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Syntheses of 2,5-Dimethylcyclopentadienyl *ansa*-Zirconocene Complexes and Their Reactivity for Ethylene/Norbornene Copolymerization

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C1-bridged and Me_2Si-bridged 2,5-dimethylcylcopentadienyl *ansa*-zirconocene complexes, $[Me(H)C(C_5H_4)(2,5\text{-}Me_2C_5H_2)]ZrCl_2$ (**6**), $[(CH_3CH_2CH_2)(H)C(C_5H_4)(2,5\text{-}Me_2C_5H_2)]ZrCl_2$ (**9**), $[(Me)(H)C(2,5\text{-}Me_2C_5H_2)_2]ZrCl_2$ (**13**), and $[Me_2Si(2,5\text{-}Me2C_5H_2)_2]ZrCl_2$ (**15**), are prepared by using 2-bromo-3-methoxy-2,5-dimethylcyclopentene (**7**) as a starting material. Solid structures of **6** and **13** were determined by X-ray crystallography. The C1-bridged zirconocene complexes **6**, **9**, and **13** are highly active for ethylene/norbornene copolymerization with high incorporation of norbornene, while the Me_2Si-bridged complex **15** shows relatively low activity. Complex **9** shows the highest activity and the highest incorporation of norbornene among the complexes, but the molecular weight of the obtained polymer is relatively low.

Introduction

The development of modified group 4 metallocene catalysts for olefin polymerization remains an active research area in both academic and industrial fields.[1] One of the merits of these metallocene-based catalysts is that the activity, the comonomer incorporation, and the polymer microstructure can be controlled by tuning the ligand structure.[2] The relationship between the tacticity and the symmetry of the metallocene complexes has been well established in propylene polymerization.[3] Recently, the electronic effects of some substituents on the properties of metallocene complexes have been reported.[4] Numerous metallocene complexes of group 4 having various substituent patterns have been synthesized and tested as catalysts for polymerization of olefins. Some changes in the ligand structure have, in some cases, a dramatic effect not only on activity but also on the microstructure of the obtained polyolefins. For example, the catalyst obtained from $Me_2Si(Me_4C_5)$-(NtBu)$TiCl_2$ (CGC) is highly active for ethylene/α-olefin copolymerization, whereas the corresponding catalyst obtained from $Me_2Si(Cp)(N\textit{t}Bu)TiCl_2$ is sluggish.[5]

We have been interested in *ansa*-metallocene complexes that have two α-methyl substituents as shown below. By placing the two methyl substituents proximal to the bridgehead carbon, the π-donor ability of the cyclopentadienyl ring can be enhanced without increasing the steric hindrance at the active site. Complex **1** was synthesized by a lengthy synthetic route (five steps) from 1,4-pentadiyne, which is not readily available, with overall low yield (6.8%).[6] Later, we developed a synthetic route for 6-alkyl(or aryl)-1,4-dimethylfulvene, and complexes **2**−**4** were successfully prepared using the fulvenes.[7] In some polymerizations, a dramatic effect of the methyl substituents was observed. In the ethylene/norbornene copolymerization, complex **1** shows excellent activity with excellent incorporation of norbornene, whereas the corresponding complex lacking the methyl substituents, $Me(H)C(Cp)_2ZrCl_2$, shows low activity with high norbornene incorporation.[8] Herein, we report

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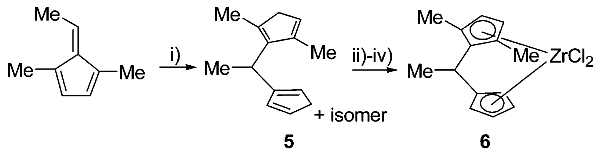
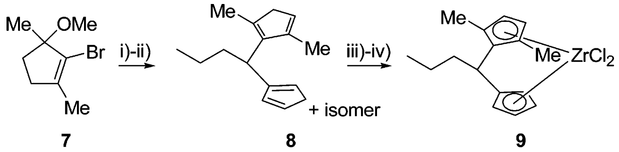
Scheme 1[a]



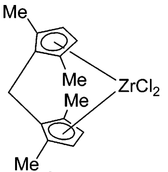
[a] Legend: (i) NaCp; (ii) MeLi (2.0 equiv); (iii) $ZrCl_2(NEt_2)_2(THF)_2$; (iv) Me_3SiCl.

Scheme 2[a]

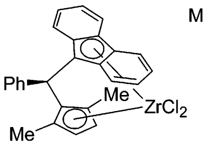


[a] Legend: (i) n-BuLi, then 6-propylfulvene; (ii) 1 N HCl; (iii) n-BuLi (2.0 equiv); (iv) $ZrCl_4(THF)_2$.

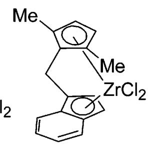
simplified syntheses of *ansa*-zirconocene complexes having methyl substituents adjacent to the bridgehead carbon and their reactivity for ethylene/norbornene copolymerization.



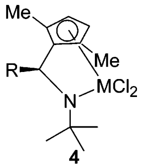
1



2



3



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Results and Discussion

Synthesis and Characterization. An *ansa*-zirconocene complex, $[Me(H)C(C_5H_4)(2,5\text{-}Me_2C_5H_2)]ZrCl_2$ (**6**), is effectively synthesized from 1,4,6-trimethylfulvene. An efficient and scalable synthesis of this fulvene was developed recently.[9] The reaction of NaCp with 1,4,6-trimethylfulvene in THF affords $Me(H)C(C_5H_5)(2,5\text{-}Me_2C_5H_3)$ (**5**) in 64% yield as a mixture of isomers, which arises by the 1,5-sigmatropic rearrangement on the C_5H_5 fragment.[10] The addition of 2 equiv of MeLi to **5** cleanly yields $Li_2[Me(H)C(C_5H_4)(2,5\text{-}Me_2C_5H_2)]$. This dilithio salt being soluble in pyridine-d_5 was characterized by ^1H and ^{13}C NMR measurement. Although the metalation reactions of the dilithium salt with $ZrCl_4$ or $ZrCl_4(THF)_2$ were not successful, its corresponding reaction with $Zr(NEt_2)_2Cl_2(THF)_2$[11] in pyridine affords the bis(diethylamido)zirconium complex, which is cleanly transformed to the dichloride complex **6** by treatment of Me_3SiCl. Single crystals suitable for X-ray crystallography were obtained by recrystallization in toluene at −30 °C, and its molecular structure was confirmed.Reaction of 6-propylfulvene with the lithiated compound of 2-bromo-3-methoxy-2,5-dimethylcyclopentene (**7**) in diethyl ether and subsequent aqueous acidic workup yields $(CH_3CH_2CH_2)(H)C(C_5H_5)(2,5\text{-}Me_2C_5H_3)$ (**8**) (Scheme 2). A 80 g scale synthesis of **7** was developed recently.[9] This route is more straightforward than that shown in Scheme 1 since the stating material 1,4,6-trimethylfulvene is synthesized from **7** by several steps. The starting material 6-propylfulvene is easily and inexpensively synthesized by the condensation of cyclopentadiene with 1-butanal.[12] However, complex **6** cannot be obtained by the route shown in Scheme 2 because 6-methylfulvene is not obtained effectively by the condensation of cyclopentadiene with acetaldehyde. Complex **9** is obtained by direct reaction of the corresponding dilithium salt with $ZrCl_4(THF)_2$ in 58% yield. Although initial efforts to obtain suitable crystals of **9** have been unsuccessful, the proposed structure is consistent with the NMR spectra and the elemental analysis. Signal patterns observed for Cp protons and carbons are very similar to those observed for **6**.

The *ansa*-zirconocene complex **13**, with two α-Me substituents on the cyclopentadienyl rings, is prepared from **7** via Scheme 3. Addition of 0.5 equiv of ethyl formate to the lithiated compound of **7** followed by treatment with MeI of the resulting alkoxide and final aqueous acidic workup yields **10** in excellent yield (∼95%). Compound **10** cannot be purified by column chromatography because it decomposes easily on the surface of silica gel. However, the crude product is so clean that it can be used for the next reaction without problems. Reaction of **10** with 3 equiv of MeLi in diethyl ether for 48 h affords a white solid, which is filtered and washed with diethyl ether to give cleanly the dilithium salt **12** in 74% yield. One equivalent of MeLi is used to form the fulvene derivative **11** with concomitant formation of MeOLi. The second equivalent of MeLi is consumed for the deprotonation of dimethylcyclopentadiene in the resulting fulvene **11**, and the remaining equivalent of MeLi attacks the 6-carbon on the fulvene to generate dilithium salt **12**. The intermediate fulvene **11** can be obtained by the addition of NaH to **10** in pentane, but it decomposes on the surface of silica gel also. Because the byproduct MeOLi is highly soluble in diethyl ether, it can be removed completely by filtration. The dilithium salt is soluble in pyridine-d_5 and is characterized by ^1H and ^{13}C NMR spectroscopy. The NMR spectra indicate that the purity of the obtained dilithium salt is satisfactory to use for metalation reaction (Supporting Information). Direct metalation with $ZrCl_4$ was not successful, but the reaction with $Zr(NEt_2)_2Cl_2(THF)_2$ in pyridine affords the desired bis(diethylamido) complex, which is transformed to the dichloride complex **13** by treatment with Me_2SiCl_2. Suitable crystals of **13** were obtained by layer diffusion of pentane to a benzene solution, and its molecular structure was confirmed by X-ray crystallography.

The Me_2Si-bridged zirconocene complex **15** is prepared starting from **7** via Scheme 4. Thus, addition of 0.5 equiv of Me_2SiCl_2 to the lithiated compound of **7** yields $Me_2Si(2,5\text{-}Me_2C_5H_3)_2$ (**14**) in 66% yield. Metalation is carried out by the reaction of the dilithium salt of **14** with $ZrCl_4(THF)_2$ in 57% yield. Only three signals (6.67, 2.08, and 0.69 ppm) in the ^1H NMR spectrum (pyridine-d_5) and five signals (131.69, 128.82, 124.17, 17.82, and 2.38 ppm) in the ^{13}C NMR spectra are observed.

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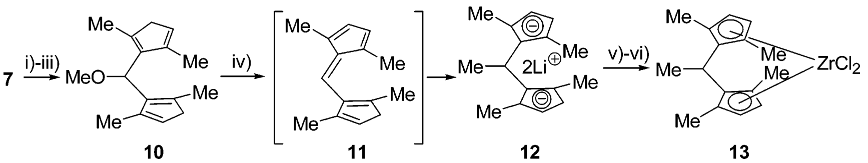
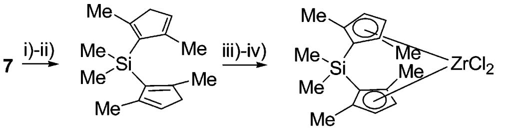
Scheme 3[a]



10 11 12 13

[a] Legend: (i) *n*-BuLi, then 0.5 equiv HC(O)OEt; (ii) MeI; (iii) 2 N HCl; (iv) MeLi (3 equiv); (v) $ZrCl_2(NEt_2)_2(THF)_2$; (vi) Me_2SiCl_2.

Scheme 4[a]



14 15

[a] Legend: (i) *n*-BuLi, then 0.5 equiv Me_2SiCl_2; (ii) 2 N HCl; (iii) *n*-BuLi (2.0 equiv); (iv) $ZrCl_4(THF)_2$.

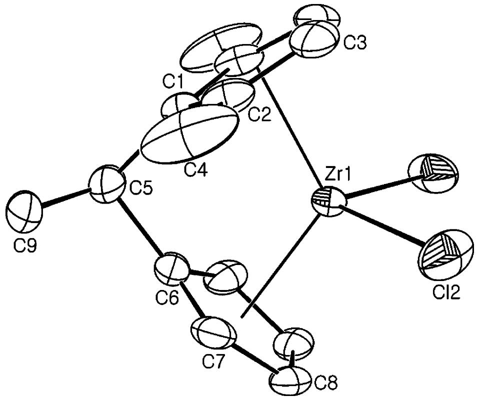


Figure 1. Thermal ellipsoid plot (30% probability level) of the structure of **6**. Selected bond distances (Å): Zr(1)–C(1), 2.436(4); Zr(1)–C(2), 2.466(3); Zr(1)–C(3), 2.538(3); Zr(1)–C(6), 2.439(4); Zr(1)–C(7), 2.455(3); Zr(1)–C(8), 2.560(3). See Table 1.

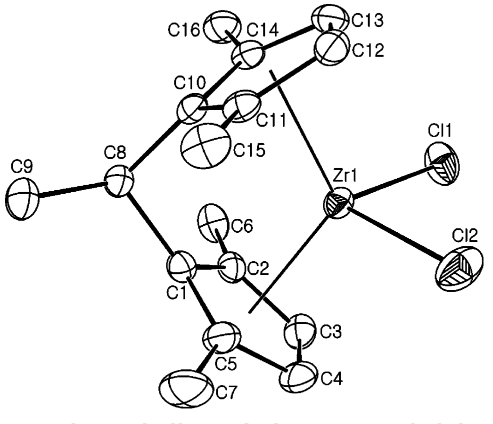


Figure 2. Thermal ellipsoid plot (30% probability level) of the structure of **13**. Selected bond distances (Å): Zr(1)–C(1), 2.448(4); Zr(1)–C(2), 2.502(4); Zr(1)–C(3), 2.551(4); Zr(1)–C(4), 2.551(4); Zr(1)–C(5) 2.498(4); Zr(1)–C(10), 2.448(3); Zr(1)–C(11), 2.498(3); Zr(1)–C(12), 2.552(4); Zr(1)–C(13) 2.556(4); Zr(1)–C(14), 2.502(4). See Table 1.

X-ray Structures of 6 and 13. The molecular structures and selected bond distances and angles for **6** and **13** are shown in Figures 1 and 2, respectively. They show characteristic strained *ansa*-zirconocene structure: small angles of Cp(c)–Zr–Cp(c) (Cp(c), centroid of Cp), deviation of C_b–C–C_b (C_b, bridgehead carbon on Cp) angles from the ideal tetrahedral value 109.5°, increase of C–Zr bond distances on going from bridgehead carbon to peripheral carbon, deviation of bridge-carbon out of the Cp plane. The bond lengths and angles of compounds **6** and **13** are compared with those observed for $Me_2C(Cp)_2ZrCl_2$[13] and $H_2C(2,5\text{-}Me_2Cp)_2ZrCl_2$ (**1**)[6] to see the effect of the methyl substituents (Table 1). Because methyl is an electron-donating group, it is expected that the Zr–(Me_2Cp(c)) distances would be shorter than the Zr–Cp(c) distances, and actually the Zr–(Me_2Cp(c)) distance (2.186 Å) observed for **6** is significantly shorter than Zr–Cp(c) distance (2.213 Å) observed for $Me_2C(Cp)_2ZrCl_2$. However, the Zr–(Me_2Cp(c)) distances observed for **13** and **1** (av 2.201 and 2.200 Å, respectively) are substantially longer when compared with that observed for **6**. The unexpected long Zr–(Me_2Cp(c)) distance in **13** and **1** may be attributed to the repulsion between the methyl groups attached on each cyclopentadienyl ring. In complex **6**, the methyl carbons are slightly deviated from the cyclopentadienyl plane (angle of H_3C–C–Cp(c), 175.49°), but in complexes **13** and **1**, the methyl carbons are more severely deviated from the plane (angle of H_3C–C–Cp(c), 171.7° and 172.0° for **13** and **1**, respectively). The severe deviation in **13** and **1** can be attributed to the repulsion between the two methyl groups. The Cp(c)–Zr–Cp(c) angle increases by attaching more methyl groups on the cyclopentadienyl ring(s) (entry 4), which implies that the openness in the active site is the most in $Me_2C(Cp)_2ZrCl_2$, middle in **6**, and the least in **13** and **1**. The C_b–C–C_b angle increases also by adding methyl substituents on the cyclopentadienyl ring(s) (entry 6).

Polymerization Studies. The newly synthesized complexes **6**, **9**, **13**, and **15** have methyl substituents proximal to the bridgehead carbon, and consequently the steric hindrance at the active site is small. Good comonomer incorporation is expected for bulky monomers such as norbornene. The ethylene/norbornene copolymer is very attractive as a novel substrate for high-density data storage devices, packaging, and optical/biomedical applications.[14] Ethylene/norbornene copolymerization reactivity of each complex is summarized in Table 1 and compared with the previously reported excellent catalyst **1**.[6] Complex **6** is so active for copolymerization that the solution temperature increases from 60 °C to 92 °C in 5 min when the polymerization is conduced in an oil bath of constant temperature, 60

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Table 1. Comparison of Selected Bond Distances (Å) and Angles (deg) Observed for $Me_2C(Cp)_2ZrCl_2$, 6, 13, and 1

entry		$Me_2C(Cp)_2ZrCl_2$	**6**	**13**[a]	**1**[a]
1	Zr−Cp(c)	2.213	2.188		
2	Zr−(Me_2Cp(c))		2.186	2.188, 2.207 2.207, 2.203	2.200, 2.203 2.199, 2.197
3	Zr−Cl	2.4321(8), 2.4406(8)	2.4353(10)	2.4338(11), 2.4469(12) 2.4409(12), 2.4304(13)	2.4327(10), 2.4444(12) 2.4368(10), 2.4390(12)
4	Cp(c)−Zr−Cp(c)	116.7	117.00	117.64, 117.59	117.13, 117.60
5	Cl−Zr−Cl	100.25(3)	102.11(7)	100.69(4), 101.73(5)	102.46(4), 102.98(4)
6	C_b−C−C_b	99.5(2)	100.7(4)	102.2(3), 101.7(3)	102.7(2), 102.9(2)
7	H_3C−C−Cp(c)		175.49	171.7[b]	172.0[b]

[a] There are two independent molecules in the asymmetric unit cell. [b] Averaged value.

°C (entry 1). The activity was calculated to be 350 × 10^6 g/mol·h by weighing the resulting polymer powder. To keep the polymerization temperature constant, the glass reactor (60 mL) was heated with mantle to the initial polymerization temperature and the mantle was removed right after injection of catalyst and ethylene gas. The evolving heat can be manually removed by using an air-gun. When the temperature was controlled at 60−62 °C, the activity was reduced to 39 × 10^6 g/mol·h (entry 2). The activity data indicate that the activity is sensitive to the reaction temperature. The activity actually increases dramatically when the polymerization temperature is raised to 80 °C (270 × 106 g/mol·h, entry 3). An increase of activity by raising the temperature is observed for all complexes studied in this work, but it is not so severe in the case of **13**, **15**, and **1**. Complex **9** shows the highest activity (310 × 10^6 g/mol·h, entry 5). The Me_2Si-bridged complex **15** shows relatively low activity when compared with the C1-bridged complexes **6**, **9**, **13**, and **1**.

The norbornene content in the copolymer can be estimated by measuring the glass transition temperature (T_g) because the T_g value shows a linear dependency on the norbornene content in the copolymer.[15] Complexes **6** and **9** are less hindered at the active site than **13** and **1**. Consequently, the catalysts generated from **6** and **9** are expected to produce polymer with higher norbornene incorporation and glass transition temperature (T_g). The T_g of the copolymer obtained with **9** is 29 °C higher than that observed for the copolymer obtained with **13** (entries 5 and 7) under the identical polymerization conditions. The T_g increases with an increase in the polymerization temperature for complexes **6** and **9**, but in the cases of **15** and **1** it changes little with an increase in temperature. Norbornene contents of some copolymers were measured by ^{13}C NMR spectroscopy, and the relationship between the T_g and the norbornene content was confirmed. The T_g of 186, 157, and 154 °C corresponds to norbornene content of 66, 55, and 53 mol %, respectively (entry 5, 7, and 9, respectively).

Molecular weights of the polymers obtained by **6** and **9** are relatively low (M_w, 62 000 and 49 000, respectively) compared with those of the polymers obtained by **15** and **1** (M_w, 144 000 and 134 000, respectively). Narrow molecular weight distributions (M_w/M_n, 1.6−2.3) are observed for all polymerizations, indicating formation of a single active species.

Experimental Section

All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk techniques. Toluene, pentane, and C_6D_6 were distilled from benzophenone ketyl. Pyridine was dried over CaH_2. Toluene used for the polymerization reaction was purchased from Aldrich (anhydrous grade) and purified further over Na/K alloy. Ethylene was purchased from Conley Gas (99.9%) and purified by contacting with molecular sieves and copper for several days under a pressure of 150 psig. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Varian Mercury plus 400. Mass spectra were obtained on a Micromass VG Autospec. Elemental analyses were carried out at the Inter-University Center Natural Science Facilities, Seoul National University. Gel permeation chromatograms (GPC) of ethylene/norbornene copolymers were obtained at 37 °C in chloroform using a Waters Millennium equipped with three Waters chromatographic columns. Differential scanning calorimetry (DSC) was performed on a Thermal Analysis 3100.

Me(H)C(C_5H_5)(2,5-$Me_2C_5H_3$) (5). To a stirred solution of NaCp (2.52 g, 28.7 mmol) in cold THF (30 mL) was added 1,4,6-trimethylfulvene (2.30 g, 19.1 mmol). The resulting solution was stirred overnight at room temperature. Water (50 mL) was added, and the compound was extracted with diethyl ether (50 mL × 3). The collected organic layer was dried over anhydrous $MgSO_4$. Removal of solvent by rotary evaporator gave a residue, which was purified by column chromatography on silica gel eluting with hexane and toluene (v/v, 10:1). The ^{1}H NMR spectrum indicated the compound existed as two isomers. Yield: 2.27 g (64%). ^{1}H NMR (C_6D_6): δ 6.46−6.02 (m, 3 H, Cp-H), 5.80 (s, 1 H, Me_2Cp-H), 3.78 (quartet, $J = 7.2$ Hz, 0.5 H, bridge-C*H*), 3.78−3.68 (m, 0.5 H, bridge-C*H*), 3.00 (quintet, $J = 1.6$ Hz, 1 H, Me_2Cp-CH_2), 2.80 (s, 3 H, Me_2Cp-CH_2 and Cp-CH_2), 1.96 (s, 3 H, CH_3), 1.85 (quartet, $J = 2.0$ Hz, 1.5 H, CH_3), 1.83 (quartet, $J = 2.0$ Hz, 1.5 H, CH_3), 1.46 (d, $J = 7.2$ Hz, 1.5 H, CHCH_3), 1.45 (d, $J = 7.2$ Hz, 1.5 H, CHCH_3) ppm. HRMS-EI: $m/z = M^+$ calcd ($C_{14}H_{18}$) 186.1409, found 186.1408.

[Me(H)C(C_5H_4)(2,5-$Me_2C_5H_2$)]$ZrCl_2$ (6). Compound **5** (2.17 g, 11.6 mmol) was dissolved in cold diethyl ether (50 mL, −30 °C), and methyllithium (14.6 mL, 23.2 mmol) was added. The solution was stirred overnight. The white solid was filtered and washed with diethyl ether to give a dilithium salt (2.31 g, 80%). ^{1}H and ^{13}C NMR analysis indicated that the dilithium salt was cleanly formed, and 0.7 equiv of diethyl ether was incorporated. ^{1}H NMR (pyridine-d_5): δ 6.29 (s, 4 H, Cp-H), 5.96 (s, 2 H, Cp-H), 4.63 (quartet, $J = 7.2$ Hz, 1 H, C*H*CH_3), 2.40 (s, 6 H, CH_3), 2.05 (d, $J = 7.2$ Hz, 3 H, CHCH_3) ppm. ^{13}C{^{1}H} NMR (pyridine-d_5): δ 131.80, 125.51, 110.33, 102.67, 102.54, 101.37, 33.55 (bridge-CH_2), 23.43 (CH_3), 16.23 (CH_3). The dilithium salt (0.900 g, 3.60 mmol) was dissolved in pyridine (9.0 mL), and $ZrCl_2(NEt_2)_2(THF)_2$ (1.62 g, 3.60 mmol) was added at room temperature. After the solution was stirred overnight, the solvent was removed by vacuum. The residue was dissolved in pentane, and the solution was filtered over Celite. The solution was concentrated and stored in a freezer

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(15) (a) Rische, T.; Waddon, A. J.; Dickinson, L. C.; MacKnight, W. J. *Macromolecules* **1998**, *31*, 1871. (b) Arndt, M.; Beulich, I. *Macromol. Chem. Phys.* **1998**, *199*, 1221. (c) Lasarov, H.; Mönkkönen, K.; Pakkanen, T. T. *Macromol. Chem. Phys.* **1998**, *199*, 1939.

(−30 °C) overnight to give light yellow crystals (0.920 g, 49%). ^{1}H NMR (C_6D_6): δ 6.27−6.22 (m, 1 H, Cp-H), 6.16−6.12 (m, 1 H, Cp-H), 5.87 (d, *J* = 3.6 Hz, 1 H, Me_2Cp-H), 5.84 (d, *J* = 3.6 Hz, 1 H, Me_2Cp-H), 5.54 (dd, *J* = 4.8, 2.4 Hz, 1 H, Cp-H), 5.33 (dd, *J* = 4.8, 2.4 Hz, 1 H, Cp-H), 3.93 (quartet, *J* = 7.2 Hz, 1 H, C*H*CH_3), 3.41−3.29 (m, 4 H, NCH_2), 3.27−3.14 (m, 4 H, NCH_2), 2.09 (s, 3 H, CH_3), 1.92 (s, 3 H, CH_3), 1.63 (d, *J* = 7.2 Hz, 1 H, CHCH_3), 1.02 (t, *J* = 6.8 Hz, 3 H, CH_3), 1.01 (t, *J* = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): 125.14 (Cp-C), 123.49 (Cp-C), 116.91 (Cp-C), 115.03 (Cp-C), 113.44 (Cp-*C*H), 113.04 (Cp-*C*H), 111.49 (Cp-*C*H), 111.24 (Cp-*C*H), 103.50 (Cp-*C*H), 101.22 (Cp-*C*H), 47.19 (N*C*H_2CH_3), 47.03 (N*C*H_2CH_3), 33.02 (bridge-*C*), 17.30 (*C*H_3), 16.83 (*C*H_3), 14.72 (NCH_2*C*H_3), 14.49 (NCH_2*C*H_3), 14.15 (*C*H_3) ppm. The bis(diethylamido)zirconium complex (0.920 g, 22.2 mmol) was dissolved in benzene (9.0 mL), and Me_3SiCl (0.846 mL, 66.6 mmol) was added. The solution was stirred overnight to give a light yellow precipitate, which was collected by filtration. The solid was pure by ^{1}H and ^{13}C NMR spectral analysis (0.730 g, 95%). Single crystals suitable for X-ray crystallography and elemental analysis were obtained by recrystallization in toluene solution at −30 °C. ^{1}H NMR (C_6D_6): δ 6.45−6.40 (m, 1 H, Cp-H), 6.35−6.33 (m, 1 H, Cp-H), 6.19 (d, *J* = 3.6 Hz, 1 H, Me_2Cp-H), 6.16 (d, *J* = 3.6 Hz, 1 H, Me_2Cp-H), 5.33 (dd, *J* = 4.2, 2.8 Hz, 1 H, Cp-H), 5.12 (dd, *J* = 4.2, 2.8 Hz, 1 H, Cp-H), 3.70 (quartet, *J* = 7.2 Hz, 1 H, C*H*CH_3), 1.83 (s, 3 H, CH_3), 1.66 (s, 3 H, CH_3), 1.27 (d, *J* = 7.2 Hz, 1 H, CHCH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): 124.39 (Cp-*C*H), 123.31 (Cp-*C*H), 122.64 (Cp-*C*H), 121.70 (Cp-*C*H), 121.15 (Cp-*C*C), 119.43 (Cp-*C*C), 118.48 (Cp-*C*C), 109.17 (Cp-*C*C), 107.47 (Cp-*C*H), 105.19 (Cp-*C*H), 33.12 (bridge-C), 17.41 (*C*H_3), 16.39 (*C*H_3), 14.78 (*C*H_3) ppm. Anal. Calcd for $C_{14}H_{16}Cl_2Zr$: C, 48.5; H, 4.66. Found: C, 48.4; H, 6.70.

($CH_3CH_2CH_2$)(H)C(C_5H_5)(2,5-$Me_2C_5H_3$) (8). To a Schlenk flask containing **7** (10.0 g, 48.8 mmol) in diethyl ether (75 mL) was added dropwise *n*-BuLi (13.5 g, 2.5 M in hexane, 48.8 mmol) at −30 °C. The solution was allowed to warm to room temperature and was stirred for 15 min. A white solid precipitated. After the slurry was cooled to −30 °C, 6-propylfulvene (5.87 g, 48.8 mmol) was added. The solution was stirred for 3 h, during which time the yellow fulvene color disappeared. Diethyl ether (75 mL) and H_2O (75 mL) were added. The water phase was discarded, and 1 N HCl (150 mL) was added. The two-phase mixture was shaken vigorously for 3 min. The HCl phase was removed, and the organic layer was rapidly neutralized with aqueous $NaHCO_3$ (150 mL). The organic layer was dried with anhydrous $MgSO_4$, and the solvent was removed by rotary evaporation to give a residue, which was purified by column chromatography on silica gel eluting with hexane (10.4 g, 98%). ^{1}H NMR (C_6D_6): δ 6.46−6.02 (m, 3 H, Cp-H), 5.78 (s, 1 H, Me_2Cp-H), 3.78 (quartet, *J* = 7.2 Hz, 0.5 H, bridge-CH_2), 3.67−3.56 (m, 0.5 H, bridge-C*H*), 2.98 (s, 1 H, Me_2Cp-CH_2), 2.79 (s, 3 H, Me_2Cp-CH_2 and Cp-CH_2), 1.98 (s, 1.5 H, CH_3), 1.96 (s, 1.5 H, CpCH_3), 1.78−1.84 (m, 3 H, CpCH_3) 1.38−1.22 (m, 4 H, CH_2C$H_2$$CH_3$), 0.95 (t, *J* = 7.2 Hz, 1.5 H, CH_2CH_3), 0.94 (t, *J* = 7.2 Hz, 1.5 H, CH_2CH_3) ppm. HRMS-EI: $m/z = M^+$ calcd ($C_{16}H_{22}$) 214.1724, found 214.1722.

[($CH_3CH_2CH_2$)(H)C(C_5H_4)(2,5-$Me_2C_5H_2$)]$ZrCl_2$ (9). To a stirred solution of **8** (10.4 g, 47.8 mmol) in cold THF (60 mL, −78 °C) was added *n*-BuLi (26.5 g, 95.7 mmol, 2.5 M in hexane) dropwise. The solution was stirred for 6 h. Solvent was removed by vacuum, and the residue was washed with pentane. The ^{1}H NMR spectrum indicated that the dilithium salt was cleanly formed and 2 equiv of THF was incorporated. ^{1}H NMR (C_6D_6 and pyridine-*d*$_5$, v/v, 10:1): δ 6.22 (s, 4 H, Cp-H), 5.94 (s, 2 H, Cp-H), 4.19 (dd, *J* = 9.6, 6.0 Hz, 1 H, C*H*CH_2), 2.60−2.40 (m, 1 H, CHCH_2), 2.32 (s, 6 H, CpCH_3), 2.2−2.0 (m, 1 H, CHCH_2), 1.12 (q, *J* = 7.6 Hz, 2 H, C$H_2$$CH_3$), 0.73 (t, *J* = 7.6 Hz, 3 H, CH_2CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6 and pyridine-*d*$_5$, v/v, 10:1): δ 131.40, 110.30, 102.58, 102.43, 101.19, 39.25, 39.03, 23.28, 16.25, 15.41 ppm. The dilithium salt (1.00 g, 2.48 mmol) was dissolved in a cosolvent of toluene (2.0 mL) and THF (8.0 mL), and $ZrCl_4(THF)_2$ (0.936 g, 2.48 mmol) was added to the solution. The resulting mixture was stirred for 5 h at room temperature. Solvent was removed by vacuum to give a residue, which was dissolved in toluene. After the solution was filtered over Celite, the solvent was removed by vacuum to give a residue, which was triturated in pentane to give a light yellow solid (0.54 g, 58%). ^{1}H NMR (C_6D_6): δ 6.45 (dd, *J* = 5.2, 3.2 Hz, 1 H, Cp-H), 6.36 (dd, *J* = 5.2, 3.2 Hz, 1 H, Cp-H), 6.21 (d, *J* = 3.6 Hz, 1 H, Me_2Cp-H), 6.19 (d, *J* = 3.6 Hz, 1 H, Me_2Cp-H), 5.35 (dd, *J* = 5.2, 3.2 Hz, 1 H, Cp-H), 5.21 (dd, *J* = 5.2, 3.2 Hz, 1 H, Cp-H), 3.77 (t, *J* = 8.4 Hz, 1 H, bridge-CH), 1.90−1.70 (m, 2 H, CHC$H_2$$CH_2$), 1.87 (s, 3 H, CpC$H_3$), 1.73 (s, 3 H, CpC$H_3$), 1.25 (sextet, *J* = 7.2 Hz, 2 H, C$H_2$$CH_3$), 0.85 (t, *J* = 7.2 Hz, 3 H, CH_2CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): 124.53 (Cp-*C*H), 123.59 (Cp-*C*H), 122.74 (Cp-*C*H), 121.85 (Cp-*C*C), 121.59 (Cp-*C*H), 119.26 (Cp-*C*C), 117.97 (Cp-*C*C), 108.61 (Cp-*C*C), 108.05 (Cp-*C*H), 105.34 (Cp-*C*H), 39.15, 32.64 (bridge-C), 21.10, 17.33, 14.79, 14.16 ppm. Anal. Calcd for $C_{16}H_{20}Cl_2Zr$: C, 51.3; H, 5.39. Found: C, 51.0; H, 5.45.

(MeO)(H)C(2,5-$Me_2C_5H_3$)$_2$ (10). To a Schlenk flask containing compound **7** (4.00 g, 19.5 mmol) in diethyl ether (20 mL) was added *n*-BuLi at −30 °C (5.41 g, 2.5 M in hexane, 19.5 mmol) dropwise. The solution was allowed to warm to room temperature and stirred for 30 min. After cooling to −30 °C, ethyl formate (0.720 g, 9.80 mmol) was added. After the solution was stirred for 1 h at room temperature, the solvent was removed by vacuum. To the residue were added DMF (20 mL) and NaH (0.47 g, 20 mmol). After the solution was stirred for 1 h, MeI (8.30 g, 58.5 mmol) was added dropwise. The solution was stirred at 35 °C for 24 h. The solution was diluted with hexane (40 mL), and water (40 mL) was added. The organic layer was collected and washed with brine (20 mL × 3). Solvent was removed by rotary evaporation, and the residue was dissolved in ethyl acetate (8.0 mL). HCl (2 N, 12 mL) was added, and the two-phase mixture was shaken vigorously for 2 min. The organic phase was rapidly neutralized with aqueous saturated $NaHCO_3$ (16 mL). After the organic layer was dried with anhydrous $MgSO_4$, solvent was removed by a rotary evaporator to give an oily residue (2.04 g, ∼91%). The crude residue is so pure by ^{1}H and ^{13}C NMR spectral analysis that it was used for the next step. ^{1}H NMR ($CDCl_3$): δ 5.83 (d, J = 1.6 Hz, 2 H, Cp-H), 5.03 (s, 1 H, CH_3OC*H*), 3.33 (s, 3 H, CH_3O), 2.83(t, J = 1.6 Hz, 4 H, Cp-CH_2), 2.04 (s, 6 H, CpCH_3), 2.83 (q, *J* = 1.6 Hz, 6 H, CpCH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): 143.42, 140.30, 136.90, 124.27, 76.08, 56.18, 44.97, 14.97, 14.44 ppm. HRMS-EI: $m/z = M^+$ calcd ($C_{16}H_{22}O$) 230.1672, found 230.1670.

[(Me)(H)C(2,5-$Me_2C_5H_2$)$_2$]Li_2 (12). To a stirred solution of **10** (1.48 g, 6.43 mmol) in cold diethyl ether (30 mL, −78 °C) was added MeLi (14.1 mL, 22.5 mmol, 1.6 M in diethyl ether) dropwise. The solution was stirred for 48 h. A light yellow solid precipitated, which was filtered and washed with diethyl ether (20 mL). The solid was dissolved in a cosolvent of benzene (10 mL) and THF (10 mL), and the solution was filtered to remove a small amount of insoluble impurities. The solvent was removed to give a light yellow solid. ^{1}H and ^{13}C NMR spectra indicated that the dilithium salt was cleanly formed and 1.8 equiv of THF was incorporated. Yield: 1.70 g, 74%. The ^{1}H and ^{13}C NMR spectra showing its purity can be seen in the Supporting Information. ^{1}H NMR (pyridine-*d*$_5$): δ 6.01 (s, 4 H, Cp-H), 4.75 (q, *J* = 7.6 Hz, 1 H, CH_3C*H*), 2.46 (s, 12 H, CH_3Cp), 2.02 (d, *J* = 6.8 Hz, 3 H, CHCH_3) ppm. ^{13}C{^{1}H} NMR (pyridine-*d*$_5$): 122.94, 111.32, 101.27, 33.15, 26.04, 16.48 ppm.

[(Me)(H)C(2,5-$Me_2C_5H_2$)$_2$]$ZrCl_2$ (13). $ZrCl_2(NEt_2)_2(THF)_2$ (0.451 g, 0.513 mmol) and the dilithium salt **12** (0.150 g, 0.52 mmol) were weighed in a vial inside a glovebox. Cold pyridine

Table 2. Ethylene/Norbornene Copolymerization Results[a]

entry	catalyst	temp (°C)[b]	activity (10^6g/ mol·h)	T_g (°C)	M_w	M_w/M_n
1	**6**	60−92[c]	350	177		
2	**6**	60−62	39	149	123 000	1.6
3	**6**	80−86	270	173	62 000	1.8
4	**9**	60−64	77	154	79 000	1.6
5	**9**	80−87	310	186 (66[d])	49 000	2.3
6	**13**	60−66	124	151	157 000	1.6
7	**13**	80−86	182	157 (55[d])	131 000	1.6
8	**15**	60−62	25	154	178 000	1.7
9	**15**	80−86	27	154 (53[d])	144 000	2.0
10	**1**	60−65	134	152	154 000	1.6
11	**1**	80−86	206	156	134 000	1.6

[a] Polymerization conditions: 30 mL of norbornene solution in toluene (3.54 M), 0.25 μmol of catalyst, Al/Zr = 6000, 100 psig ethylene, 5 min. [b] Temperature was controlled by cooling with an air-gun. [c] Temperature was not controlled. [d] Norbornene content in mol % determined by ^{13}C NMR spectroscopy.

(15 mL, −20 °C) was added, and the resulting mixture was stirred overnight at room temperature. Solvent was removed to give a residue, which was dissolved in pentane. The solution was filtered, and the solvent was removed by vacuum to give an oily residue. ^{1}H NMR (C_6D_6): δ 5.99 (d, J = 3.2 Hz, 2 H, Cp-H), 5.97 (d, J = 3.2 Hz, 2 H, Cp-H), 4.19 (q, J = 7.6 Hz, 1 H, C*H*CH$_3$), 3.38 (q, J = 6.8 Hz, 8 H, NCH$_2$), 2.28 (s, 6 H, CpCH$_3$), 2.00 (s, 6 H, CpCH$_3$), 1.80 (d, J = 7.6 Hz, 3 H, CHC*H*$_3$), 1.06 (q, J = 6.8 Hz, 12 H, NCH$_2$C*H*$_3$) ppm. The residue was dissolved in benzene (1.0 mL), and Me_2SiCl_2 (0.12 mL, 0.51 mmol) was added. After the solution was stirred for 3 h at room temperature, the solvent was removed by vacuum to give a residue, which was triturated in pentane. A light yellow solid was obtained by filtration. The solid was dissolved in benzene again, and the solution was filtered over Celite to remove a slight amount of insoluble impurity. Solvent in the filtrate was removed under vacuum to give a yellow solid (0.75 g, 40%). Single crystals suitable for X-ray crystallography were obtained by layer diffusion of pentane to a benzene solution. ^{1}H NMR (C_6D_6): δ 6.27 (d, J = 3.2 Hz, 2 H, Cp-H), 6.25 (d, J = 3.2 Hz, 2 H, Cp-H), 4.08 (q, J = 7.6 Hz, 1 H, C*H*CH$_3$), 2.06 (s, 6 H, CpCH$_3$), 1.80 (s, 6 H, CpCH$_3$), 1.50 (d, J = 7.6 Hz, 3 H, CHC*H*$_3$) ppm. ^{13}C NMR (C_6D_6): δ 126.29, 123.78, 123.19, 121.60, 107.67, 33.12, 17.83, 16.29, 15.98 ppm. Anal. Calcd for $C_{16}H_{20}Cl_2Zr$: C, 51.3; H, 5.39. Found: C, 51.2; H, 5.52.

$Me_2Si(2,5\text{-}Me_2C_5H_3)_2$ (14). To a Schlenk flask containing **7** (5.00 g, 24.4 mmol) in diethyl ether (30 mL) was added *n*-BuLi (6.76 g, 2.5 M in hexane, 24.4 mmol) at −30 °C dropwise. The solution was allowed to warm to room temperature and stirred for 15 min at room temperature. After cooling to −30 °C, Me_2SiCl_2 (1.50 mL, 12.2 mmol) was added, and the solution was stirred for 5 h at room temperature. The solution was diluted with ethyl acetate (20 mL), and water (20 mL) was added. The water phase was removed, and 2 N HCl (50 mL) was added. The two-phase mixture was shaken vigorously for 3 min. The organic phase was rapidly neutralized with aqueous saturated $NaHCO_3$ (50 mL). The organic layer was dried with anhydrous $MgSO_4$, and solvent was removed by a rotary evaporator to give an oily residue, which was purified by column chromatography on silica gel eluting with hexane (1.95 g, 66%). ^{1}H NMR (CDCl$_3$): δ 5.78 (dd, J = 2.0, 1.2 Hz, 2 H, Cp-CH), 2.87 (quintet, J = 2 Hz, 4 H, Cp-CH$_2$), 2.18 (s, 6 H, CpCH$_3$), 1.97 (s, 6 H, CpCH$_3$), 0.46 (s, 3 H, SiCH$_3$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): 156.34, 147.18, 138.04, 123.98, 47.82 (Cp-CH$_2$), 17.44 (CH$_3$), 17.05 (CH$_3$), 1.81 (SiCH$_3$) ppm. HRMS-EI: $m/z = M^+$ calcd ($C_{16}H_{24}Si$) 244.1647, found 244.1648.

$[Me_2Si(2,5\text{-}Me_2C_5H_3)_2]ZrCl_2$ (15). To a stirred solution of **14** (1.95 g, 7.98 mmol) in cold THF (30 mL, −78 °C) was added *n*-BuLi (4.42 g, 16.0 mmol, 2.5 M in hexane) dropwise. The solution was stirred overnight to give a white precipitate, which was collected by filtration and washed with hexane. The ^{1}H and ^{13}C NMR indicated clean formation of the dilithium salt and 1.2 equiv of THF was incorporated (2.50 g, 92%). ^{1}H NMR (pyridine-d_5): δ 6.49 (s, 4 H, Cp-H), 2.79 (s, 12 H, CH$_3$), 1.22 (s, 6 H, SiCH$_3$) ppm. ^{13}C{^{1}H} NMR (pyridine-d_5): δ 122.50, 109.83, 106.27, 18.61, 6.17 ppm. The dilithium salt (0.150 g, 0.440 mmol) was dissolved in pyridine (5 mL), and $ZrCl_4(THF)_2$ (0.165 g, 0.440 mmol) was added at room temperature. The solution was stirred for 3 h. Solvent was removed by vacuum to give a residue, which was dissolved again in toluene. After the solution was filtered over Celite, the solvent was removed by vacuum to give a white solid (0.100 g, 57%). ^{1}H NMR (pyridine-d_5): δ 6.67 (s, 4 H, Cp-H), 2.08 (s, 12 H, CH$_3$), 0.69 (s, 6 H, SiCH$_3$) ppm. ^{13}C{^{1}H} NMR (pyridine-d_5): δ 131.69, 128.82, 124.17, 17.82, 2.38 ppm. Anal. Calcd for $C_{16}H_{22}SiCl_2Zr$: C, 47.5; H, 5.49. Found: C, 47.3; H, 5.50.

Table 3. Crystallographic Parameters of 6 and 13

	6	**13**
formula	$C_{14}H_{16}Cl_2Zr$	$C_{16}H_{20}Cl_2Zr$
fw	346.39	374.44
color	white	white
size, mm^3	0.30 × 0.30 × 0.10	0.30 × 0.15 × 0.15
a, Å	11.262(1)	17.5740(6)
b, Å	13.876(1)	8.8569(3)
c, Å	9.054(1)	20.5210(6)
α, deg	90	90
β, deg	90	91.407(2)
γ, deg	90	90
V, Å^3	1414.9(2)	3193.15(18)
cryst syst	orthorhombic	monoclinic
space group	*Pnma*	*P*21/*n*
D(calc), g cm^{-1}	1.626	1.558
Z	4	8
μ, mm^{-1}	1.130	1.008
no. of data collected	2913	12 489
no. of unique data	1658	7319
no. of variables	95	353
R (%)	0.0360	0.0517
R_w (%)	0.0941	0.0796
goodness of fit	1.088	1.002

[a] Data collected at 293(2) K with Mo Kα radiation (λ(Kα) = 0.7107 Å), $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ with $F_o > 2.0\sigma(I)$, $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o)^2]^2]^{1/2}$ with $F_o > 2.0\sigma(I)$.

Crystallographic Studies. Crystals of **6** and **13** coated with grease (Apiezon N) were mounted inside a thin glass tube with epoxy glue and placed on an Enraf-Nonius CCD single-crystal X-ray diffractometer. The structures were solved by direct methods (SHELXL-97)[16] and refined against all F^2 data (SHELXL-97). All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were treated as idealized contributions. The crystal data and refinement results are summarized in Table 3.

Ethylene/Norbornene Copolymerization. In a drybox, to a dried 70 mL glass reactor was added 30 mL of norbornene solution in toluene (3.54 M). The reactor was assembled and brought out from the drybox. The reactor was heated to a given temperature by mantle. After an activated catalyst prepared by mixing 0.25 μmol of catalyst and MAO (Akzo, MMAO type 4, 6.4 wt % of Al, 0.63 g, 1.5 mmol Al) was added via a syringe, ethylene (100 psig) was fed immediately. The evolving heat was manually removed by using an air-gun to control the temperature. After polymerization had been conducted for 5 min, ethylene was vented and acetone was added to the reactor to give white precipitates, which were collected by filtration and dried under vacuum. Table 2 summarizes the polymeri-

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(16) Sheldrick, G. M. *SHELXL-97*, Program for the Refinement of Crystal Structures; University of Göttingen: Germany, 1997.

zation results. Glass transition temperatures (T_g) were determined on a second heating at a heating rate of 15 °C/min on DSC.

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Supporting Information Available: Complete details of the crystallographic studies of **6** and **13** and ^{1}H and ^{13}C NMR spectra of **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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