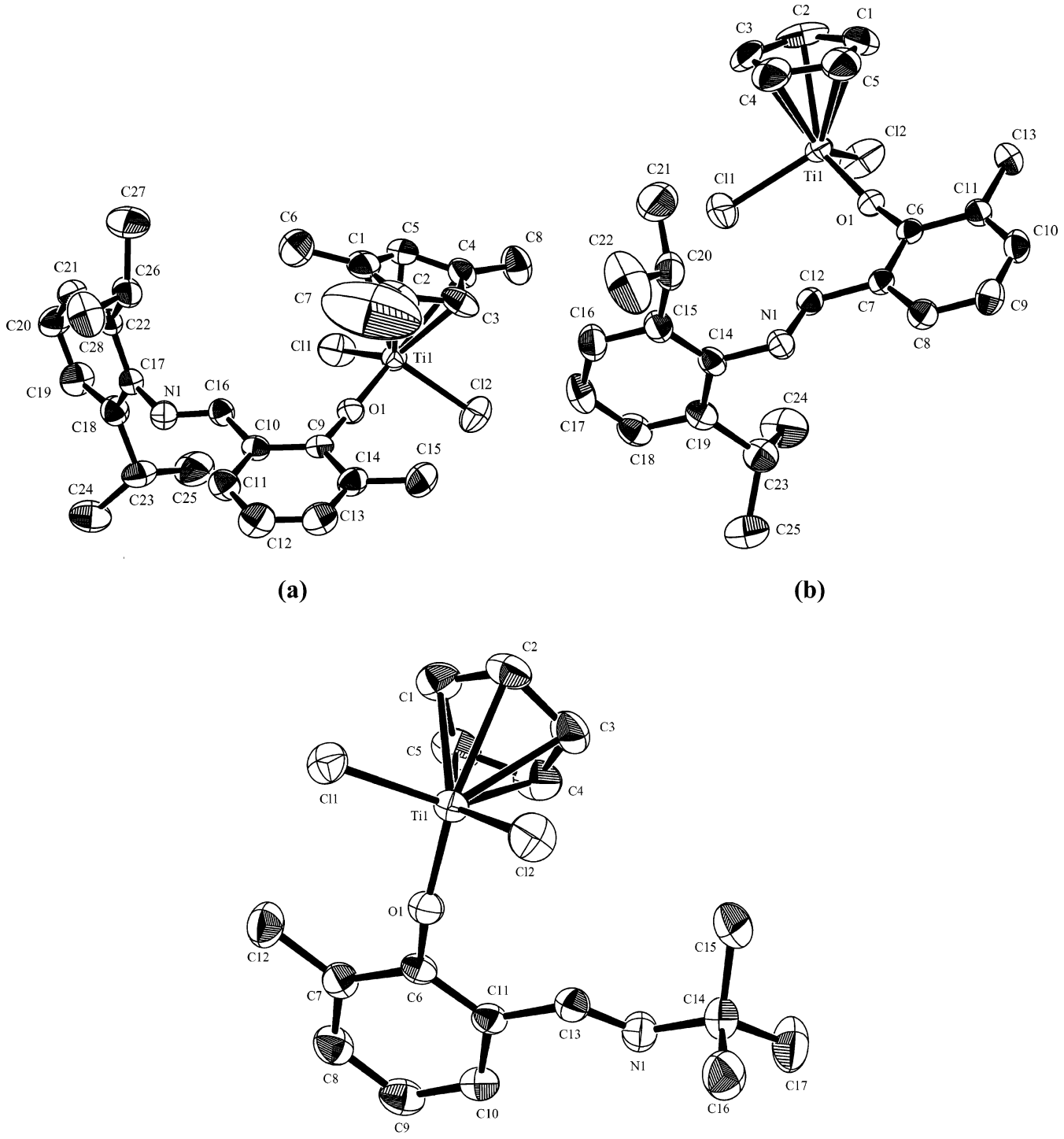
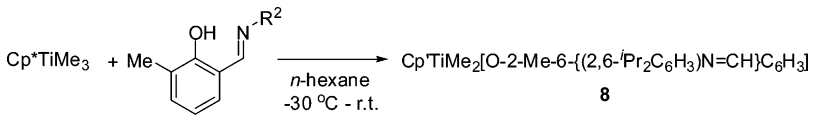


Figure 2. ORTEP drawings for Cp′$TiCl_2$[O-2-Me-6-(R^2N═CH)C_6H_3]. Cp′, R^2 = (a) 1,2,4-$Me_3C_5H_2$, 2,6-^{i}Pr$_2C_6H_3$ (**5**), (b) Cp, 2,6-^{i}Pr$_2C_6H_3$ (**6**), (c) Cp, ^{t}Bu (**7**). Thermal ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

Scheme 2



2,6-$Ph_2C_6H_3$) [1.811(3) Å].[33] This is explained as due to the influence of the bulky *ortho*-substituent, (2,6-^{i}Pr$_2C_6H_3$)N═CH−, in the phenoxy group. The Ti−Cl distances [2.2643(10), 2.2724(13) Å] are similar to those in $CpTiCl_2$(O-2,6-^{i}Pr$_2C_6H_3$) [2.262(1) Å],[18a,b] as well as those in various Cp*$TiCl_2$(OAr) [2.258(1)−2.273(6) Å, Ar = 2,6-$Me_2C_6H_3$,[31] 2,6-^{t}Bu$_2C_6H_3$,[32] 2,6-$Ph_2C_6H_3$,[33] 2,6-Ph_2-3,5-^{t}Bu$_2C_6H$[34]] except Cp*$TiCl_2$(O-2,6-^{i}Pr$_2C_6H_3$) [2.305(2) Å].[18a,b] The Cl−Ti−Cl angle [101.92(5)°] is slightly smaller than those in Cp*$TiCl_2$(O-2,6-$Me_2C_6H_3$) [103.3(2)°][31] and Cp*$TiCl_2$(O-2,6-^{i}Pr$_2C_6H_3$) [103.45(5)°][18a,b] and

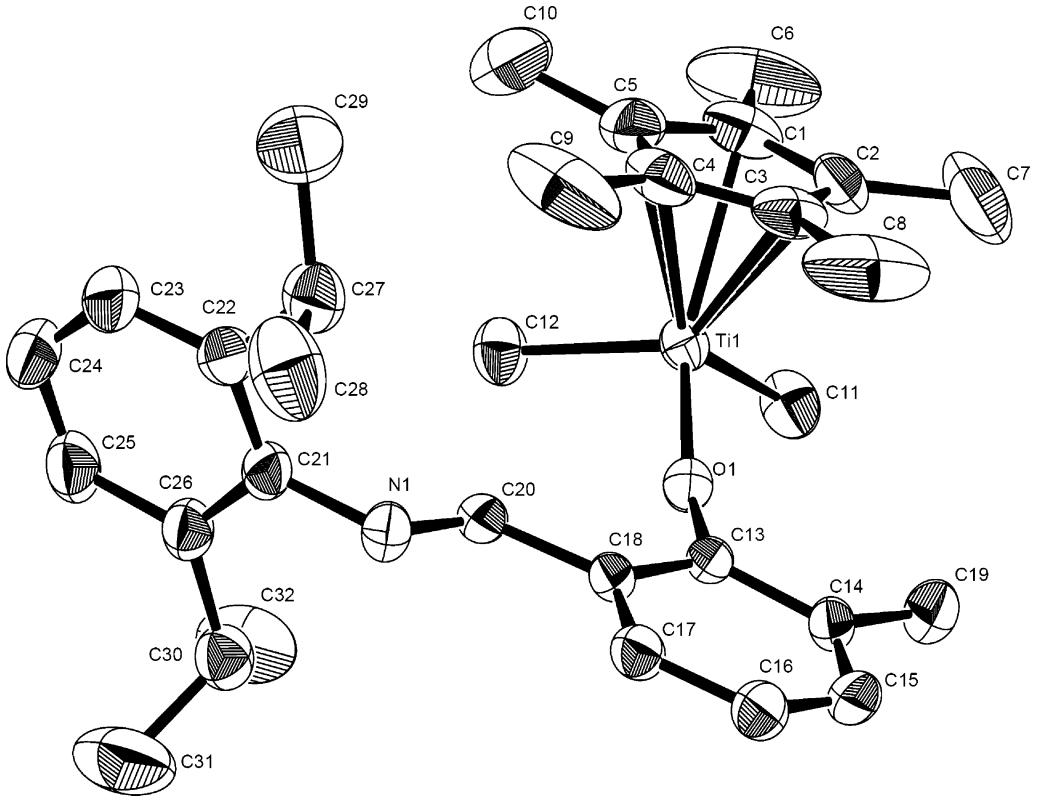


Figure 3. ORTEP drawings for Cp*TiMe$_2$[O-2-Me-6-{(2,6-^{i}Pr$_2$−C$_6$H$_3$)N═CH}C$_6$H$_3$] (**8**). Thermal ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Various Cp*TiCl$_2$[O-2-R^1-6-(R^{2}N═CH)C$_6$H$_3$] [R^1, R^2 = Me, 2,6-^{i}Pr$_2$C$_6$H$_3$ (1), ^{t}Bu, 2,6-^{i}Pr$_2$C$_6$H$_3$ (2), Me, ^{t}Bu (3)].

	R^1, R^2		
	Me, 2,6-^{i}Pr$_2$C$_6$H$_3$ (**1**)	^{t}Bu, 2,6-^{i}Pr$_2$C$_6$H$_3$ (**2**)	Me, ^{t}Bu (**3**)
Ti(1)−Cl(1)	2.2724(13)	2.2765(7)	2.2596(10)
Ti(1)−Cl(2)	2.2643(10)	2.2559(8)	2.2722(9)
Ti(1)−O(1)	1.7968(16)	1.8001(13)	1.808(2)
N(1)−C(18)	1.261(3)	1.260(2)$_{N(1)-C(17)}$	1.241(4)
O(1)−C(11)	1.357(2)	1.366(2)	1.349(3)
N(1)−C(19)	1.421(2)	1.426(2)$_{N(1)-C(22)}$	1.469(4)
C(16)−C(18)	1.472(2)	1.468(2)$_{C(12)-C(17)}$	1.485(4)
Cl(1)−Ti(1)−Cl(2)	103.40(4)	102.49(2)	104.03(4)
Cl(2)−Ti(1)−O(1)	102.30(5)	104.31(5)	101.10(8)
Ti(1)−O(1)−C(11)	162.16(13)	169.55(13)	156.5(2)
Cl(1)−Ti(1)−O(1)	101.92(5)	100.23(4)	102.78(7)
N(1)−C(18)−C(16)	122.0(2)	121.41(18)$_{N(1)-C(17)-C(12)}$	120.8(3)
C(18)−N(1)−C(19)	116.9(2)	118.48(18) $_{C(17)-N(1)-C(22)}$	121.5(3)

larger than those in Cp*TiCl$_2$(O-2,6-^{t}Bu$_2$C$_6$H$_3$) [98.10(4)°][31] and Cp*TiCl$_2$(O-2,6-Ph$_2$C$_6$H$_3$) [98.70(5)°].[33] The Ti−O−C(phenyl) angle [162.16(13)°] is close to that in Cp*TiCl$_2$(O-2,6-Me$_2$C$_6$H$_3$) [162.3(2)°].[29] These results thus indicate that these bond angles and distances are similar to those in a series of Cp*TiCl$_2$(OAr) in most cases.

Note that the imino-nitrogen was not coordinated to Ti; this observation is an interesting contrast to that in CpTiCl$_2$[O-2-^{t}-Bu-6-{(2,4,6-Me$_3$C$_6$H$_2$)N═CH}C$_6$H$_3$] (Ti−N = 2.268 Å),[26] where the Ti atom is five-coordinate with the Cp ligand in the apical site of a distorted square-pyramid and the N,O-chelating ligand forms a plane that includes the phenoxide ring and the imino nitrogen.

The structures for the other Cp* analogues, Cp*TiCl$_2$[O-2-^{t}Bu-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N═CH}C$_6$H$_3$] (**2**) and Cp*TiCl$_2$[O-2-Me-6-(^{t}BuN═CH)C$_6$H$_3$] (**3**), were also determined by X-ray crystallography (Figures 1b,c, respectively), and selected bond distances and angles are summarized in Table 1. These complexes have a distorted tetrahedral geometry around the Ti metal center, and the imino nitrogens were not coordinated to Ti. Slight differences in the Ti−O and Ti−Cl bond distances were seen, but these values are in the same range as in the various Cp*TiCl$_2$(OAr) introduced above.[18a,b,31−34] In contrast, Ti−O−C(phenyl) bond angles are strongly influenced by the substituents in both the *ortho*-phenoxy and the imino groups, and the bond angle increased in the order 169.55(13)° (**2**, R^1, R^2 = ^{t}Bu, 2,6-^{i}Pr$_2$C$_6$H$_3$) > 162.16(13)° (**1**, R^1, R^2 = Me, 2,6-^{i}Pr$_2$C$_6$H$_3$) > 156.5(2)° (**3**, R^1, R^2 = Me, ^{t}Bu). The bond angle in **2** is larger than those in ordinary Cp*TiCl$_2$(OAr) [155.5(2)−162.3(2)°][31−34] and somewhat similar to that in

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(33) Sturla, S. J.; Buchwald, S. L. *Organometallics* **2002**, *21*, 739.
(34) Thorn, M. G.; Vilardo, J. S.; Lee, J.; Hanna, B.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **2000**, *19*, 5636.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Cp′TiCl$_2$[O-2-Me-6-(R^{2}N═CH)C$_6$H$_3$] [Cp′; R^2 = 1,2,4-Me$_3$C$_5$H$_2$, 2,6-^{i}Pr$_2$C$_6$H$_3$ (5), Cp; 2,6-^{i}Pr$_2$C$_6$H$_3$ (6), Cp; ^{t}Bu (7)]

	Cp′ R^2		
	1,2,4-Me$_3$Cp 2,6-^{i}Pr$_2$C$_6$H$_3$ (**5**)	Cp 2,6-^{i}Pr$_2$C$_6$H$_3$ (**6**)	Cp ^{t}Bu (**7**)
Ti(1)−Cl(1)	2.260(2)	2.2546(6)	2.2555(4)
Ti(1)−Cl(2)	2.2623(16)	2.2515(7)	2.2592(4)
Ti(1)−O(1)	1.781(3)	1.7761(14)	1.7840(10)
N(1)−C(16)	1.263(6)	1.259(2)$_{N(1)-C(12)}$	1.2496(17)$_{N(1)-C(13)}$
O(1)−C(6)	1.370(5)$_{O(1)-C(9)}$	1.363(2)	1.3633(17)
N(1)−C(14)	1.418(6) $_{N(1)-C(17)}$	1.435(2)	1.488(2)
C(10)−C(16)	1.477(7)	1.466(2)$_{C(7)-C(12)}$	1.4751(18)$_{C(11)-C(13)}$
Cl(1)−Ti(1)−Cl(2)	103.53(7)	101.79(3)	103.387(19)
Cl(2)−Ti(1)−O(1)	102.61(11)	102.40(4)	103.15(2)
Ti(1)−O(1)−C(6)	171.0(3)$_{Ti(1)-O(1)-C(9)}$	166.05(14)	156.40(8)
Cl(1)−Ti(1)−O(1)	101.82(13)	104.87(5)	103.15(2)
N(1)−C(16)−C(10)	121.2(2)	122.68(18)$_{N(1)-C(12)-C(7)}$	121.30(14)$_{N(1)-C(13)-C(11)}$
C(16)−N(1)−C(17)	121.1(4)	116.25(17)$_{C(12)-N(1)-C(14)}$	119.65(14)$_{C(13)-N(1)-C(14)}$

Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) [173.0(3)°],[18a,b] which exhibit notable catalytic activity for olefin polymerization in the presence of MAO.

The structures for Cp′TiCl$_2$[O-2-Me-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N═CH}C$_6$H$_3$] [Cp′ = 1,2,4-Me$_3$C$_5$H$_2$ (**5**); Cp′ = Cp (**6**)] were also determined by X-ray crystallography (Figures 2a,b, respectively) to explore the effect of the cyclopentadienyl fragment by comparison with **1**, and selected bond distances and angles are summarized in Table 2. Complexes **5** and **6** have a distorted tetrahedral geometry around the titanium metal center, and the imino nitrogens were not coordinated to Ti; the results also showed unique contrast to that in CpTiCl$_2$[O-2-^{t}Bu-6-{(2,4,6-Me$_3$C$_6$H$_2$)N═CH}C$_6$H$_3$].[26] The Ti−Cl bond distances for **5** and **6** [2.2515(7)−2.2623(16) Å] are similar or slightly shorter than those in **1** [2.2643(10) and 2.2724(13) Å], and the Ti−O bond distances [1.781(3), 1.7761(14) Å for **5**, **6**, respectively] are slightly shorter than that in **1** [1.7968(16) Å]. This is explained as due to an electronic effect in the cyclopentadienyl fragments, because the Ti−O bond distances increased in the order **1** (Cp′ = C$_5$Me$_5$) > **5** (1,2,4-Me$_3$C$_5$H$_2$) > **6** (Cp). In contrast, the Ti−O−C(phenyl) bond angle increased in the order **5** [171.0(3)°] > **6** [166.05(14)°] > **1** [162.16(13)°], although the reason is not clear at this moment. The structure for CpTiCl$_2$[O-2-Me-6-(^{t}BuN═CH)C$_6$H$_3$] (**7**) was also determined, and selected results are summarized in Table 2. Complex **7** also possesses a distorted tetrahedral geometry around the titanium metal center, and the imino nitrogen was not coordinated to Ti. No significant differences in the bond distances were seen from those in **6**, and the Ti−O−C(phenyl) bond angle [156.40(8)°] is smaller than that in **6** [166.05(14)°] but similar to that in **3** [156.5(2)°] probably due to the influence of bulky *tert*-butyl substituent in the imino group for **3** and **6**. Taking into account these results, we may conclude that the bond distances and angles [especially Ti−Cl and Ti−O distances, Ti−O−C(phenyl) angle] are influenced by the substituents in both the cyclopentadienyl and aryloxo (phenoxy-imine) ligands.

Yellow prism microcrystals of **8** were grown from a concentrated chilled *n*-hexane solution, and the structure was determined by X-ray crystallography (Figure 2). Selected bond distances and angles are summarized in Table 3. The Ti−C(Me) bond distances [2.371(14), 2.393(5) Å] as well as the Ti−O distance [1.813(2) Å] are somewhat longer than those in Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) [2.093(3), 2.101(3), and 1.790(2) Å],[35] and this might be due to the influence of the bulky substituent in **8** [2-Me-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N═CH}-C$_6$H$_3$ vs 2,6-^{i}Pr$_2$C$_6$H$_3$]. The Ti−O distance is also slightly longer than in the dichloro analogue [**1**, 1.7968(16) Å]. The Ti−O−C(phenyl) bond angle [159.1(2)°] is smaller than that in Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) [168.7(1)°][35] but similar to that in the dichloro analogue [**1**, 162.16(13)°].

Table 3. Selected Bond Distances (Å) and Angles (deg) for Cp*TiMe$_2$[O-2-Me-6-{(2,6-^{i}Pr$_2$-C$_6$H$_3$)N═CH}C$_6$H$_3$] (8)

Bond Distances	
Ti(1)−C(1) 2.393(5)	Ti(1)−C(2) 2.371(4)
Ti(1)−O(1) 1.813(2)	N(1)−C(20) 1.263(5)
O(1)−C(13) 1.352(4)	N(1)−C(21) 1.415(4)
C(18)−C(20) 1.468(4)	
Bond Angles	
C(11)−Ti(1)−C(12) 100.86(4)	C(11)−Ti(1)−O(1) 102.05(15)
Ti(1)−O(1)−C(13) 159.1(2)	C(12)−Ti(1)−O(1) 102.33(13)
N(1)−C(20)−C(18) 123.5(3)	C(20)−N(1)−C(21) 117.2(3)

3. Ligand Effects in Ethylene Polymerization and Syndiospecific Styrene Polymerization Using Cp′TiX$_2$[O-2-R^1-6-(R^{2}N═CH)C$_6$H$_3$] (1−8)−MAO Catalyst Systems. Ethylene polymerizations by Cp′TiCl$_2$[O-2-R^1-6-(R^{2}N═CH)C$_6$H$_3$] (**1**−**7**) in the presence of methylaluminoxane (MAO) were examined to explore the effect of substituents on both the cyclopentadienyl and the phenoxy-imine ligands toward the catalytic activity (ethylene 4 atm, 25−70 °C, under the optimized Al/Ti molar ratio), and the results are summarized in Table 4.

The catalytic activities at 25 °C for ethylene polymerization using catalyst systems consisting of a series of Cp* analogues, Cp*TiCl$_2$[O-2-R^1-6-(R^{2}N═CH)C$_6$H$_3$] (**1**−**4**), and MAO increased in the order (ethylene 4 atm) 11 070 kg PE/mol Ti·h (**4**, R^1, R^2 = ^{t}Bu, ^{t}Bu, run 9) > 8460 (**3**, R^1, R^2 = Me, ^{t}Bu, run 6) > 6360 (**2**, R^1, R^2 = ^{t}Bu, 2,6-^{i}Pr$_2$C$_6$H$_3$, run 3) > 3540 (**1**, R^1, R^2 = Me, 2,6-^{i}Pr$_2$C$_6$H$_3$, run 1). The results suggest that the activities are highly affected by the substituents; the bulky substituents in both the phenoxy group in the *ortho*-position (^{t}Bu > Me) and the imino group (^{t}Bu > 2,6-^{i}Pr$_2$C$_6$H$_3$) seem to be important for high catalytic activity. Both the activities and the M_w values for resultant polyethylene decreased at higher temperature. The Cp* analogues showed higher catalytic activities than the Cp analogues (**6**, **7**) [activities at 25 °C: 3540, 8460 kg PE/mol Ti·h by **1**, **3**, respectively, vs 132, 243 kg PE/mol Ti·h by **6**, **7**, respectively], suggesting that an electronic effect on the Cp′ affects the catalytic activity as seen in the series Cp′TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) in both ethylene and 1-hexene polymerizations.[18a,b,32] In contrast, the M_w values using the Cp analogues (**6**, **7**) were higher than those prepared by the Cp* analogues, although we do not have the exact reason for the

(35) Nomura, K.; Fudo, A. *Inorg. Chim. Acta* **2004**, *345*, 37.

Table 4. Ethylene Polymerization by Cp′TiCl$_2$[O-2-R^1-6-(R^{2}N═CH)C$_6$H$_3$] (1−8)−MAO Catalyst Systems[a]

run	cat. (μmol)	temp/°C	polymer yield/mg	activity[b]	M_w[c] ×10^{-4}	M_w/M_n[c]
1	**1** (0.2)	25	118	3540	2.91	1.8
2	**1** (0.2)	40	99	2970	2.57	1. 9
3	**2** (0.2)	25	212	6360	4.49	2.4
4	**2** (0.2)	40	171	5130	3.65	2.2
5	**2** (0.2)	70	100	3000	1.14	2.7
6	**3** (0.2)	25	282	8460	3.25	2.7
7	**3** (0.2)	40	237	7110	2.43	2.7
8	**3** (0.2)	70	131	3930	1.93	3.0
9	**4** (0.2)	25	369	11070	1.75	2.7
10	**4** (0.2)	70	271	8130	1.66	2.4
11	**5** (0.2)	25	161	4830	1.45	2.4
12	**5** (0.2)	40	135	4050	1.29	2.4
13	**6** (2.0)	25	44	132	109	3.1
14	**6** (2.0)	70	31	93	65.3	2.2
15	**7** (2.0)	25	81	243	224.3	3.0
16	**7** (2.0)	70	36	108	97.1	2.9
17[d]	**8**(0.2)	25	107	3210	2.44	2.0

[a] Cp′ = Cp* and R^1, R^2 = Me, 2,6-^{i}Pr$_2$C$_6$H$_3$ (**1**), ^{t}Bu, 2,6-^{i}PrC$_6$H$_3$ (**2**), Me, ^{t}Bu (**3**), ^{t}Bu, ^{t}Bu (**4**); Cp′ = 1,2,4-Me$_3$C$_5$H$_2$ and R^1, R^2 = Me, 2,6-^{i}Pr$_2$C$_6$H$_3$ (**5**); Cp′, R^1 = Cp, Me and R^2 = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**6**), ^{t}Bu (**7**), and Cp*TiMe$_2$[O-2-Me-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N═CH}C$_6$H$_3$] (**8**). Conditions: catalyst 0.2 or 2.0 μmol, MAO (prepared by removing AlMe$_3$ and toluene from PMAO) 3.0 mmol, ethylene 4 atm, toluene total 50 mL, 25 °C, 10 min (100 mL scale autoclave). [b] Activity in kg PE/mol Ti·h. [c] GPC data in *o*-dichlorobenzene vs polystyrene standards. [d] Al^{i}Bu$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$/Ti = 500:1:1 (molar ratio).

Table 5. Syndiospecific Styrene Polymerization by Cp′TiCl$_2$[O-2-R^1-6-(R^{2}N═CH)C$_6$H$_3$] (1−7)−MAO Catalyst Systems[a]

run	cat. (μmol)	temp/°C	polymer yield[b]/mg	activity[c]	M_w[d] ×10^{-4}	M_w/M_n[d]
18	**1** (2.0)	25	47	141	19.9	2.2
19	**1** (2.0)	40	64	192	21.3	2.1
20	**1** (2.0)	55	95	285	19.3	2.2
21	**1** (2.0)	70	184	552	18.5	2.3
22	**2** (2.0)	25	trace			
23	**2** (2.0)	40	42	126	19.3	2.3
24	**2** (2.0)	55	77	231	18.2	2.2
25	**2** (2.0)	70	126	378	17.1	2.2
26	**3** (2.0)	55	31	93	8.37	2.2
27	**3** (2.0)	70	50	150	8.34	2.2
28	**4** (2.0)	70	trace			
29	**5** (2.0)	25	44	132	15.0	2.2
30	**5** (2.0)	40	170	510	17.2	2.2
31	**5** (2.0)	55	248	744	14.4	2.1
32	**5** (2.0)	70	298	894	14.3	2.1
33	**6** (2.0)	25	117	351	2.67	2.1
34	**6** (2.0)	40	446	1338	2.47	2.4
35	**6** (2.0)	55	665	1995	2.42	2.3
36	**6** (2.0)	70	970	2910	1.74	2.5
37	**7** (2.0)	25	130	390	7.55	2.1
38	**7** (2.0)	40	546	1638	6.23	2.1
39	**7** (2.0)	55	999	2997	5.91	2.1
40	**7** (2.0)	70	1529	4587	5.84	2.1

[a] Cp′ = Cp* and R^1, R^2 = Me, 2,6-^{i}Pr$_2$C$_6$H$_3$ (**1**), ^{t}Bu, 2,6-^{i}PrC$_6$H$_3$ (**2**), Me, ^{t}Bu (**3**), ^{t}Bu, ^{t}Bu (**4**); Cp′ = 1,2,4-Me$_3$C$_5$H$_2$ and R^1, R^2 = Me, 2,6-^{i}Pr$_2$C$_6$H$_3$ (**5**); Cp′, R^1 = Cp, Me and R^2 = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**6**), ^{t}Bu (**7**). Conditions: catalyst 2.0 μmol, MAO (prepared by removing AlMe$_3$ and toluene from PMAO) 3.0 mmol (Al/Ti = 1500, molar ratio), styrene 10 mL, styrene + toluene total 30 mL, 25 °C, 10 min and 100 mL scale autoclave. [b] Yield of acetone-insoluble fraction. [c] Activity in kg sPS/mol Ti·h. [d] GPC data in *o*-dichlorobenzene vs polystyrene standards.

better results at this moment.[36] The activities of the 1,2,4-Me$_3$C$_5$H$_2$ analogue (**5**) were similar to or rather higher than those of the Cp* analogue (**1**) under the same conditions (runs 1, 2 vs runs 10, 11).

The observed catalytic activity at 25 °C of the dimethyl analogue (**8**)−Ph$_3$CB(C$_6$F$_5$)$_4$ system in the presence of Al^{i}Bu$_3$ was somewhat similar to that of the dichloro analogue (**1**) in the presence of MAO. Since the M_w values for the resultant polymers prepared by **1** and **8** were close with uniform distributions (runs 1 and 17), we assume that similar catalytically active species, Cp′TiR[O-2-Me-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N═CH}-C$_6$H$_3$]$^+$ (R = alkyl), play a role in the ethylene polymerization.

We previously demonstrated that efficient catalyst precursor-(s) for ethylene (1-hexene) polymerization using the series Cp′TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) or Cp′TiCl$_2$(NR^{1}R^2) in the presence of MAO can be tuned to efficient catalyst precursor(s) for syndiospecific styrene polymerization only by modification (replacement) of the cyclopentadienyl fragment.[8b,18d,37] We thus explored syndiospecific styrene polymerization (at 25−70 °C) by Cp′TiCl$_2$[O-2-R^1-6-(R^{2}N═CH)C$_6$H$_3$] (**1**−**7**) to explore the ligand effects on the catalytic activity. The results are summarized in Table 5.[38]

The catalytic activities increased at higher temperature, as seen previously,[37b] and the activities at 70 °C were higher than those at 25 °C; however, complex **4** showed negligible activity. The resultant polymers were syndiotactic polystyrene (sPS) that possessed rather high molecular weights with uniform molecular weight distributions in all cases (M_w = (1.74−21.3) × 10^4, M_w/M_n = 2.06−2.53). The M_w values for resultant syndiotactic polystyrene prepared by the Cp* analogues (**1**−**3**) were higher than those by the Cp analogues (**6**, **7**), as seen in the previous report.[37b]

The catalytic activity at 70 °C using a series of Cp′TiCl$_2$[O-2-Me-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N═CH}C$_6$H$_3$]−MAO catalyst systems increased in the order **6** (Cp′ = Cp, 2910 kg sPS/mol Ti·h) > **5** (1,2,4-Me$_3$C$_5$H$_2$, 894) > **1** (Cp*, 552). The results thus clearly demonstrate that an efficient catalyst precursor for ethylene polymerization using a series of Cp′TiCl$_2$[O-2-Me-6-{(2,6-^{i}-Pr$_2$C$_6$H$_3$)N═CH}C$_6$H$_3$] can be tuned to efficient catalyst precursors for syndiospecific styrene polymerization by modification of the cyclopentadienyl fragment. We believe that the results presented here show one of the unique characteristics of *nonbridged* half-titaniocenes that make them suitable as catalyst precursors for olefin (styrene) polymerization, as demonstrated previously.[8b]

The catalytic activity at 70 °C using a series of Cp*TiCl$_2$-[O-2-R^1-6-(R^{2}N═CH)C$_6$H$_3$]−MAO catalyst systems increased in the order **1** (R^1, R^2 = Me, 2,6-^{i}Pr$_2$C$_6$H$_3$, 552 kg sPS/mol Ti·h, run 21) > **2** (R^1, R^2 = ^{t}Bu, 2,6-^{i}Pr$_2$C$_6$H$_3$, 378, run 25) > **3** (R^1, R^2 = Me, ^{t}Bu, 150, run 27) ≫ **4** (R^1, R^2 = ^{t}Bu, ^{t}Bu, trace, run 28). The observed trend was opposite of that in the ethylene polymerization. Moreover, among the Cp analogues, CpTiCl$_2$[O-2-R^1-6-(R^{2}N═CH)C$_6$H$_3$], activities of **7** (R^1, R^2 = ^{t}Bu, ^{t}Bu, 4587 kg sPS/mol Ti·h, run 40) were higher than those of **6** (R^1, R^2 = Me, ^{t}Bu, 2910, run 36). These facts clearly suggest that the activities were highly affected by the anionic donor ligand employed, although the effect should be negligible if the cationic Ti(III) species are considered as the catalytically

(36) As a reviewer noted, the M_w values for the resultant PEs prepared by the Cp* analogues [Cp*TiCl$_2$(X) (X = aryloxo, amide, anilide etc.]−MAO catalyst systems were generally higher than the Cp analogues, except the Cp′−ketimide analogues, CpTiCl$_2$(N═C^{t}Bu$_2$).[8b] Although the exact reason was not clear , the observation might be a promising characteristic for using the present type of complex for olefin polymerization.

(37) (a) Nomura, K.; Komatsu, T.; Imanishi, Y. *Macromolecules* **2000**, *33*, 8122. (b) Byun, D.-J.; Fudo, A.; Tanaka, A.; Fujiki, M.; Nomura, K. *Macromolecules* **2004**, *37*, 5520.

(38) As reported previously,[37] the resultant polymer generally consisted of (acetone-soluble) atactic polystyrene produced by MAO and (acetone-insoluble) syndiotactic polystyrene (SPS) prepared by the titanium catalyst. SPS was isolated as the acetone-insoluble fraction.

Table 6. Copolymerization of Ethylene with Norbornene (NBE) by Cp′TiCl$_2$[O-2-R^1-6-(R^{2}N═C)-C$_6$H$_3$]−MAO Catalyst Systems[a]

run	cat. (μmol)	NBE conc[b]/ mmol/mL	polymer yield/mg	activity[c]	NBE cont.[d]/ mol %	M_w[e] ×10^{-4}	M_w/M_n[e]
1	**1** (0.2)		118	3540		2.91	1.8
41	**1** (5.0)	0.50	359	431	<1.5	1.65	1.9
3	**2** (0.2)		212	6360		4.49	2.4
42	**2** (5.0)	0.20	351	421		1.84	2.3
43	**2** (5.0)	0.50	116	139	5.4	1.35	3.1
6	**3** (0.2)		282	8460		3.25	2.7
44	**3** (5.0)	0.20	227	272		1.82	2.7
45	**3** (5.0)	0.50	159	191	4.8	1.18	2.6
13	**6** (0.2)		44	132		109	3.1
46	**6** (2.0)	0.20	258	774	7.6	5.01	2.8
47	**6** (5.0)	0.50	621	745	28.1	4.32	2.4
48	**6** (5.0)	1.00	161	193	32.5	3.27	2.0
15	**7** (0.2)		81	243		224	3.00
49	**7** (5.0)	0.20	221	265	4.9	3.02	2.8
50	**7** (5.0)	0.50	178	214	10.1	2.87	2.4

[a] Cp′ = Cp* and R^1, R^2 = Me, 2,6-^{i}Pr$_2$C$_6$H$_3$ (**1**), ^{t}Bu, 2,6-^{i}PrC$_6$H$_3$ (**2**), Me, ^{t}Bu (**3**); Cp′, R^1 = Cp, Me and R^2 = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**6**), ^{t}Bu (**7**). Conditions: toluene 50 mL, MAO (prepared by removing AlMe$_3$ and toluene from PMAO) 3.0 mmol, ethylene 4 atm, 25 °C, 10 min. [b] Norbornene (NBE) concentration charged. [c] Activity in kg polymer/mol Ti·h. [d] NBE content (mol %) estimated by ^{13}C NMR spectra. [e] GPC data in *o*-dichlorobenzene vs polystyrene standards.

active species.[39,40] Taking into account the above results, the catalytic activity of a series of Cp′TiCl$_2$[O-2-R^1-6-(R^{2}N═CH)-C$_6$H$_3$]−MAO catalyst systems was highly affected by substituents in both the cyclopentadienyl and phenoxy-imine ligands.

4. Copolymerization of Ethylene with Norbornene and 1-Hexene by Cp′TiX$_2$[O-2-R^1-6-(R^{2}N═CH)C$_6$H$_3$] (1−7)−MAO Catalyst Systems. Copolymerizations of ethylene with norbornene (NBE) using a series of Cp′TiX$_2$[O-2-R^1-6-(R^2-NCH)C$_6$H$_3$] (**1**−**3**, **6** ,**7**)−MAO catalyst systems were conducted, because CpTiCl$_2$(N═C^{t}Bu$_2$) exhibited both remarkable catalytic activity and efficient NBE incorporation for ethylene/NBE copolymerization[41] and the activity as well as NBE incorporations were dependent upon the anionic donor ligand employed.[41] The results are summarized in Table 6.[42,43]

The catalytic activities of the Cp* analogues (**1**−**3**) significantly decreased in the presence of NBE; the resultant copolymers possessed low NBE content, suggesting that these complexes showed inefficient NBE incorporation. In contrast, the catalytic activities of the Cp analogues (**6**, **7**) increased or did not change in the presence of NBE (NBE 0.50 mmol/mL); **6** showed better NBE incorporation than **7** and the Cp* analogues (**1**−**3**) under the same conditions. These results clearly indicate that an efficient catalyst precursor for the ethylene copolymerization can be tuned to an efficient catalyst precursor for ethylene/NBE copolymerization by modification of both Cp′ and anionic donor ligands.[8b,41]

Table 7. Copolymerization of Ethylene with 1-Hexene by Cp′TiCl$_2$[O-2-R^1-6-(R^{2}N═C)C$_6$H$_3$]−MAO Catalyst Systems[a]

run	cat. (μmol)	polymer yield/mg	activity[b]	1-hexene content[c]	M_w[d] ×10^{-4}	M_w/M_n[d]
51	**1** (5.0)	189	227	3.2	0.79	2.9[e]
52	**2** (5.0)	146	175	2.7	0.56	2.9[e]
53	**3** (5.0)	184	221	2.2	0.39	2.3[e]
54	**5** (5.0)	43	52		0.4	2.5[e]

[a] Cp′ = Cp* and R^1, R^2 = Me, 2,6-^{i}Pr$_2$C$_6$H$_3$ (**1**), ^{t}Bu, 2,6-^{i}PrC$_6$H$_3$ (**2**), Me, ^{t}Bu (**3**); Cp′ = 1,2,4-Me$_3$C$_5$H$_2$ and R^1, R^2 = Me, 2,6-^{i}Pr$_2$C$_6$H$_3$ (**5**). Conditions: catalyst 5.0 μmol, toluene 40 mL, MAO (prepared by removing AlMe$_3$ and toluene from PMAO) 3.0 mmol, ethylene 4 atm, 25 °C, 10 min., 1-hexene, 0.2 mmol/mL. [b] Activity in kg polymer/mol Ti·h. [c] 1-Hexene content (mol %) estimated by ^{13}C NMR spectra. [d] GPC data in *o*-dichlorobenzene vs polystyrene standards. [e] Trace amount of high M_w shoulder (M_w = 263.4) was observed in the GPC trace.

The resultant copolymers especially prepared by the **6**−MAO catalyst system possessed rather high molecular weights with unimodal molecular weight distributions (runs 46−48); resonances corresponding to the isolated, alternating NBE sequences in addition to NBE dyads were observed in the ^{13}C NMR spectra for the resultant poly(ethylene-*co*-NBE)s.[43] The NBE incorporation by **6** was slightly less efficient than that by CpTiCl$_2$(N═C^t-Bu$_2$) [NBE 40.7−41.5 mol %[41] vs 32.5 mol % by **6** (run 48), ethylene 4 atm, NBE 1.00 mmol/mL], suggesting that **6** is suited as the catalyst precursor for efficient NBE incorporation. However, the activity decreased at high NBE concentration (run 48).

Copolymerization of ethylene with 1-hexene with the Cp* and 1,2,4-Me$_3$C$_5$H$_2$ analogues (**1**−**3**, **5**)−MAO catalyst systems was conducted, and the results are summarized in Table 7. The catalytic activities of the Cp* analogues−MAO catalyst systems decreased in the presence of 1-hexene (runs 51−53), and the resultant polymers possessed low molecular weights with rather broad molecular weight distributions. The 1-hexene contents in the resultant copolymers were low, suggesting that these complexes were not suited as the catalyst precursor for the copolymerization; the results are similar to that for CpTiCl$_2$[O-2,4-^{t}Bu$_2$-6-{(C$_6$F$_5$)N═CH}-C$_6$H$_2$] reported previously.[26a] The activity of the 1,2,4-Me$_3$C$_5$H$_2$ analogue (**5**) was low, and those of the Cp* analogues were higher than that of 1,2,4-Me$_3$C$_5$H$_2$.

In conclusion, we have prepared a series of Cp′TiCl$_2$[O-2-R^1-6-(R^{2}N═CH)C$_6$H$_3$] [Cp′ = Cp* (C$_5$Me$_5$) and R^1, R^2 = Me, 2,6-^{i}Pr$_2$C$_6$H$_3$ (**1**); ^{t}Bu, 2,6-^{i}Pr$_2$C$_6$H$_3$ (**2**); Me, ^{t}Bu (**3**); ^{t}Bu, ^{t}Bu

(39) Example of a mechanistic study concerning both styrene polymerization and propylene/styrene copolymerization: (a) Grassi, A.; Zambelli, A.; Laschi, F. *Organometallics* **1996**, *15*, 480−482. (b) Mahanthappa, M. K.; Waymouth, R. M. *J. Am. Chem. Soc.* **2001**, *123*, 12093−12904. (c) Minieri, G.; Corradini, P.; Guerra, G.; Zambelli, A.; Cavallo, L. *Macromolecules* **2001**, *34*, 5379−5385.

(40) Related mechanistic study concerning syndiospecific styrene polymerization and ethylene/styrene copolymerization: Zhang, H.; Byun, D.-J.; Nomura, K. *Dalton Trans.* **2007**, 1802.

(41) Nomura, K.; Wang, W.; Fujiki, M.; Liu, J. *Chem. Commun.* **2006**, 2659.

(42) Selected examples of copolymerization of ethylene with NBE using metallocenes and linked half-titanocene including an estimation of NBE content in the poly(ethylene-*co*-NBE)s: (a) Provasoli, A; Ferro, D. R.; Tritto, I.; Boggioni, L. *Macromolecules* **1999**, *32*, 6697. (b) Tritto, I.; Marestin, C.; Boggioni, L.; Zetta, L.; Provasoli, A.; Ferro, D. R. *Macromolecules* **2000**, *33*, 8931. (c) Tritto, I.; Marestin, C.; Boggioni, L.; Sacchi, M. C.; Brintzinger, H.-H.; Ferro, D. R. *Macromolecules* **2001**, *34*, 5770. (d) Tritto, I.; Boggioni, L.; Jansen, J. C.; Thorshaug, K.; Sacchi, M. C.; Ferro, D. R. *Macromolecules* **2002**, *35*, 616. (e) Thorshaug, K.; Mendichi, R.; Boggioni, L.; Tritto, I.; Trinkle, S.; Friedrich, C.; Mülhaupt, R. *Macromolecules* **2002**, *35*, 2903. (f) Tritto, I.; Boggioni, L.; Ferro, D. R. *Macromolecules* **2004**, ***37***, 9681.

(43) Selected ^{13}C NMR spectra for resultant poly(ethylene-*co*-NBE)s are shown in the Supporting Information.

(**4**); Cp′ = 1,2,4-$Me_3C_5H_2$ and R^1, R^2 = Me, 2,6-^{i}Pr$_2$C$_6$H$_3$ (**5**); Cp′ = Cp and R^1, R^2 = Me, 2,6-^{i}Pr$_2$C$_6$H$_3$ (**6**); Me, ^{t}Bu (**7**)], and the structures were determined by X-ray crystallography. The imino nitrogen atoms in **1**−**3** and **5**−**8** were not coordinated to Ti in all cases, and these are unique contrasts to those reported previously[25−28] and may suggest the presence of an equilibrium between coordination and dissociation of the nitrogen to Ti in the catalytic reaction. The bond angles for Ti−O−C(Ph) were affected by substituents in both the cyclopentadienyl and phenoxy-imine ligands. The catalytic activities for ethylene polymerization and syndiospecific styrene polymerization using **1**−**7**−MAO catalyst systems were highly affected by the substituents in both the cyclopentadienyl and the phenoxy-imine ligands; the Cp* analogues (**3**, **4**) exhibited remarkable catalytic activities for ethylene polymerization, whereas the Cp analogues (**6**, **7**) showed notable catalytic activities for syndiospecific styrene polymerization. The Cp analogue **6** showed efficient NBE incorporation in the ethylene/NBE copolymerizations, whereas the activities of the Cp* analogues decreased in the presence of NBE. These results suggest that efficient catalyst precursors for the desired (co)polymerizations can be tuned by modification (replacement) of the cyclopentadienyl fragment.

Experimental Section

General Procedures. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox unless otherwise specified. Anhydrous grade tetrahydrofuran, diethyl ether, hexane, dichloromethane, and toluene (Kanto Kagaku Co. Ltd) were transferred into a bottle containing molecular sieves (mixture of 3 Å and 4 Å 1/16, and 13X) under a nitrogen stream in the drybox and were used without further purification. $CpTiCl_3$ and Cp^*TiCl_3 were purchased from Strem Chemical Co., Ltd. Styrene of reagent grade (Kanto Kagaku Co. Ltd.) was stored in a freezer after passing through an alumina short column under nitrogen flow in the drybox. Ethylene for polymerization was of polymerization grade (purity >99.9%, Sumitomo Seika Co., Ltd.) and was used as received. Reagent grade $[PhN(H)Me_2][B(C_6F_5)_4]$ (Asahi Glass Co. Ltd.), and Al^{i}Bu$_3$ (Kanto Kagaku Co. Ltd.) were stored in the drybox and were used as received. Elemental analyses were performed by using a PE2400II Series (Perkin-Elmer Co.). Some analysis runs were employed twice to confirm the reproducibility in independent analysis/synthesis runs.

All ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz, ^{1}H). All deuterated NMR solvents were stored over molecular sieves under a nitrogen atmosphere, and all chemical shifts are given in ppm and are referenced to Me_4Si. ^{13}C NMR spectra for polyethylene and polystyrene were recorded on a JEOL JNM-LA400 spectrometer (100.40 MHz, ^{13}C) with proton decoupling. The pulse interval was 5.2 s, the acquisition time was 0.8 s, the pulse angle was 90°, and the number of transients accumulated was ca. 6000. The analysis samples of copolymers were prepared by dissolving polymers in a mixed solution of 1,2,4-trichlorobenzene/benzene-d_6 (90/10 wt), and the spectra were measured at 110 °C. The NBE contents in the resultant poly(ethylene-*co*-norbornene)s were estimated by the ^{13}C NMR spectra of copolymer according to the previous reports,[22,43] and the 1-hexene contents in poly(ethylene-*co*-1-hexene)s were also estimated according to the previous reports.[20,44]

Molecular weights and molecular weight distributions for the poly(ethylene-*co*-styrene)s were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) with a polystyrene gel column (TSK gel GMH_{HR}-H HT × 2, 30 cm × 7.8 mm i.d.), ranging from $<10^2$ to $<2.8 \times 10^8$ MW) at 140 °C using *o*-dichlorobenzene containing 0.05 wt/v% 2,6-di-*tert*-butyl-*p*-cresol as the solvent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples.

Synthesis of Cp*TiCl$_2$[O-2-Me-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N═CH}-C$_6$H$_3$] (1). Into a stirred Et_2O (10 mL) solution containing 2-Me-6-(2,6-^{i}Pr$_2$C$_6$H$_3$)N═CH−C$_6$H$_3$OH (443 mg, 1.5 mmol), *n*-BuLi (1.0 mL, 1.58 M in hexane, 1.0 equiv) was added dropwise at −30 °C. The reaction mixture was warmed slowly to room temperature and was stirred for 4 h. The solution was then chilled at −30 °C, and the chilled solution was added into a Et_2O solution containing Cp^*TiCl_3 (435 mg, 1.5 mmol) at −30 °C. The reaction mixture was then warmed slowly to room temperature and was stirred for an additional 14 h. The mixture was then filtered through a Celite pad, and the filter cake was washed with Et_2O (15 mL × 2). The combined filtrate and wash were taken to dryness under reduced pressure to give a red-orange solid. The solid was then dissolved in a minimum amount of CH_2Cl_2 layered by a small amount of hexane. The chilled solution gave red prism shaped microcrystals. Yield: 486 mg (59.1%). ^{1}H NMR ($CDCl_3$): δ 8.54 (s, 1H, −C*H*═N−), 7.04−7.21 (m, 6H, Ar-*H*), 3.05 (m, 2H, $(CH_3)_2CH$−), 2.22 (s, 3H, $CH_3C_6H_3$), 2.10 (s, 15H, $C_5(CH_3)_5$), 1.15 (d, 12H, J = 6.4 Hz, $(CH_3)_2CH$−). ^{13}C NMR ($CDCl_3$): δ 163.9, 156.9, 149.6, 137.1, 133.8, 133.4, 129.9, 126.4, 124.7, 123.8, 123.0, 122.6, 28.0, 23.0, 17.2, 13.1. Anal. Calcd for $C_{30}H_{39}Cl_2NOTi$: C, 65.70; H, 7.17; N, 2.55. Found: C, 65.41; H, 7.01; N, 2.49.

Synthesis of Cp*TiCl$_2$[O-2-^{t}Bu-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N═CH}-C$_6$H$_3$] (2). Synthesis of **2** was carried out by the same procedure as that for **1** except that Cp^*TiCl_3 (500 mg, 1.73 mmol) and 2-^{t}Bu-6-(2,6-^{i}Pr−C$_6$H$_3$N═CH)C$_6$H$_3$OH (403 mg, 1.73 mmol) in place of 2-Me-6-(2,6-^{i}Pr$_2$C$_6$H$_3$)N═CH−C$_6$H$_3$OH were used. Yield: 621 mg (60.8%). ^{1}H NMR ($CDCl_3$): δ 8.61 (s, 1H, −C*H*═N−), 7.47 (dd, 1H, Ar-*H*), 7.12−7.05 (m, 2H, Ar-*H*), 3.00 (m, 2H, $(CH_3)_3CH$−), 2.02 (s, 15H, $C_5(CH_3)_5$), 1.42 (s, 9H, $C(CH_3)_3$), 1.16 (d, J = 7.0 Hz, 12H, $(CH_3)_2CH$). ^{13}C NMR ($CDCl_3$): δ 165.4, 156.9, 149.2, 140.3, 137.2, 134.0, 130.1, 128.4, 125.7, 123.9, 122.9, 122.5, 35.3, 30.6, 28.0, 22.7, 13.2. Anal. Calcd for $C_{33}H_{45}Cl_2NOTi$: C, 67.12; H, 7.68; N, 2.37. Found: C, 67.01; H, 7.63; N, 2.28.

Synthesis of Cp*TiCl$_2$[O-2-Me-6-(^{t}BuN═CH)C$_6$H$_3$] (3). Synthesis of **3** was carried out by the same procedure as that for **1** except that Cp^*TiCl_3(579 mg, 2.0 mmol) and 2-Me-6-(^{t}BuN═CH)-C$_6$H$_3$OH (383 mg, 2.0 mmol) in place of 2-Me-6-(2,6-^{i}Pr$_2$C$_6$H$_3$)N═CH−C$_6$H$_3$OH were used. Yield: 476 mg (53.6%). ^{1}H NMR ($CDCl_3$): δ 8.67 (s, 1H, −C*H*═N−), 7.79 (dd, 1H, Ar-*H*), 7.14 (m, 1H, Ar-*H*), 6.94 (t, 1H, J = 7.7 Hz, Ar-*H*), 2.26 (s, 3H, $CH_3C_6H_3$), 2.17 (s,15H, $C_5(CH_3)_5$), 1.27 (s, 9H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 162.8, 151.2, 132.8, 132.2, 128.7, 127.6, 124.7, 122.9, 57.6, 29.6, 16.7, 12.8. Anal. Calcd for $C_{22}H_{31}Cl_2NOTi$: C, 59.48; H, 7.03; N, 3.15. Found: C, 59.40; H, 7.00; N, 3.10.

Synthesis of Cp*TiCl$_2$[O-2-^{t}Bu-6-(^{t}BuN═CH)C$_6$H$_3$] (4). Synthesis of **4** was carried out by the same procedure as that for **1** except that Cp^*TiCl_3(500 mg, 1.73 mmol) and 2-^{t}Bu-6-(^{t}BuN═CH)-C$_6$H$_3$OH (403 mg, 1.73 mmol) in place of 2-Me-6-(2,6-^{i}Pr$_2$C$_6$H$_3$)N═CH−C$_6$H$_3$OH were used. Yield: 438 mg (50.6%). ^{1}H NMR ($CDCl_3$): δ 8.70 (s, 1H, −C*H*═N−), 7.94 (d, 1H, J = 7.7 Hz, Ar-*H*), 7.33 (d, 1H, J = 7.7 Hz, Ar-*H*), 6.99 (t, 1H, J = 7.7 Hz, Ar-*H*), 2.12 (s, 15H, $C_5(CH_3)_5$), 1.37 (s, 9H, $C(CH_3)_3$), 1.28 (s, 9H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 164.5, 151.7, 138.9, 133.4, 129.4, 128.3, 125.9, 122.8, 57.9, 35.1, 30.4, 29.5, 13.03. Anal. Calcd for $C_{20}H_{27}Cl_2NOTi$: C, 57.71; H, 6.54; N, 3.37. Found: C, 57.62; H, 6.52; N, 3.35.

Synthesis of (1,2,4-Me$_3$C$_5$H$_2$)TiCl$_2$[O-2-Me-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)-N═CH}C$_6$H$_3$] (5). Synthesis of **5** was carried out by the same procedure as that for **1** except that (1,2,4-Me_3)$CpTiCl_3$ (392 mg, 1.50 mmol) was used. Yield: 443 mg (56.7%). ^{1}H NMR ($CDCl_3$):

(44) Assignments of resonances in the ^{13}C NMR spectra and estimation of 1-hexene content in poly(ethylene-*co*-1-hexene)s: Randall, J. C. *JMS Rev. Macromol. Chem. Phys.* **1989**, *C29* (2&3), 201.

Table 8. Crystal Data and Structure Refinement Parameters for Complexes 1, 2, 3, and 5

	1	2	3	5
empirical formula	$C_{30}H_{39}Cl_2NOTi$	$C_{33}H_{45}Cl_2NOTi$	$C_{22}H_{31}Cl_2NOTi$	$C_{28}H_{35}Cl_2NOTi$
fw	548.45	590.53	444.3	520.4
cryst color, habit	red, prism	red, prism	red, platelet	red, platelet
cryst size (mm)	0.80 × 0.80 × 0.36	0.80 × 0.80 × 0.60	0.80 × 0.80 × 0.25	0.80 × 0.42 × 0.30
cryst syst	monoclinic	orthorhombic	triclinic	monoclinic
space group	*Cc* (#9)	*Pbca* (#61)	$P\bar{1}$ (#2)	$P2_1/c$ (#14)
a (Å)	23.967(10)	18.083(3)	7.405(3)	14.914(5)
b (Å)	8.126(4)	15.268(3)	9.169(5)	15.886(5)
c (Å)	15.972(6)	23.643(5)	17.929(10)	24.206(10)
α (deg)			80.16	
β (deg)	107.487(18)		82.88(2)	104.932(12)
γ (deg)			72.895(19)	
volume (Å^3)	2966.9(20)	6527.4(22)	1142.8(9)	5541.3(34)
Z	4	8	2	8
D_{calc} (g/cm^3)	1.228	1.202	1.291	1.247
$F_{(000)}$	1160.00	2512.00	468.00	2192.00
no. of reflns measd	14 169	57 211	11 291	47 817
no. of observns	5737	5108	4093	7236
no. of variables	355	388	275	665
goodness-of-fit	1.024	1.007	1.003	1.001
residuals: R_1; wR_2	0.0335; 0.0873	0.0370; 0.0976	0.0541; 0.1142	0.0669; 0.1310

δ 8.58 (s, 1H, −C*H*═N−), 7.13−7.07 (m, 6H, Ar-*H*), 6.17 (s, 2H, C_5H_2), 2.96 (m, 2H, 2(CH_3)$_3$C*H*−), 2.34 (s, 3H, C$H_3C_6H_3$), 2.16 (s, 6H, C_5(CH_3)$_2$), 2.08 (s, 3H, C_5(CH_3)), 1.16 (d, *J* = 6.9 Hz, 12H, 2(CH_3)$_2$CH). ^{13}C NMR ($CDCl_3$): *δ* 165.8, 157.1, 149.4, 137.3, 135.7, 135.3, 133.9, 129.4, 126.2, 125.0, 124.0, 123.6, 122.9, 121.9, 27.9, 23.3, 17.2, 16.1, 14.6. Anal. Calcd for $C_{28}H_{35}Cl_2NOTi$: C, 64.63; H, 6.78; N, 2.69. Found: C, 64.63; H, 6.90; N, 2.64.

Synthesis of CpTiCl$_2$[O-2-Me-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N═CH}C$_6$H$_3$] (6). Synthesis of **6** was carried out by the same procedure as that for **1** except that $CpTiCl_3$ (262 mg, 1.2 mmol) and 2-Me-6-(2,6-^{i}Pr$_2$C$_6$H$_3$)N═CH−C$_6$H$_3$OH (354 mg, 1.20 mmol) were used. Yield: 407 mg (70.9%). ^{1}H NMR ($CDCl_3$): *δ* 8.54 (s, 1H, −C*H*═N−), 8.01 (d, 1H, *J* = 6.2 Hz Ar-*H*), 7.35−7.09 (m, 5H, Ar-*H*), 6.66 (s, 5H, C_5H_5), 2.97 (m, 2H, 2(CH_3)$_2$C*H*−), 2.35 (s, 3H, C$H_3C_6H_3$), 1.17 (d, *J* = 7.0 Hz, 12H, 2(CH_3)$_2$CH−). ^{13}C NMR ($CDCl_3$) *δ*: 167.1, 157.7, 149.3, 137.1, 133.9, 128.1, 125.4, 124.7, 123.9, 122.7, 121.0, 27.8, 23.2, 16.8. Anal. Calcd for $C_{25}H_{29}Cl_2NOTi$: C, 62.78; H, 6.11; N, 2.93. Found (1): C, 62.70; H, 6.01; N, 2.90. Found (2): C, 62.68; H, 5.99; N, 2.87.

Synthesis of CpTiCl$_2$[O-2-Me-6-(^{t}BuN═CH)C$_6$H$_3$] (7). Synthesis of **7** was carried out by the same procedure as that for **1** except that $CpTiCl_3$(327 mg, 1.50 mmol) and 2-Me-6-(^{t}BuNCH)-C$_6$H$_3$OH (287 mg, 1.5 mmol) in place of 2-Me-6-(2,6-^{i}Pr$_2$C$_6$H$_3$)N═CH−C$_6$H$_3$OH were used. Yield: 407 mg (72.5%). ^{1}H NMR ($CDCl_3$): *δ* 8.66 (s, 1H, −C*H*═N−), 7.75 (d, 1H, *J* = 7.7 Hz, Ar-*H*), 7.19 (d, 1H, *J* = 7.3 Hz, Ar-*H*), 7.01 (t, 1H, *J* = 7.5 Hz, Ar-*H*), 6.66 (s, 5H, C_5H_5), 2.27 (s, 3H, C$H_3C_6H_3$), 1.31 (s, 9H, C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$): *δ* 167.1, 151.5, 132.3, 127.3, 126.5, 124.6, 124.2, 121.0, 57.7, 29.6, 16.7. Anal. Calcd for $C_{17}H_{21}Cl_2NOTi$: C, 54.58; H, 5.66; N, 3.74. Found: C, 54.15; H, 5.62; N, 3.50.

Synthesis of Cp*TiMe$_2$[O-2-Me-6-{(2,6-^{i}Pr−C$_6$H$_3$)N═CH}-C$_6$H$_3$] (8). Into a stirred solution of Cp*$TiMe_3$ (114 mg, 0.5 mmol) in dry *n*-hexane (20 mL) 2-Me-6-{(2,6-^{i}Pr−C_6H_3)N═CH}C_6H_3-OH (148 mg, 0.5 mmol) was added dropowise at −30 °C. The reaction mixture was warmed slowly to room temperature and was stirred for 4 h. The mixture was then filtered through a Celite pad, and the filter cake was washed with hexane (10 mL × 2). The combined filtrate and wash were taken to dryness under reduced pressure to give a yellow solid. Yield: 234 mg (92%). ^{1}H NMR (C_6D_6): *δ* 8.78 (s, 1H, −C*H*═N−), 8.62 (d, 1H, *J* = 7.7 Hz, Ar-*H*), 7.21−6.97 (m, 5H, Ar-*H*), 3.34 (t, H, *J* = 6.8 Hz, (CH_3)$_3$C*H*−), 2.21 (s, 3H, C$H_3C_6H_3$), 1.67 (s, 15H, C_5(CH_3)$_5$), 1.32 (d, 12H, *J* = 7.0 Hz, (CH_3)$_2$CH−), 0.73 (s, 6H, Ti−CH_3). ^{13}C NMR (C_6D_6): *δ* 168.4, 165.2, 161.8, 159.5, 152.6, 140.7, 135.0, 130.5, 127.1, 126.2, 125.4, 124.5, 124.0, 123.9, 122.4, 57.4, 28.3, 24.1, 18.3, 12.4. Anal. Calcd for $C_{32}H_{45}NOTi$: C, 75.72; H, 8.94; N, 2.76. Found: C, 75.86; H, 9.06; N, 2.75.

Reaction of Cp*TiMe$_2$[O-2-Me-6-{(2,6-^{i}Pr-C$_6$H$_3$)N═CH}-C$_6$H$_3$] (8) with [PhN(H)Me$_2$][B(C$_6$F$_5$)$_4$]. A solution of **8** (31 mg, 0.061mmol) in bromobenzene-d_5 was added dropwise to a solution of [PhN(H)Me_2][$B(C_6F_5)_4$] (56 mg, 0.061mmol) in bromobenzene-d_5 at −30 °C. The resulting mixture was shaken and was then transferred into a Young's Teflon NMR tube to measure the NMR spectroscopic data at room temperature (25 °C). ^{1}H NMR (C_6D_5Br): *δ* 8.64 (s, 1H, −C*H*═N−), 7.36−6.57 (m, 11H, Ar-*H*), 2.84 (s, 2H, (CH_3)$_3$C*H*−), 2.62 (s, 6H, NMe_2), 2.01 (s, 3H, C$H_3C_6H_3$), 1.43 (s, 15H, C_5(CH_3)$_5$), 1.28 (d, 3H, *J* = 6.6 Hz, (CH_3)$_2$-CH−), 1.12 (d, 3H, *J* = 6.6 Hz, (CH_3)$_2$CH−), 0.93 (s, 3H, Ti-*Me*), 0.12 (s, 3H, CH_4). ^{19}F NMR (C_6D_5Br): *δ* −133.37, −163.85, −167.66.

Crystallographic Analysis. All measurements were made on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo Kα radiation. All structures were solved by direct methods and expanded using Fourier techniques,[45] and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the Crystal Structure[46,47] crystallographic software package. Selected crystal collection parameters are summarized in Tables 8 and 9.

Polymerization of Ethylene. Ethylene polymerizations were conducted in toluene by using a 100 mL scale autoclave. Solvent (29.0 mL) and MAO as a white solid (174 mg, 3.0 mmol), prepared by removing toluene and $AlMe_3$ from commercially available MAO (PMAO-S, Tosoh Finechem Co.), were charged into the autoclave in the drybox, and the apparatus was placed under ethylene atmosphere (1 atm). After the addition of a toluene solution (1.0 mL) containing a prescribed amount of **1** via a syringe, the reaction apparatus was pressurized to 3 atm (total 4 atm), and the mixture was stirred magnetically for 10 min. After the above procedure, ethylene was purged, and the mixture was then poured into EtOH (150 mL) containing HCl (10 mL). The resultant polymer was collected on a filter paper by filtration and was adequately washed

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Table 9. Crystal Data and Structure Refinement Parameters for Complexes 6, 7, and 8

	6	7	8
empirical formula	$C_{25}H_{29}Cl_2NOTi$	$C_{17}H_{21}Cl_2NOTi$	$C_{32}H_{45}NOTi$
fw	478.32	374.16	507.61
cryst color, habit	red, prism	orange, prism	yellow, block
cryst syst	orthorhombic	monoclinic	monoclinic
space group	*Pbca* (#61)	$P2_1/a$ (#14)	*Cc* (#9)
a (Å)	13.129(4)	13.556(6)	24.043(3)
b (Å)	14.930(3)	7.224(3)	8.1281(8)
c (Å)	24.791(6)	18.814(7)	16.5418(17)
β (deg)		102.982(18)°	108.631(3)°
volume (Å^3)	4859.3(20)	1795.2(12)	3063.2(6)
Z	8	4	4
D_{calc} (g/cm^3)	1.308	1.384	1.101
$F_{(000)}$	2000.00	776.00	1096.00
cryst size (mm)	0.80 × 0.60 × 0.60	0.80 × 0.70 × 0.50	0.80 × 0.80 × 0.60
no. of reflns measd	43 760	16 760	11 753
no. of observns	5515	3493	3483
no. of variables	300	220	361
goodness-of-fit on F^2	1.013	0.999	0.999
residuals: R_1; wR_2	0.0443; 0.0973	0.0259; 0.0798	0.0364; 0.0828

with EtOH and then dried *in vacuo*. Polymerization results in Table 4 are data at the optimized Al/Ti molar ratios.

Syndiospecific Polymerization of Styrene. Toluene (19 mL), styrene (10 mL), and the MAO solid (174 mg, 3.0 mmol) were added into the autoclave (100 mL scale stainless steel) in the drybox, and the reaction apparatus was then replaced and filled with nitrogen at room temperature (25 °C). A toluene solution (1.0 mL) containing a prescribed amount of **1** was then added into the autoclave. The mixture was magnetically stirred for 10 min, and the mixture was then poured into EtOH (50 mL) containing HCl (5 mL). The resultant polymer was collected on a filter paper by filtration and was adequately washed with EtOH and then dried *in vacuo*. According to a previous report,[21] the resultant polymer mixture was separated into two fractions, and atactic polystyrene prepared only by MAO itself was extracted with acetone; syndiotactic polystyrene prepared by **1**−MAO catalyst was isolated as the acetone-insoluble fraction.

Copolymerization of Ethylene with Norbornene and 1-Hexene. Experimental procedures for the copolymerization of ethylene with norbornene were the same as those for the ethylene polymerization described above except that a prescribed amount of norbornene was added into the autoclave. Experimental procedures for the ethylene/1-hexene polymerizations were the same as those for the ethylene polymerizations except that a prescribed amount of 1-hexene was charged and the total volume of toluene and 1-hexene was set to 40 or 50 mL.

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Supporting Information Available: CIF files for complexes $Cp^*TiCl_2[O\text{-}2\text{-}R^1\text{-}6\text{-}(R^2N{=}CH)C_6H_3]$ [R^1, R^2 = Me, 2,6-^{i}Pr$_2$C$_6$H$_3$ (**1**), ^{t}Bu, 2,6-^{i}PrC$_6$H$_3$ (**2**), Me, ^{t}Bu (**3**)], $(1,2,4\text{-}Me_3C_5H_2)TiCl_2[O\text{-}2\text{-}Me\text{-}6\text{-}\{(2,6\text{-}^iPrC_6H_3)N{=}CH\}C_6H_3]$ (**5**), $CpTiCl_2[O\text{-}2\text{-}R^1\text{-}6\text{-}(R^2N{=}CH)C_6H_3]$ [R^1, R^2 = Me, 2,6-^{i}Pr$_2$C$_6$H$_3$ (**6**), Cp, Me, ^{t}Bu (**7**)], and $Cp^*TiMe_2[O\text{-}2\text{-}Me\text{-}6\text{-}\{(2,6\text{-}^iPr_2C_6H_3)N{=}CH\}C_6H_3]$ (**8**). ^{1}H and ^{19}F NMR spectrum for reaction of **8** with 1.0 equiv of $[PhN(H)Me_2][B(C_6F_5)_4]$, ^{13}C NMR spectra for poly(ethylene-co-NBE)s and poly(ethylene-*co*-1-hexene)s, and the structure reports for **1**−**3** and **5**−**8**. These materials are available free of charge via the Internet at http://pubs.acs.org.

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