ORGANOMETALLICS

Article

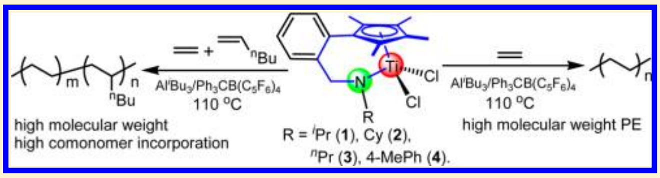
pubs.acs.org/Organometallics

New Titanium(IV) Complexes with 2-Cyclopentadienylbenzylamido Ligands: Synthesis, Characterization, and Catalytic Properties for Ethylene Polymerization and Copolymerization with 1-Hexene

Xin Tao, Qiaolin Wu, Hang Huo, Wei Gao, and Ying Mu*

The State Key Laboratory for Supramolecular Structure and Materials, School of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, People's Republic of China

Supporting Information

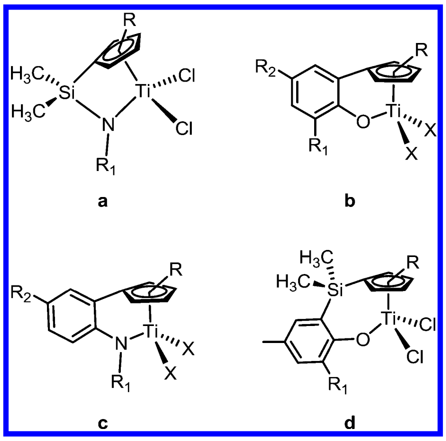


ABSTRACT: A series of new half-sandwich titanium(IV) complexes chelated with 2-(tetramethylcyclopentadienyl)-benzylamido ligands, 2-Me$_4$CpC$_6$H$_4$CH$_2$(R)NTiCl$_2$ (R = ^{i}Pr (**1**), Cy (**2**), ^{n}Pr (**3**), 4-MePh (**4**)), have been synthesized from the chlorotrimethylsilane elimination reactions of TiCl$_4$ with the double-trimethylsilyl-substituted preligands 2-Me$_4$(TMS)-CpC$_6$H$_4$CH$_2$(R)N(TMS) (R = ^{i}Pr (TMS$_2$**L1**), Cy (TMS$_2$**L2**), ^{n}Pr (TMS$_2$**L3**), 4-MePh (TMS$_2$**L4**)). The free ligands H$_2$**L1**−H$_2$**L4** were synthesized by reduction of the corresponding imine compounds 2-Me$_4$CpHC$_6$H$_4$CH═NR with LiAlH$_4$, while the imine compounds were formed in situ by a condensation reaction of 2-tetramethylcyclopentadienylbenzaldehyde with the corresponding amine. The free ligands were characterized by LC-MS and ^{1}H NMR spectroscopy, and the titanium complexes were characterized by ^{1}H and ^{13}C NMR, elemental analyses, and single-crystal X-ray crystallography. The X-ray crystallography analysis reveals that these titanium complexes possess a three-legged piano-stool geometry with the amide N atom in a mitered six-membered chelating ring and the two chloride atoms as the legs. The angle between the cyclopentadienyl plane and the attached phenyl plane in these complexes (59.2, 62.7, and 61.9° for complexes **1**, **2**, and **4**, respectively) is much less than 90° in the solid state. Upon activation with Al^{i}Bu$_3$ and Ph$_3$CB(C$_6$F$_5$)$_4$, complexes **1**−**4** exhibit reasonable catalytic activity for ethylene homopolymerization and copolymerization with 1-hexene at 110 °C, producing high-molecular-weight polyethylenes and poly(ethylene-*co*-1-hexenes) with relatively high comonomer incorporation. Complex **4** was found to show higher catalytic activity for ethylene/1-hexene copolymerization than complexes **1**−**3** under similar conditions, while complexes **1**−**3** produce poly(ethylene-*co*-1-hexenes) with higher comonomer incorporation.

■ INTRODUCTION

Group 4 metallocene catalysts have attracted extensive interest in the past decades due to their unique properties and advantages as olefin polymerization catalysts.[1−5] Many research efforts have been focused on the development of new homogeneous metallocene catalysts for producing a variety of high-performance polyolefin materials and understanding the relationship between the structure and their catalytic property of a type of catalyst with respect to polymer chain composition and architecture.[6−9] Since the so-called constrained-geometry titanium complexes were reported to exhibit excellent catalytic performance in the copolymerization of ethylene with α-olefins,[10−12] a variety of monocyclopentadienyltitanium complexes with a chelating side arm containing a nitrogen, oxygen, or phosphorus donor have been developed.[13−17] Several typical titanium complexes of this type are shown in Chart 1. The silylene-bridged Cp-amido titanium complexes **a**, the typical constrained-geometry catalysts, have been known to show several advantages over the bis(cyclopentadienyl) metallocene catalysts in thermal stability, high α-olefin incorporation, and producing high molecular weight polymers in the ethylene/α-olefin copolymerization.[14] The cyclopentadienyl-phenoxytitanium complexes **b** were reported to exhibit high catalytic activity and α-olefin incorporation for ethylene/α-olefin copolymerization but produce polymers with low molecular weights due to their too open coordination environment.[15] The *o*-phenylene-bridged Cp-amido titanium complexes **c**[16] and the

Chart 1. Typical Monocyclopentadienyl Titanium Complexes with a Chelating Side Arm



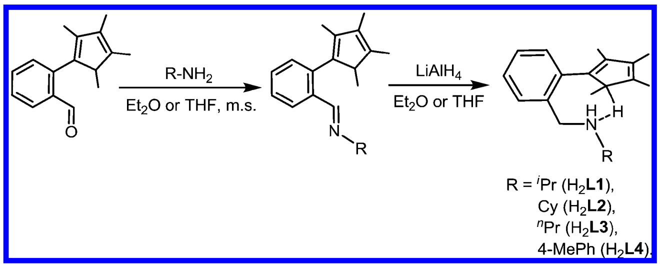
Received: May 5, 2013

so-called PHENICS complexes **d** (phenoxy induced complex of Sumitomo),[17] with more crowded coordination environments in both cases, were reported to show good catalytic activity and efficient comonomer incorporation in ethylene/*α*-olefin copolymerization and produce polymers with relatively high molecular weights. It is therefore of interest to develop analogous titanium(IV) complexes with more bulky ligands and explore their catalytic performance for ethylene/*α*-olefin copolymerization. We have recently synthesized a number of new titanium(IV) complexes of the type 2-$Me_4CpC_6H_4CH_2(R)NTiCl_2$ (R = ^{i}Pr (**1**), Cy (**2**), ^{n}Pr (**3**), 4-MePh (**4**)) and found that they show good catalytic activity for ethylene/1-hexene copolymerization at 110 °C and produce high-molecular-weight poly(ethylene-*co*-1-hexenes) with high comonomer incorporation. In this paper we report the synthesis and characterization of these complexes and their catalytic performance in ethylene polymerization and ethylene/1-hexene copolymerization.

■ RESULTS AND DISCUSSION

Synthesis of Ligands. The free ligands 2-$Me_4CpHC_6H_4CH_2(R)NH$ (R = ^{i}Pr (H_2**L1**), Cy (H_2**L2**), ^{n}Pr (H_2**L3**), 4-MePh (H_2**L4**)) were synthesized in high yields (about 60−70%) by a two-step procedure: a condensation reaction of 2-(tetramethylcyclopentadienyl)benzaldehyde with the corresponding amine derivatives[18] followed by reduction of the formed imine compounds with $LiAlH_4$, as illustrated in Scheme 1. The imine compounds were directly reduced in aprotic solvent (Et_2O or THF) without isolation due to their poor stability. H_2**L1** and H_2**L3** were synthesized from reactions carried out in Et_2O, while the sterically bulkier free ligands H_2**L2** and H_2**L4** could only be obtained from reactions carried out in THF in high yields, presumably due to the relatively good solubility of $LiAlH_4$ in THF. These free ligands were characterized by LC-MS and ^{1}H NMR spectroscopy. LC-MS shows that these compounds were obtained in about 95% purity, and the [M + H] ions were clearly observed. The ^{1}H NMR spectra of all free ligands show mainly three singlets and one doublet for the CpCH_3 protons and one quartet for the Cp*H* proton, indicating that these compounds exist in the form of one major isomer. In addition, the two methylene protons of PhCH_2 in these free ligands are magnetically inequivalent and show two sets of doublets in their ^{1}H NMR spectra. These results might be explained by the formation of a C−H···N hydrogen bond between the acidic H atom of the Cp ring and the nitrogen atom.[19] Similar results have also been observed for related 2-(tetramethylcyclopentadienyl)phenol[15] and 2-(tetramethylcyclopentadienyl)-*N*,*N*-dimethylaniline[19] derivatives, and the C−H···N hydrogen bond has been confirmed by single-crystal X-ray crystallography in the latter case.

Scheme 1. Synthetic Route for the Free Ligands H_2L1−H_2L4

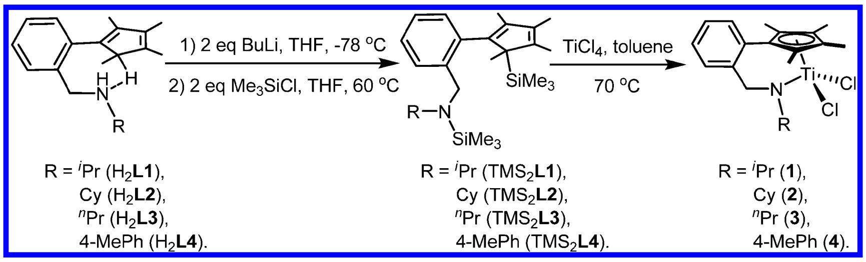


Synthesis of Complexes. The new titanium complexes **1**−**4** were synthesized in moderate yields (35−50%) from the chlorotrimethylsilane elimination reactions[20] of $TiCl_4$ with the double-trimethylsilyl-substituted preligands 2-Me_4(TMS)-$CpC_6H_4CH_2(R)N(TMS)$ (R = ^{i}Pr (TMS_2**L1**), Cy (TMS_2**L2**), ^{n}Pr (TMS_2**L3**), 4-MePh (TMS_2**L4**)), as shown in Scheme 2. The double-trimethylsilyl-substituted preligands were synthesized by treatment of the corresponding free ligands with 2 equiv of *n*-BuLi and 2 equiv of Me_3SiCl sequentially in THF. Crude preligands TMS_2**L1**−TMS_2**L4** were obtained after removal of the formed LiCl by filtration and used directly for the chlorotrimethylsilane elimination reaction without further purification due to their poor stability. The titanium complexes **1**−**4** were purified by recrystallization from CH_2Cl_2/hexane. These complexes are fairly soluble in CH_2Cl_2 and toluene and slightly soluble in petroleum ether and hexane. They were all characterized by ^{1}H and ^{13}C NMR spectroscopy along with elemental analyses, and the structures of complexes **1**, **2**, and **4** were confirmed by X-ray crystallography.

The ^{1}H NMR spectra of complexes **1**−**4** all show two sets of singlets for the CpCH_3 protons and one singlet for the PhCH_2 protons. In comparison with the corresponding signals of their free ligands, the signals observed for the methine protons of the ^{i}Pr group in complex **1** and the methine protons of the Cy group in complex **2** shift downfield from 2.54−2.64 and 2.19−2.29 ppm to 5.82−5.95 and 5.37−5.46 ppm, respectively. Similarly, the signal of NCH_2Et protons in complexes **3** shifts downfield from 2.39−2.43 to 4.25−4.30 ppm. The ^{1}H and ^{13}C NMR spectroscopic analysis of these complexes confirms that the N atom and the Cp ring have been attached to the titanium metal center of these complexes, and all complexes are C_s-symmetric in solution.

Crystallographic Analysis of Complexes 1, 2, and 4. The molecular structures of complexes **1**, **2**, and **4** were determined by single-crystal X-ray diffraction analysis. The molecular structures of these complexes with the atom-numbering schemes are shown in Figures 1−3, and selected bond lengths and angles are given in Table 1. Crystallographic data indicate that crystals of complexes **2** and **4** belong to the monoclinic system and $P2_1/n$ space group, while complex **1**

Scheme 2. Synthetic Route for Complexes 1−4



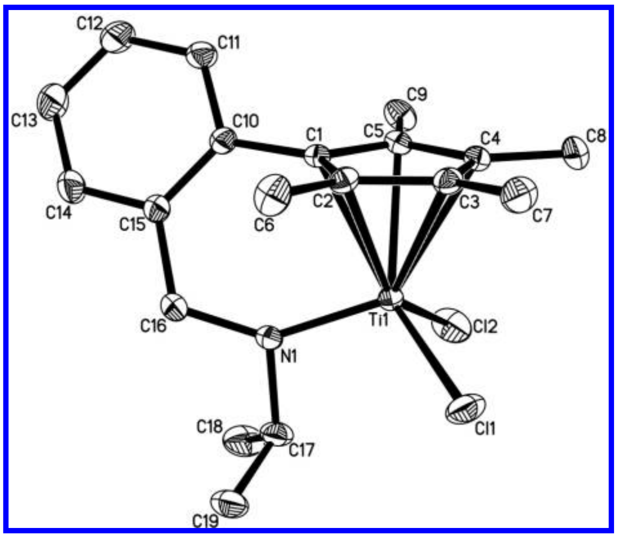


Figure 1. Perspective view of **1** with thermal ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity.

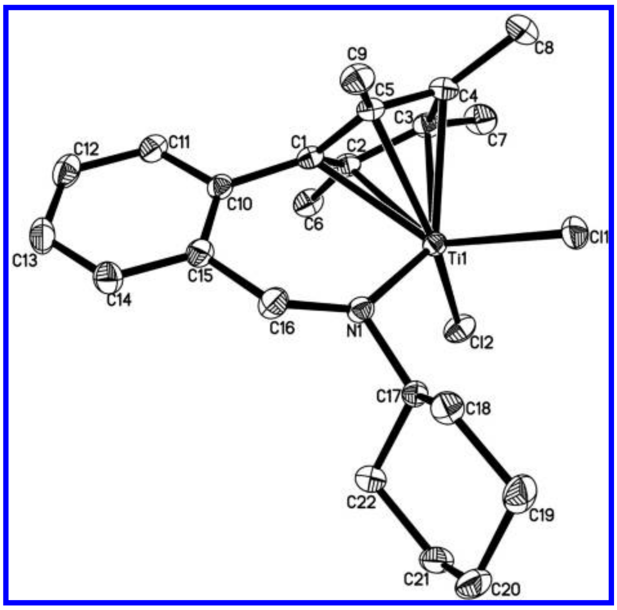


Figure 2. Perspective view of **2** with thermal ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity.

crystallizes in the monoclinic system and $C2/c$ space group. All three complexes possess a three-legged piano-stool geometry with a distorted-octahedral coordination environment around the central titanium atom. As can be seen from their crystal structures, the coordination of the nitrogen atom to the central metal in these complexes builds a six-membered chelating ring in a position approximately vertical to the cyclopentadienyl ring. The six-membered chelating ring, together with the group at the nitrogen atom, constructs a relatively crowded coordinating environment surrounding the central titanium atom. The Ti−N distances in complexes **1**, **2**, and **4** (1.868(15) Å for **1**, 1.869(16) Å for **2**, and 1.895(15) Å for **4**) are slightly shorter than those observed for complexes **a** (1.901−1.907 Å)[21] and **c** (1.900−1.923 Å)[16] in Chart 1. Complex **4** has the longest Ti−N bond distance among these complexes, which is reasonable, since the amido N atom with the 4-methylphenyl group in complex **4** has relatively poor electron-donating ability in comparison to those in complexes **1** and **2**. The Ti−N bond distances in these complexes are all shorter than the estimated value (2.02 Å) for a Ti−N single bond according to Pauling's covalent radii,[22] demonstrating a Ti═N double-bond character. The Ti−Cl bond distances (2.276−2.305 Å) in these complexes are in agreement with those observed for related N- or O-functionalized cyclopentadienyl titanium dichloride complexes.[14−17,21] Ti−Cp(cent) distances are close to each other for complexes **1** (2.020 Å), **2** (2.019 Å), and **4** (2.023 Å). Similarly, the $\mathrm{Ti{-}C_{Cp}}$(av) (av = average) distances (2.353 Å for **1**, 2.354 Å for **2**, and 2.357 Å for **4**) are also close to each other. In these complexes, the individual $\mathrm{Ti{-}C_{Cp}}$ bond distances range from 2.321 to 2.376 Å, with the Ti−C3 and Ti−C4 distances (2.3755(18) and 2.3726(18) Å for **1**, 2.3688(19) and 2.3762(18) Å for **2**, and 2.3744(18) and 2.3681 Å for **4**) being obviously longer than the remaining $\mathrm{Ti{-}C_{Cp}}$ bond lengths (average 2.3386, 2.3411, and 2.3470 Å for **1**, **2**, and **4**, respectively), indicating that the central titanium atom is not located exactly below the center of the Cp ring due to the coordination of the amido N atom. The N−Ti−Cp(cent) angles of complexes **1**, **2**, and **4** (110.5° for **1** and **4** and 110.4° for **2**) are obviously larger than those observed in the known N-functionalized titanocene complexes **a** (107.0−107.6°)[21] and **c** (104.6−106.1°),[16] which is indicative of these complexes possessing a more crowded coordinating environment surrounding the central titanium atom than the reported similar complexes. The two N−Ti−Cl angles (104.9(5) and 106.4(5)° for **1**, 105.7(5) and 107.0(5)° for **2**, and 105.0(5) and 109.3(5)° for **4**) in each complex are different, since these complexes are not C_s-symmetric in the solid state, with the angles between the Cp plane and the attached phenyl plane (59.2° for **1**, 62.7° for **2**, and 61.9° for **4**) being much less than the 90° of ideal C_s-symmetric molecules. The Cl−Ti−Cl angles (104.3(3)° for **1**, 103.8(2)° for **2**, and 102.3(2)° for **4**) change in the order **1** > **2** > **4**. In addition, the sum of the bond angles around the amido nitrogen atom is 359.6° for **1**, 359.4° for **2**, and 358.9° for **4**, respectively, indicating π donation of an electron pair onthe N atom to the titanium through sp^2 hybridization. These structural features may affect their catalytic performance by influencing the rate of olefin molecule coordination to the titanium atom and insertion into the

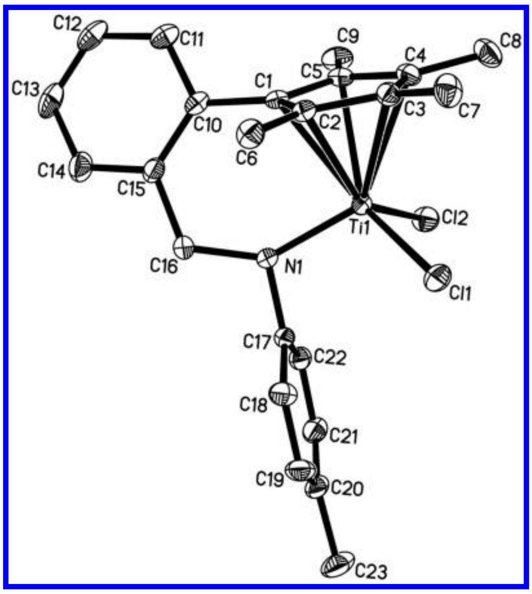


Figure 3. Perspective view of **4** with thermal ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for Complexes 1, 2, and 4

	1	**2**	**4**
Ti(1)−N(1)	1.868(15)	1.869(16)	1.895(15)
Ti(1)−Cl(1)	2.301(6)	2.297(6)	2.276(6)
Ti(1)−Cl(2)	2.302(6)	2.305(6)	2.295(6)
Ti(1)−C_{Cp} (range)	2.321(17)−2.376(18)	2.328(17)−2.376(18)	2.334(17)−2.374(18)
Ti(1)−C_{Cp} (av)	2.353	2.354	2.357
Ti(1)−Cp(cent)	2.020	2.019	2.023
C(16)−N(1)	1.458(2)	1.463(2)	1.474(2)
C(17)−N(1)	1.493(2)	1.480(2)	1.451(2)
Cl(1)−Ti(1)−Cl(2)	104.32(3)	103.82(2)	102.34(2)
N(1)−Ti(1)−Cl(1)	104.88(5)	105.74(5)	105.00(5)
N(1)−Ti(1)−Cl(2)	106.36(5)	106.95(5)	109.27(5)
Cp(cent)−Ti−N(1)	110.5	110.4	110.5
C(16)−N(1)−Ti(1)	140.93(13)	141.81(12)	140.34(12)
C(17)−N(1)−Ti(1)	104.84(12)	103.49(11)	108.02(11)
C(16)−N(1)−C(17)	113.84(15)	114.09(15)	110.51(14)
N(1)−C(16)−C(15)	115.66(16)	114.85(17)	115.66(16)
Cp∠Ph[a]	59.2	62.7	61.9

[a] Angle between a cyclopentadienyl plane and an attached phenyl plane.

growing polymer chain, as well as the rate of the polymer chain termination.

Table 2. Summary of Ethylene Polymerization Catalyzed by 1−4/$\mathrm{Al}^i\mathrm{Bu}_3$/$\mathrm{Ph_3CB(C_6F_5)_4}$ Systems[a]

entry	cat.	Al/Ti	temp (°C)	yield (g)	activity[b]	M_η[c] ($\times10^4$)	T_m[d] (°C)
1	**1**	120	110	0.41	820	92.6	139.2
2	**1**	150	110	0.68	1360	82.8	139.8
3	**1**	180	110	0.85	1700	78.2	140.1
4	**1**	210	110	0.79	1580	73.6	138.5
5	**1**	240	110	0.61	1220	63.2	138.9
6	**1**	180	80	0.71	1420	96.5	140.4
7	**2**	180	110	1.39	2780	85.7	140.1
8	**2**	180	80	1.26	2520	102.6	139.6
9	**3**	180	110	0.58	1160	65.4	137.2
10	**3**	180	80	0.41	820	82.3	138.0
11	**4**	180	110	1.78	3560	101.1	141.3
12	**4**	180	80	1.66	3320	116.4	141.1

[a] Polymerization conditions: solvent, 60 mL of toluene; catalyst, 2×10^{-6} mol; B/Ti molar ratio, 1.5; ethylene pressure, 5 bar; time, 15 min. [b] In units of kg of PE (mol of Ti)$^{-1}$ h^{-1}. [c] Measured in decahydronaphthalene at 135 °C. [d] Determined by DSC at a heating rate of 10 °C min^{-1}.

Polymerization. Ethylene polymerizations using complexes **1**−**4** as precatalysts under different conditions were examined, and the results are summarized in Table 2. Upon activation with $\mathrm{Al}^i\mathrm{Bu}_3$ and $\mathrm{Ph_3CB(C_6F_5)_4}$, complexes **1**−**4** all exhibit moderate catalytic activity for the ethylene polymerization reaction. Under similar conditions, the catalytic activity decreases in the order **4** > **2** > **1** > **3**, which indicates that the catalytic activity of these complexes is notably influenced by the nature of the substituents on their amido N atoms. As is known for group 4 metallocene catalysts, electron-donating substituents on the ligands stabilize the catalytically active cationic species during the polymerization and improve the catalytic activity of the catalyst; bulky ligands weaken the interaction between the catalytically active cationic species and the anionic cocatalyst[15b,c,23] and therefore could increase the catalytic activity of the catalyst as well. The fact that the catalytic activity of complex **4** with a bulkier but less electron donating **L4** ligand is higher than that of complex **2** with a less bulky but more electron-donating **L2** ligand further demonstrates the importance of the steric effect of the ligand. As observed in other olefin polymerization catalyst systems, the catalytic activity of these titanium catalyst systems is dependent on the Al/Ti molar ratio. The maximum catalytic activity data were obtained at Al/Ti molar ratios of about 180. The catalytic performance of these catalyst systems was also examined at different polymerization temperatures (80 and 110 °C), and relatively high catalytic activities were observed at 110 °C, demonstrating good thermal stability of these catalyst systems. It was found that the molecular weight of the resultant polyethylenes is remarkably dependent on the structure of the catalyst, with the highest molecular weight polyethylenes being produced by catalyst **4**, due probably to the relatively large steric hindrance of its ligand in the chain-transfer reaction.[24] The influence of the Al/Ti molar ratio and the polymerization temperature on the polymer molecular weight was also investigated. As expected, the molecular weight of the obtained polyethylenes decreases with the increase in Al/Ti molar ratio and the elevation in polymerization temperature due to the acceleration of both the chain transfer reaction to alkylaluminum and the β-hydride elimination reaction. In addition, the melting temperature of the resultant polyethylenes (137.2−141.3 °C) is in the normal range for linear polyethylene.

Copolymerization reactions of ethylene with 1-hexene using complexes **1**−**4** as precatalysts, activated with $\mathrm{Al}^i\mathrm{Bu}_3$ and $\mathrm{Ph_3CB(C_6F_5)_4}$, were also explored, and the experimental results are summarized in Table 3. As observed in the ethylene homopolymerization, the catalytic activity of these catalyst systems for the ethylene/1-hexene copolymerization under similar conditions also changes in the order **4** > **2** > **1** > **3**. It is worth noting that the catalytic activity data of these catalytic systems for most copolymerization reactions are higher than those observed for the ethylene homopolymerization reactions due to the comonomer effect. The comonomer effect for these catalyst systems can be clearly seen from the data in Table 3. Similar results have previously been observed in the ethylene/1-hexene copolymerization reaction with other half-sandwich titanium(IV) catalyst systems.[23,25] The obtained poly(ethylene-

Table 3. Summary of Ethylene/1-Hexene Copolymerization Catalyzed by 1−4/Al^iBu_3/$Ph_3CB(C_6F_5)_4$ Systems[a]

entry	cat.	amt of 1-hexene (mol/L)	yield (g)	activity[b]	1-hexene content[c] (mol %)	M_w[d] ($\times10^4$)	M_w/M_n[d]
13	**1**	0.5	0.69	1380	14.7	13.16	3.13
14	**1**	1.0	0.91	1820	21.4	11.88	3.48
15	**1**	1.5	0.76	1520	30.0	9.71	3.92
16	**2**	0.5	0.82	1640	12.6	15.56	2.61
17	**2**	1.0	1.43	2860	19.5	13.90	2.88
18	**2**	1.5	1.05	2010	27.9	10.24	3.11
10	**3**	0.5	0.22	440	13.8	9.16	2.63
20	**3**	1.0	0.34	680	20.6	8.74	2.96
21	**3**	1.5	0.27	540	28.7	8.19	3.13
22	**4**	0.5	2.18	4360	3.6	22.98	2.48
23	**4**	1.0	2.59	5180	5.3	21.58	2.67
24	**4**	1.5	2.32	4640	7.9	21.33	2.98

[a] Polymerization conditions: toluene + 1-hexene, total 60 mL; catalyst, 2×10^{-6} mol; Al/Ti molar ratio, 180; B/Ti molar ratio, 1.5; time, 15 min; temperature, 110 °C; ethylene pressure, 5 bar. [b] In units of kg of polymer (mol of Ti)$^{-1}$ h^{-1}. [c] Calculated on the basis of ^{13}C NMR spectra. [d] Measured by GPC analysis.

co-1-hexenes) were analyzed by ^{13}C NMR and GPC. The ^{13}C NMR spectra for typical copolymer samples are shown in the Supporting Information. On the basis of the ^{13}C NMR analysis,[26] the comonomer content in the poly(ethylene-*co*-1-hexenes) was calculated and the data are given in Table 4. It can be seen from these results that the comonomer incorporation ability of these catalyst systems is evidently dependent on the structure of the catalyst. The comonomer contents of the copolymers obtained with complexes **1**−**3** are quite high, being comparable to those produced by similar N- or O-functionalized titanocene catalyst systems under similar conditions.[16a,17f] In comparison, complex **4** produces copolymers with relatively low comonomer contents due probably to the relatively large steric hindrance of its ligand. It has been known that the comonomer incorporation ability of a catalyst system can be affected by several factors. In the present work, the steric bulk of the ligands in these complexes seems to be a major issue. A large steric hindrance from the ligands would block the coordination of the comonomer to the metal center of the catalyst. Table 4 summarizes the monomer sequence distribution and the r_Er_H values for typical poly(ethylene-*co*-1-hexene) samples estimated on the basis of ^{13}C NMR spectroscopy. The calculated r_Er_H values of about 0.2 imply that the 1-hexene incorporation in the present system does not proceed in a random manner as observed in the constrained-geometry catalyst systems.[27] GPC analysis on the copolymers reveals that the poly(ethylene-*co*-1-hexenes) produced by these catalysts possess relatively high molecular weights (M_w = (8−23) × 10^4) in comparison to those formed by similar catalyst systems[16a,17f] and that the molecular weight distribution is basically unimodal and narrow, being characteristic for metallocene polyolefins. The aforementioned capability of the new catalyst systems to efficiently catalyze the copolymerization of ethylene with α-olefins and produce high-molecular-weight copolymers with high comonomer incorporation is just what is required for this type of catalyst.

■ CONCLUSION

A series of new titanium(IV) complexes with chelated 2-(tetramethylcyclopentadienyl)benzylamido ligands, 2-$Me_4CpC_6H_4CH_2(R)NTiCl_2$, have been synthesized from the reactions of $TiCl_4$ with the double-trimethylsilyl-substituted preligands 2-$Me_4(TMS)CpC_6H_4CH_2(R)N(TMS)$. The free ligands H_2**L1**−H_2**L4** can be synthesized by reduction of the corresponding in situ formed imine compounds 2-$Me_4CpHC_6H_4CH{=}NR$ with $LiAlH_4$. ^{1}H NMR spectroscopic analysis indicates that the free ligands exist mainly in one form of their three isomers due to the formation of a C−H···N hydrogen bond between the acidic H atom of the Cp ring and the nitrogen atom. X-ray crystallographic analysis demonstrates that the half-metallocene titanium(IV) complexes adopt a pseudo-octahedral coordination environment, with the N atom bonding to the Ti metal center. Upon activation with Al^iBu_3 and $Ph_3CB(C_6F_5)_4$, complexes **1**−**4** exhibit moderate catalytic activity for ethylene homopolymerization and copolymerization with 1-hexene at 110 °C, producing high-molecular-weight polyethylenes and poly(ethylene-*co*-1-hexenes) with high comonomer incorporation. Complex **4** shows a higher catalytic activity for ethylene/1-hexene copolymerization than complexes **1**−**3** under similar conditions, while complexes **1**−**3** produce poly(ethylene-*co*-1-hexenes) with higher comonomer incorporation.

■ EXPERIMENTAL SECTION

All manipulations involving air- and/or moisture-sensitive compounds were carried out under a nitrogen atmosphere (ultrahigh purity) using either standard Schlenk techniques or glovebox techniques. Toluene, diethyl ether, THF, and *n*-hexane were distilled under nitrogen in the presence of sodium and benzophenone. CH_2Cl_2 and 1-hexene were purified by distilling over calcium hydride before use. 2-(Tetramethylcyclopentadienyl)benzaldehyde[18] and $Ph_3CB(C_6F_5)_4$ were prepared according to literature procedures. Polymerization grade ethylene was further purified by passage through columns of 5 Å molecular sieves and MnO. Al^iBu_3, *n*-BuLi, TMSCl, $LiAlH_4$, and $TiCl_4$

Table 4. Monomer Sequence Distributions for Poly(ethylene-co-1-hexenes) Obtained with the 1−4/Al^iBu_3/$Ph_3CB(C_6F_5)_4$ Systems[a]

			triad[c] (%)						dyad[d] (%)			
entry	cat.	content of 1-hexene (mol %)[b]	EEE	EEH + HEE	HEH	EHE	EHH + HHE	HHH	EE	EH + HE	HH	r_Er_H[e]
13	**1**	14.7	64.8	11.7	trace	23.5	trace	trace	70.7	29.3	trace	
15	**1**	30.0	32.9	21.3	2.8	36.0	7.0	trace	43.6	52.9	3.5	0.22
18	**2**	27.9	37.6	18.5	2.3	36.1	5.5	trace	46.9	50.4	2.7	0.20
21	**3**	28.7	36.7	18.1	2.6	36.3	6.4	trace	45.7	51.1	3.2	0.22
24	**4**	7.9	80.6	7.2	trace	12.2	trace	trace	84.2	15.8	trace	

[a] For polymerization condition,: see Table 3. [b] 1-Hexene content in mol % estimated on the basis of ^{13}C NMR spectra. [c] Calculated by ^{13}C NMR spectra. [d] [EE] = [EEE] + $^1/_2$[EEH + HEE], [EH + HE] = [HEH] + [EHE] + $^1/_2${[EEH + HEE] + [HHE+EHH]}, [HH] = [HHH] + $^1/_2$[HHE +EHH]. [e] r_Er_H = 4[EE][HH]/[EH + HE].[2]

were purchased from Aldrich or Acros. ^{1}H and ^{13}C NMR spectra were measured using a Varian Mercury-300 NMR spectrometer. ^{13}C NMR spectra of the copolymers were recorded on a Varian Unity-400 NMR spectrometer at 135 °C with o-$C_6D_4Cl_2$ as the solvent. LC-MS were recorded on a DIONEX Ultimate 3000 liquid chromatograph and a Bruker HCT mass spectrometer in ESI mode. The molecular weight of the polyethylenes was measured in decahydronaphthalene at 135 °C by a Ubbelohde viscometer according to the following equation: $[\eta] = (6.77 \times 10^{-4})M_{\eta}^{0.67}$. Molecular weights and molecular weight distributions of the copolymer samples were measured on a PL-GPC 220 instrument at 150 °C with 1,2,4-trichlobenzene as the eluent. The melting points of the polymers were measured by differential scanning calorimetry (DSC) on a NETZSCH DSC 204 instrument at a heating/cooling rate of 10 °C/min from 35 to 160 °C, and the data from the second heating scan were used.

Synthesis of 2-$Me_4CpHC_6H_4CH_2(^{i}Pr)NH$ (H_2L1). To a solution of 2-(2,3,4,5-tetramethylcyclopentadienyl)benzaldehyde (2.26 g, 10.0 mmol) in absolute diethyl ether (30 mL) were added isopropylamine (0.591 g, 10.0 mmol), 4 Å molecular sieves (MS), and formic acid (2 drops), and the mixture was stirred at room temperature under a nitrogen atmosphere. After the disappearance of the aldehyde was confirmed by ^{1}H NMR spectroscopy, the molecular sieves were filtered off. To the solution was slowly added $LiAlH_4$ at 0 °C, and the reaction mixture that formed was warmed to room temperature and stirred for 1 h under a nitrogen atmosphere. After the reaction mixture changed color from orange to colorless, the reaction was quenched with 1 mL of water and the insoluble solids were filtered off. Further 3 M NaOH (1 mL) and H_2O (3 mL) were added to the filtrate, and the product was extracted with diethyl ether. The organic layer was dried over anhydrous $MgSO_4$, and the solvent was evaporated under reduced pressure. The obtained oily substance was purified by silica gel chromatography to give the pure product (1.76 g, 6.54 mmol, 65.4%) as a colorless oily substance. ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ 7.43−6.95 (m, 4H, ArH), 3.62 (d, J = 13.2 Hz, 1H, ArCH_2N), 3.57 (d, J = 13.2 Hz, 1H, ArCH_2N), 2.77−2.65 (m, 1H, CpH), 2.64−2.54 (m, 1H, NCH($CH_3)_2$), 1.88 (s, 3H, CpCH_3), 1.70 (s, 3H, CpCH_3), 1.55 (s, 3H, CpCH_3), 1.13 (d, J = 7.5 Hz, 3H, CpCH_3), 0.94 (d, J = 6.2 Hz, 6H, NCH(C$H_3)_2$) ppm. MS: m/z 270 [M + H].

Synthesis of 2-$Me_4CpHC_6H_4CH_2$(Cy)NH (H_2L2). Compound H_2**L2** was synthesized in the same manner as for H_2**L1** with cyclohexylamine (0.991 g, 10.0 mmol) as starting material. However, this reaction was carried out in absolute THF. The pure product (1.91 g, 6.18 mmol, 61.8%) was obtained as a colorless oily substance. ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ 7.43−6.96 (m, 4H, ArH), 3.64 (d, J = 13.2 Hz, 1H, ArCH_2N), 3.59 (d, J = 13.2 Hz, 1H, ArCH_2N), 2.75−2.64 (m, 1H, CpH), 2.29−2.19 (tt, J = 10.1, 3.6 Hz, 1H, NCH in Cy), 1.88 (s, 3H, CpCH_3), 1.70 (s, 3H, CpCH_3), 1.55 (s, 3H, CpCH_3), 1.13 (d, J = 7.7 Hz, 3H, CpCH_3), 1.75−0.90 (m, 10H, NCHC$_5H_{10}$) ppm. MS: m/z 310 [M + H].

Synthesis of 2-$Me_4CpHC_6H_4CH_2(^{n}Pr)NH$ (H_2L3). Compound H_2**L3** was synthesized in the same manner as for H_2**L1** with propylamine (0.59 g, 10.0 mmol) as starting material. The pure product (1.81 g, 6.72 mmol, 67.2%) was obtained as a colorless oily substance. ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ 7.40−6.99 (m, 4H, ArH), 3.62 (d, J = 13.5 Hz, 1H, ArCH_2N), 3.57 (d, J = 13.5 Hz, 1H, ArCH_2N), 2.75−2.68 (m, 1H, CpH), 2.43−2.39 (t, J = 6.0 Hz, 2H, NC$H_2C_2H_5$), 1.87 (s, 3H, CpCH_3), 1.69 (s, 3H, CpCH_3), 1.54 (s, 3H, CpCH_3), 1.49−1.34 (m, 2H, NCH$_2$CH_2CH$_3$), 1.13 (d, J = 9 Hz, 3H, CpCH_3), 0.86−0.81 (t, J = 6.0 Hz, 3H, N(CH$_2)_2$CH_3) ppm. MS: m/z 270 [M + H].

Synthesis of 2-$Me_4CpHC_6H_4CH_2$(4-MePh)NH (H_2L4). Compound H_2**L4** was synthesized in the same manner as for H_2**L2** with 4-methylaniline (1.07 g, 10.0 mmol) as starting material. The pure product (2.03 g, 6.39 mmol, 63.9%) was obtained as a colorless oily substance. ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ 7.77−6.92 (m, 8H, ArH), 3.94 (d, J = 13.2 Hz, 1H, ArCH_2N), 3.79 (d, J = 13.2 Hz, 1H, ArCH_2N), 2.75−2.68 (m, 1H, CpH), 2.36 (s, 3H, ArCH_3), 1.88 (s, 3H, CpCH_3), 1.71 (s, 3H, CpCH_3), 1.56 (s, 3H, CpCH_3), 1.12 (d, J = 7.5 Hz, 3H, CpCH_3) ppm. MS: m/z 318 [M + H].

Synthesis of Complex 1. To a solution of free ligand H_2**L1** (1.35 g, 5.00 mmol) in 20 mL of THF was added dropwise a solution of n-butyllithium (5.43 mL, 10.0 mmol) in n-hexane at −78 °C. The reaction mixture was warmed to room temperature and stirred for 3 h. Trimethylsilyl chloride (1.27 mL, 10.0 mmol) was added, and the mixture was then heated at 60 °C for 5 h. The solvents were removed under reduced pressure, and the residue was redissolved in toluene (20 mL). The LiCl precipitate was filtered off, and the solution was slowly added to a solution of $TiCl_4$ (0.55 mL, 5.00 mmol) in toluene (30 mL) at room temperature. The reaction mixture was stirred at room temperature for 1 h and then at 70 °C overnight. The precipitate was filtered off, and the solvent was removed under reduced pressure to leave an orange residue. Recrystallization from CH_2Cl_2/hexane gave pure product **1** (0.938 g, 48.6%) as orange crystals. Anal. Calcd for $C_{19}H_{25}Cl_2NTi$ (385.08): C, 59.09; H, 6.53; N, 3.63. Found: C, 59.19; H, 6.62; N, 3.71. ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ 7.42−7.34 (m, 4H, ArH), 5.95−5.82 (m, 1H, NCH(CH$_3)_2$), 4.55 (s, 2H, ArCH_2N), 2.27 (s, 6H, CpCH_3), 1.85 (s, 6H, CpCH_3), 1.21 (d, J = 6.1 Hz, 6H, NCH(C$H_3)_2$) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): δ 141.7, 131.1, 130.6, 130.5, 128.3, 128.2, 127.4, 127.1, 57.7, 49.7, 18.4, 13.6, 13.2 ppm.

Synthesis of Complex 2. Complex **2** was synthesized in the same way as described above for the synthesis of complex **1** with the ligand H_2**L2** (1.55 g, 5.00 mmol), n-BuLi (5.43 mL, 10.0 mmol), Me_3SiCl (1.27 mL, 10.0 mmol), and $TiCl_4$ (0.55 mL, 5 mmol) as starting materials. Pure **2** (0.848 g, 39.8%) was obtained as yellow crystals. Anal. Calcd for $C_{22}H_{29}Cl_2NTi$ (425.12): C, 61.99; H, 6.86; N, 3.29. Found: C, 62.11; H, 6.97 ; N, 3.36. ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ 7.44−7.30 (m, 4H, ArH), 5.46−5.37 (tt, J = 10.2, 3.3 Hz, 1H, NCHC$_5$H$_{10}$), 4.57 (s, 2H, ArCH_2N), 2.27 (s, 6H, CpCH_3), 1.84 (s, 6H, CpCH_3), 1.91−1.08 (m, 10H, NCHC$_5H_{10}$) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): δ 141.8, 131.0, 130.6, 128.2, 128.1, 127.7, 127.4, 127.1, 59.2, 57.9, 28.9, 26.9, 25.9, 13.6, 13.2 ppm.

Synthesis of Complex 3. Complex **3** was synthesized in the same way as described above for the synthesis of complex **1** with the ligand H_2**L3** (1.35 g, 5.00 mmol), n-BuLi (5.43 mL, 10.0 mmol), Me_3SiCl (1.27 mL, 10.0 mmol), and $TiCl_4$ (0.55 mL, 5 mmol) as starting materials. Pure **3** (0.679 g, 35.2%) was obtained as dark red crystals. Anal. Calcd for $C_{19}H_{25}Cl_2NTi$ (385.08): C, 59.09; H, 6.53; N, 3.63. Found: C, 59.21; H, 6.48; N, 3.74. ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ 7.43−7.28 (m, 4H, ArH), 4.64 (s, 2H, ArCH_2N), 4.30−4.25 (t, J = 7.5 Hz, 2H, NC$H_2C_2H_5$), 2.27 (s, 6H, CpCH_3), 1.86 (s, 6H, CpCH_3), 1.68−1.56 (m, 2H, NCH$_2$CH_2CH$_3$), 1.03−0.99 (t, J = 7.5 Hz, 3H, N(CH$_2)_2$CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): δ 141.4, 137.2, 130.7, 128.3, 128.1, 127.9, 127.4, 127.2, 65.4, 56.2, 21.4, 20.8, 13.6, 13.2 ppm.

Synthesis of Complex 4. Complex **4** was synthesized in the same way as described above for the synthesis of complex **1** with the ligand H_2**L4** (1.59 g, 5.00 mmol), n-BuLi (5.43 mL, 10.0 mmol), Me_3SiCl (1.27 mL, 10.0 mmol), and $TiCl_4$ (0.55 mL, 5 mmol) as starting materials. Pure **4** (0.827 g, 38.2%) was obtained as orange crystals. Anal. Calcd for $C_{23}H_{25}Cl_2NTi$ (433.08): C, 63.62; H, 5.80; N, 3.23. Found: C, 63.77; H, 5.89; N, 3.38. ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ7.46−7.16 (m, 8H, ArH), 4.93 (s, 2H, ArCH_2N), 2.37 (s, 3H, NArCH_3), 2.29 (s, 6H, CpCH_3), 2.05 (s, 6H, CpCH_3) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): δ 148.4, 141.3, 137.9, 132.4, 130.7, 130.4, 130.3, 129.7, 128.4, 127.5, 127.4, 127.3, 71.6, 21.5, 13.9, 13.6 ppm.

X-ray Crystallographic Studies. The crystals were mounted on glass fibers using an oil drop. Data obtained with the $\omega-2\theta$ scan mode were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved using direct methods,[28] and further refinements with full-matrix least squares on F^2 were obtained with the SHELXTL program package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms. All calculations were performed using the SHELXTL crystallographic software packages.[29]

Polymerization Reaction. The ethylene polymerization experiments were carried out as follows: a dry 250 mL steel autoclave with a magetic stirrer was charged with 60 mL of toluene, thermostated at the desired temperature, and saturated with ethylene (1.0 atm). The polymerization reaction was started by addition of a mixture of catalyst and Al^{i}Bu$_3$ in toluene (5 mL) and a solution of Ph$_3$CB(C$_6$F$_5$)$_4$ in toluene (5 mL) at the same time. The vessel was pressurized to 5 atm with ethylene immediately, and the pressure was kept by continuous feeding of ethylene. The reaction mixture was stirred at the desired temperature for 15 min. The polymerization was then quenched by injecting acidified ethanol containing HCl (3 M). The polymer was collected by filtration, washed with water and ethanol, and dried to a constant weight under vacuum. For the ethylene/1-hexene copolymerization experiments, appropriate amounts of 1-hexene were added in toluene.

■ ASSOCIATED CONTENT

Supporting Information

Figures giving ^{13}C NMR spectra for typical copolymer samples and CIF files giving X-ray crystallographic data for complexes **1**, **2**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Y.M.: tel, (86)-431-85168376; fax, (86)-431-85193421; e-mail, ymu@jlu.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research work was supported by the National Natural Science Foundation of China (Nos. 21074043, 51173061, and 21274050).

■ REFERENCES

(1) Kaminsky, W.; Sinn, H. *Transition Metals and Organometallics for Catalysts for Olefin Polymerization*; Springer: New York, 1988.

(2) Natta, G.; Pino, P.; Giannini, U. *J. Am. Chem. Soc.* **1957**, *79*, 2975.

(3) Halterman, R. L. *Chem. Rev.* **1992**, *92*, 965.

(4) Möhring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1.

(5) (a) Nomura, K. *Dalton Trans.* **2009**, *41*, 8811. (b) Nomura, K.; Liu, J.; Padmanabhan, S.; Kitiyanan, B. *J. Mol. Catal. A: Chem.* **2007**, *267*, 1.

(6) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.

(7) Kaminsky, W. *Macromol. Chem . Phys.* **1996**, *197*, 3907.

(8) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587.

(9) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 428.

(10) Stevens, J. C.; Timmers, F. J.; Wilson, D. R.; Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. W.; Lai, S. (Dow Chemical Co.) Eur. Patent Appl. EP 416 815-A2, 1991.

(11) Canich, J. M. (Exxon Chemical Co.) Eur. Patent Appl. EP 420 436-A1, 1991.

(12) (a) Shapiro, P. J.; Bunel, E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867. (b) Okuda, J. *Chem. Ber.* **1990**, *123*, 1649.

(13) (a) Bredeau, S.; Altenhoff, G.; Kunz, K.; Döring, S.; Grimme, S.; Kehr, G.; Erker, G. *Organometallics* **2004**, *23*, 1836. (b) Kunz, K.; Erker, G.; Döring, S.; Fröhlich, R.; Kehr, G. *J. Am. Chem. Soc.* **2001**, *123*, 6181.

(14) (a) Irwin, L. J.; Miller, S. A. *J. Am. Chem. Soc.* **2005**, *127*, 9972. (b) Grandini, C.; Camurati, I.; Guidotti, S.; Mascellani, N.; Resconi, L.; Nifant'ev, I. E.; Kashulin, I. A.; Ivchenko, P. V.; Mercandelli, P.; Sironi, A. *Organometallics* **2004**, *23*, 344. (c) De Rosa, C.; Auriemma, F.; Ruiz de Ballesteros, O.; Resconi, L.; Fait, A.; Ciaccia, E.; Camurati, I. *J. Am. Chem. Soc.* **2003**, *125*, 10913. (d) Klosin, J.; Kruper, W. J., Jr.; Nickias, P. N.; Roof, G. R.; De Waele, P.; Abboud, K. A. *Organometallics* **2001**, *20*, 2663. (e) Wang, C.; Erker, G.; Kehr, G.; Wedeking, K.; Fröhlich, R. *Organometallics* **2005**, *24*, 4760. (f) Gibson, V. C.; Spitzmesser, S . K. *Chem. Rev.* **2003**, *103*, 283.

(15) (a) Zhang, Y.; Mu, Y.; Lu, C.; Li, G.; Xu, J.; Zhang, Y.; Zhu, D.; Feng, S. *Organometallics* **2004**, *23*, 540. (b) Chen, Y.-X.; Fu, P.-F.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 5958. (c) Chen, Y. X.; Marks, T. J. *Organometallics* **1997**, *16*, 3649.

(16) (a) Cho, D. J.; Wu, C. J.; S, S.; Han, W.-S.; Kang, S. O.; Lee, B. Y. *Organometallics* **2006**, *25*, 2133. (b) Wu, C. J.; Lee, S. H.; Yu, S. T.; Na, S. J.; Yun, H.; Lee, B. Y. *Organometallics* **2008**, *27*, 3907. (c) Wu, C. J.; Lee, S. H.; Yun, H.; Lee, B. Y. *Organometallics* **2007**, *27*, 6685.

(17) (a) Katayama, H.; Nabika, M.; Imai, A.; Miyashita, A.; Watanabe, T.; Johoji, H.; Oda, Y.; Hanaoka, H. (Sumitomo) PCT Appl. WO 97/03992, 1997. (b) Imai, A.; Ogawa, A.; Takei, A.; Nishiyama, T.; Johoji, H. MetCon2000, 2000. (c) Imai, A.; Katayama, H.; Nabika, M.; Watanabe, T. MetCon2001, 2001. (d) Imai, A.; Johoji, H.; Hozumi, H.; Nishiyama, T. MetCon2002, 2002. (e) Hanaoka, H.; Hino, T.; Souda, H.; Yanagi, K.; Oda, Y.; Imai, A. *J. Organomet. Chem.* **2007**, *692*, 4059. (f) Nabika, M.; Katayama, H.; Tsuyoshi, W.; Hiroshi, K.; Yanagi, K.; Imai, A. *Organometallics* **2009**, *28*, 3785. (g) Senda, T.; Hanaoka, H.; Okada, Y.; Oda, Y.; Tsurugi, H.; Mashima, K. *Organometallics* **2009**, *28*, 6915.

(18) Zhang, L.; Gao, W.; Tao, X.; Wu, Q.; Mu, Y.; Ye, L. *Organometallics* **2011**, *30*, 433.

(19) Enders, M.; Ludwig, G.; Pritzkow, H. *Organometallics* **2001**, *20*, 827.

(20) Christie, S. D. R.; Man, K. W.; Whitby, R. J. *Organometallics* **1999**, *18*, 348.

(21) Carpenetti, D. W.; Kloppenburg, L.; Kupec, J. T.; Petersen, J. L. *Organometallics* **1996**, *15*, 1572.

(22) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(23) Liu, K.; Wu, Q.; Gao, W.; Mu, Y.; Ye, L. *Eur. J. Inorg. Chem.* **2011**, *12*, 1901.

(24) (a) Zhang, F.; Mu, Y.; Zhao, L.; Zhang, Y.; Bu, W.; Chen, C.; Zhai, H.; Hong, H. *J. Organomet. Chem.* **2000**, *613* (1), 68. (b) Zhang, F.; Mu, Y.; Wang, J.; Shi, Z.; Bu, W.; Hu, S.; Zhang, Y.; Feng, S. *Polyhedron* **2000**, *19*, 1941.

(25) Zhang, Y.; Wang, J.; Mu, Y.; Shi, Z.; Lv, C.; Zhang, Y.; Qiao, L.; Feng, S. *Organometallics* **2003**, *22*, 3877.

(26) Randall, J. C. *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **1989**, *C29* (2&3), 201.

(27) (a) Devore, D. D.; Timmers, F. J.; Hasha, D. L.; Rosen, R. K.; Marks, T. J.; Deck, P. A.; Stern, C. L. *Organometallics* **1995**, *14*, 3132. (b) Suhm, J.; Schneider, M. J.; Mülhaupt, R. *J. Mol. Catal. A: Chem.* **1998**, *128*, 215.

(28) Sheldrick, G. M. *SHELXTL, Version 5.1*; Siemens Industrial Automation, Inc., 1997.

(29) *SMART and SAINT software packages*; Siemens Analytical X-ray instruments, Inc., Madison, WI, 1996.