Notes

Synthesis of [2,2′-Methylenebis(1,3-dimethylcyclopentadienyl)]zirconium Dichloride and Its Reactivity in Ethylene–Norbornene Copolymerization

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*Summary: An ansa-zirconocene compound, [2,2′-methylenebis(1,3-dimethylcyclopentadienyl)]zirconium dichloride (**5**), bearing methyl substituents on the carbons adjacent to a bridgehead carbon, was synthesized by key steps of the catalytic Pauson–Khand reaction and the retro-Diels–Alder reaction. The crystal structure of **5** was determined. The small angle (117.15°) between the two centroids of the cyclopentadienyls and a zirconium atom and the absence of any substituents on the positions β with respect to the bridgehead carbon indicate that the coordination site for catalysis is widely opened. Compound **5**, when activated with MAO, showed good performance for copolymerization of ethylene with a bulky monomer such as norbornene. The activity and norbornene incorporation ability are much better than those of [Ph₂C(Fluo)(Cp)]ZrCl₂.*

Introduction

The metallocene compounds of group 4 have been developed as catalysts for polymerization of olefins[1,2] and are now reaching the early stages of commercialization.[3] The catalytic activity, comonomer incorporation and distribution, tacticity, and molecular weight of the

polymer depend heavily on the ligand structure. While searching for catalysts showing good comonomer incorporation, we envisaged novel *ansa*-zirconocene compounds bearing substituents only on the carbons adjacent to a bridgehead carbon. In those compounds, the electronic effect can be controlled by the substituents while the steric hindrance is kept to a minimum. Good polymerization reactivity is expected for a bulk monomer such as norbornene.[4–6] In this paper, we report the synthesis of the novel *ansa*-zirconocene compound [2,2′-methylenebis(1,3-dimethylcyclopentadienyl)]zirconium dichloride and its catalytic reactivity toward ethylene–norbornene copolymerization.

Results and Discussion

Ligands for *ansa*-metallocene compounds have been conventionally afforded by nucleophilic attack of a substituted cyclopentadienyl anion to an electrophile such as dialkyldichlorosilane, dibromoethane, or fulvene. By this method, ligands bearing substituents only on the carbons adjacent to the bridgehead carbon cannot be obtained because a substituent on the cyclopentadienyl anion is situated at the β-position from the bridgehead carbon for steric reasons. We could synthesize the ligand by using the Pauson–Khand reaction (Scheme 1).[7] The catalytic intermolecular Pauson–Khand reaction of 1,4-pentadiyne with norbornadiene afforded the tricyclo compound **1**.[8,9] Addition of Me₂CuLi to **1** gave

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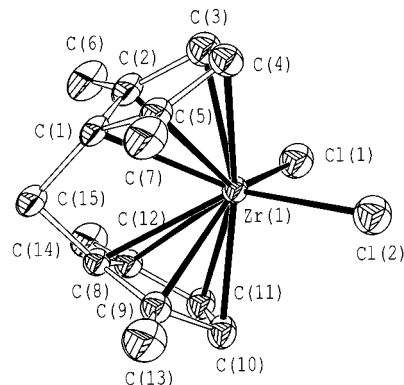(5) Ruchatz, D.; Fink, G. *Macromolecules* **1998**, *31*, 4674.
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Scheme 1[a]

1   **2**   **3**   **4**   **5**
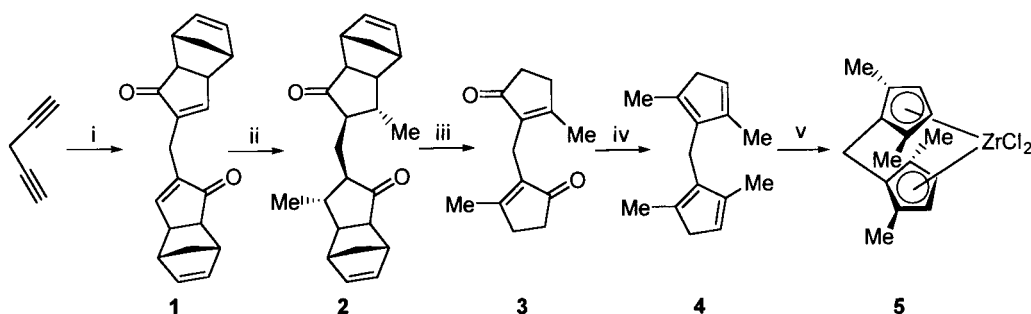
[a] Legend: (i) Co₂(CO)₈ (1 mol %), CO (10 bar); (ii) Me₂CuLi; (iii) 420 °C (2 min); (iv) MeLi and then aqueous HCl; (v) *n*-BuLi (2.0 equiv) and then ZrCl₄.

cleanly a 1,4-addition product, **2**.[10] When a quartz tube containing **2** was immersed in a furnace at 420 °C for a short time (2 min), a retro-Diels–Alder reaction and subsequent isomerization of double bonds occurred to give **3** in 66% yield. 1,2-Addition of MeLi followed by elimination of water by an aqueous HCl workup gave the desired cyclopentadiene compound **4**, in moderate yield (63%). Stirring the slurry of dilithium salt, generated by addition of 2 equiv of *n*-BuLi to **4**, and ZrCl₄ in toluene gave **5** in a rather low yield (20%). The ¹H NMR spectrum of **5** was very simple: δ 6.45 ppm in CDCl₃ for cyclopentadienyl hydrogens, δ 4.07 ppm for methylene bridge hydrogens, and δ 2.21 ppm for methyl hydrogens. Five peaks were observed in the ¹³C{¹H} NMR spectrum: δ 124.3, 122.5, and 104.1 ppm for cyclopentadienyl carbons, δ 21.7 ppm for the methylene bridge carbon, and δ 16.5 ppm for methyl carbons.

Single crystals of **5** suitable for X-ray crystallography were grown by vapor-phase diffusion of pentane into a toluene solution. Figure 1 shows the structure of **5** with selected bond lengths and angles. The unit cell contains two independent molecules. The two cyclopentadienyl rings are almost in an eclipsed conformation. The small angle of C(1)–C(15)–C(8) (102.7(2)/102.9(2)°) indicates that the bridge methylene carbon is distorted from a normal tetrahedral structure (109°) due to the metallocenophane character. The angle between the two centroids of cyclopentadienyls and a zirconium atom (117.15°) is comparable to that of [Ph₂C(Fluo)(Cp)]ZrCl₂ (117.6°),[11] which implies that the Zr atom in complex **5** displaces from the mouth of the ligand as far as in [Ph₂C(Fluo)(Cp)]ZrCl₂. The Cl–Zr–Cl angle (102.46(4)/ 102.98(4)°) is quite large when compared with that of [Ph₂C(Fluo)(Cp)]ZrCl₂ (95.9°), presumably due to the absence of any substituent on the β-carbons. The Zr–C distance increases progressively from the bridgehead

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Figure 1. ORTEP view of **5**, showing the atom-numbering scheme. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Zr(1)–Cl-(1), 2.4327(4); Zr(1)–Cl(2), 2.4444(12); Zr(1)–C(1), 2.453-(3); Zr(1)–C(2), 2.496(3); Zr(1)–C(3), 2.552(3); C(1)–C(15), 1.520(4); Cl(1)–Zr(1)–Cl(1), 102.46(4); C(1)–C(15)–C(8), 102.7(8); Cp(centroid)–Zr(1)–Cp(centroid), 117.15.

Table 1. Ethylene–Norbornene Copolymerization Results[a]

entry	cat.	pressure (psig)	time (min)	yield (g)	activity[b]	T_g (°C)	M_w	M_w/M_n
1	**5**	100	10	5.7	68	171	130 000	2.0
2	**5**	75	10	4.8	58	179	158 000	2.2
3	**5**	50	10	2.2	26	196	164 000	2.3
4	**5**	25	10	0.85	10	226	173 000	2.0
5	**6**[c]	100	6	3.2	64	136	490 000	3.3
6	**6**	75	6	1.8	36	145	555 000	3.2
7	**6**	50	6	0.84	17	161	534 000	3.4
8	**6**	25	6	0.54	11	193	435 000	2.3

[a] Polymerization conditions: 30 mL of norbornene solution in toluene (3.54 M), 0.5 μmol catalyst, Al/Zr = 4000, 60 °C. [b] In units of 10⁶ g/(mol h). [c] [Ph₂C(Fluo)(Cp)]ZrCl₂.

carbon (average 2.450(4) Å) to α-carbons (average 2.496-(4) Å) and to the β-carbons (average 2.544(6) Å). All these data indicate that the coordination site for catalysis is widely opened.

Compound **5** activated with MAO (Al/Zr, 4000) was tested for the copolymerization of norbornene with ethylene. For comparison, [Ph₂C(Fluo)(Cp)]ZrCl₂ (**6**)[5,12] showing a high activity for the copolymerization was studied. The results are summarized in Table 1. The norbornene content in the copolymer can be estimated by measuring T_g, because the T_g value shows a linear dependence on the norbornene content in the copoly-

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mer.[13] Compound **5** showed better activity and norbornene incorporation ability than **6**. Owing to the absence of any substituent on the β-carbons, there is no steric hindrance on the reaction site. Thus, a bulky norbornene easily approaches the reaction site, which results in an increase of the norbornene content in the polymer. The role of methyl substituents in **5** is crucial to the high activity. The corresponding compound MeCH(Cp)$_2$ZrCl$_2$ without methyl substituents was reported to have a low activity, even though its norbornene incorporation ability is high.[5] In comparison to [Ph$_2$C(Fluo)(Cp)]ZrCl$_2$, **5** gave lower molecular weight polymers (M_w, 130 000–173 000) and the molecular weight of the copolymer increases with the increase of the norbornene content, which is the general trend shown by *anza*-zirconocene complexes.[6] After norbornene insertion, the chain transfer via β-elimination is impossible because the basic requirement for β-elimination, coplanarity of Zr–C(α)–C(β)–H, cannot be attainable. The narrow molecular weight distribution (M_w/M_n, 2.0–2.3) of the copolymers implies that complex **5** gives a single active species when it is activated with MAO. The comparative complex, [Ph$_2$C(Fluo)(Cp)]ZrCl$_2$, gave polymers of rather broad molecular weight distribution (2.3–3.4). and the polymers did not show good correlation between norbornene content and molecular weight. Similar results were observed with the same complex by Kaminsky.[12]

Experimental Section

General Consideration. All manipulations were performed under an inert atmosphere (dinitrogen or argon) using a standard Schlenk technique or a VAC glovebox. Pentane, toluene, and diethyl ether were distilled from benzophenone ketyl. Anhydrous grade toluene was purchased from Aldrich for polymerization and was purified further by distillation over Na/K alloys. Methylaluminoxane (MAO) was purchased as a solution in toluene from Akzo (6.4 w% of Al, MMAO type 4). Ethylene in high purity grade (99.9%) was purchased from Matheson and dried by passing it through columns of activated molecular sieves and copper. NMR spectra were obtained on a Bruker ARX-300. IR spectra were recorded on a Bio-Rad FTA-60A instrument. Elemental analyses were carried out on a Perkin-Elmer 2400 CHN microanalyzer. Gel permeation chromatograms (GPC) were obtained at 140 °C in trichlorobenzene using a Waters Model 150-C+ GPC, and the data were analyzed using a polystyrene analyzing curve. Differential scanning calorimetry (DSC) was performed on a Thermal Analysis 3100.

4,4′-Methylenebis(tricyclo[5.2.1.0²,⁶]deca-4,8-dien-3-one) (1). Compound **1** was synthesized according to the published method.[8] The crude compound was purified by flash column chromatography, with with hexane and ethyl acetate (v/v, 10/1) as eluent. The yield was 50%. Although the Pauson–Khand reaction gave only an exocyclic product, a mixture of two diastereomers was obtained because two chiral fragments were connected by a methylene bridge. Splitting of some peaks was observed in the ^{13}C{^{1}H} NMR spectrum. ^{1}H NMR (CDCl$_3$): δ 7.26–7.23 (m, 2 H, C(O)C=C*H*), 6.28 (dd, 5.6, 3.0 Hz, 2 H, vinyl *H*), 6.20 (dd, 5.6, 3.0 Hz, 2 H, vinyl *H*), 3.07 (s, 2 H), 2.90 (s, 2 H), 2.72 (s, 2 H), 2.68 (s, 2 H), 2.28 (d, 5 Hz, 2 H), 1.37 (d, 9.3 Hz, 2 H, CHC*H*$_2$CH), 1.17 (d, 9.3 Hz, 2 H, CHC*H*$_2$CH) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 209.45 (carbonyl),

161.31 and 161.24 (splitting, vinyl *C*), 147.31 and 147.25 (splitting, vinyl *C*), 138.85 (vinyl-*C*), 137.46 and 137.44 (splitting, vinyl *C*), 52.79, 48.13, 44.04 and 44.02 (splitting), 43.33 and 43.29 (splitting), 41.62 and 41.58 (splitting), 21.58 and 21.56 (splitting) ppm. IR (KBr pellet): 1705, 1620 cm^{-1}. Anal. Calcd for C$_{21}$H$_{20}$O$_2$: C, 82.86; H, 6.62. Found: C, 82.75; H, 6.68.

4,4′-Methylenebis(5-methyltricyclo[5.2.1.0²,⁶]deca-8-en-3-one) (2). To a Schlenk flask containing CuI (4.7 g, 25 mmol) and diethyl ether (75 mL) was added MeLi (33 mL, 1.5 M in diethyl ether, 50 mmol) at −20 °C. The solution was stirred at −20 °C for 30 min and cooled to −78 °C. Compound **1** (3.0 g, 9.9 mmol) was added as a solid. The resulting solution was warmed to room temperature. After the solution was stirred at room temperature for 5 h, it was poured into chilled water (5 mL). The mixture was filtered over Celite, and the ethereal solution was separated. The aqueous solution was extracted with diethyl ether (50 mL). The combined ethereal solution was dried over anhydrous MgSO$_4$. Evaporation of the solvent gave a white solid which was purified by chromatography on a silica gel column with hexane and ethyl acetate (v/v, 15/1) as eluent. Yield: 85%. ^{1}H NMR (CDCl$_3$): δ 6.17 (dd, 6.3, 2.9 Hz, 2 H, vinyl *H*), 6.12 (dd, 6.3, 2.9 Hz, 2 H, vinyl *H*), 3.11 (s, 2 H), 2.73 (s, 2 H), 2.55–2.40 (m, 2 H), 2.31 (d, 9.3 Hz, 2 H), 1.99 (dt, 14, 6.8 Hz, 1 H, bridge C*H*$_2$), 1.84 (dd, 8.6, 6.3 Hz, 2 H), 1.38 (d, 8.9 Hz, 2 H, CHC*H*$_2$CH), 1.40–1.26 (m, 3 H), 1.28 (s, 6 H, C*H*$_3$), 1.02 (d, 8.9 Hz, 2 H, CHC*H*$_2$CH) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 218.59 (carbonyl), 138.71 (vinyl *C*), 137.76 (vinyl *C*), 58.49, 54.43, 49.09, 46.86, 45.41, 44.71, 41.64, 26.08, 21.43 (*C*H$_3$) ppm. IR (KBr pellet): 1737 cm^{-1}. Anal. Calcd for C$_{23}$H$_{28}$O$_2$: C, 82.10; H, 8.39. Found: C, 82.32; H, 8.60.

2,2′-Methylenebis(3-methyl-2-cyclopenten-1-one) (3). Compound **2** (1.50 g, 0.46 mmol) was placed in a quartz tube which was connected via a flexible hose to a Schlenk flask. After the system was purged with nitrogen, the quartz tube was placed in a furnace whose temperature had been set to 420 °C, and the Schlenk flask was immersed in a liquid nitrogen bath. After 2 min, the quartz tube was removed from the furnace. The product was purified by chromatography on a silica gel column with hexane and ethyl acetate (v/v, 1/1) as eluent. Yield: 0.60 g (66%). ^{1}H NMR (CDCl$_3$): δ 3.05 (s, 2 H, bridge C*H*$_2$), 2.5–2.4 (m, 4 H), 2.35–2.25 (m, 4 H), 2.18 (s, 6 H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 209.64 (carbonyl), 173.09 (vinyl *C*), 137.76 (vinyl *C*), 34.57, 32.22, 18.23 (*C*H$_3$), 17.51 (bridge *C*H$_2$) ppm. IR (KBr pellet): 1690, 1640 cm^{-1}. Anal. Calcd for C$_{13}$H$_{16}$O$_2$: C, 76.42; H, 7.91. Found: C, 76.21; H, 7.50.

2,2′-Methylenebis(1,3-dimethyl-1,3-cyclopentadiene) (4). To a Schlenk flask containing **3** (1.24 g, 6.05 mmol) in diethyl ether (30 mL) was added MeLi (12 mL, 1.5 M in Et$_2$O, 18 mmol) at −78 °C. The solution was warmed to room temperature. After the solution was stirred for 20 h, 10 mL of water was added. After diethyl ether was removed by a rotary evaporator, ethyl acetate (60 mL) was added. The mixture was poured into a separatory funnel. The aqueous layer was removed, and aqueous HCl solution (2 M, 60 mL) was added. The separatory funnel was vigorously shaken for 2 min. The aqueous layer was removed and the organic layer was washed with aqueous NaHCO$_3$ solution (30 mL). The organic layer was collected and dried over anhydrous MgSO$_4$. Evaporation of the solvent gave a residue which was purified by chromatography on a silica gel column with hexane and benzene (v/v, 10/1) as eluent. Yield: 0.770 g (63%). ^{1}H NMR (CDCl$_3$): δ 5.80 (s, 2 H, vinyl *H*), 3.27 (s, 2 H, bridge C*H*$_2$), 2.76 (s, 4 H, C*H*$_2$), 1.93 (s, 6 H, C*H*$_3$), 1.82 (s, 6 H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 144.40 (vinyl *C*), 137.61 (vinyl *C*), 137.45 (vinyl *C*), 123.56 (vinyl *C*H), 43.90, 23.53, 14.55, 13.90 ppm.

[2,2′-Methylenebis(1,3-dimethylcyclopentadienyl)]zirconium Dichloride (5). To a Schlenk flask containing **4** (0.770 g, 3.84 mmol) in 10 mL of diethyl ether was added *n*-BuLi (3.1 mL, 2.5 M in hexane) at −78 °C. The solution was

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warmed to room temperature. After the mixture was stirred overnight, it was filtered. After the solid was washed with diethyl ether (10 mL × 2) and dried under vacuum, 0.77 g of lithium salt was obtained (96%). The lithium salt (0.719 g, 3.39 mmol) and $ZrCl_4$ (0.789 g, 3.39 mmol) were reacted in toluene (30 mL) at room temperature for 3 days. Filtration followed by removal of the solvent gave a pure product. Single crystals suitable for X-ray crystallography were obtained by slow diffusion of pentane vapor into a toluene solution for 12 h. Yield: 0.250 g (20%) of white crystals. Mp: >200 °C dec. ^{1}H NMR (CDCl$_3$): δ 6.45 (s, 4 H, Cp *H*), 4.07 (s, 2 H, bridge C*H$_2$*), 2.21 (s, 12 H, C*H$_3$*) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 124.29 (Cp *C*H), 122.54 (Cp *C*), 104.06 (Cp *C*), 21.73 (bridge *C*H$_2$), 16.47 (*C*H$_3$) ppm. Anal. Calcd for C$_{15}$H$_{18}$ZrCl$_2$: C, 49.98; H, 5.04. Found: C, 50.05; H, 5.01.

Ethylene−Norbornene Copolymerization. In a drybox, in 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 immersed in an oil bath whose temperature had been set to 60 °C, and the mixture was stirred for 15 min. An activated catalyst prepared by mixing 0.50 μmol of catalyst and MAO (0.84 g, 2.0 mmol of Al) was added via a syringe. Ethylene was fed immediately

under the predetermined pressure. After polymerization had been conducted for a given time, the polymerization reaction was quenched by venting ethylene and pouring the mixture into acetone. White precipitates were collected by filtration and dried under vacuum. Table 1 summarizes the polymerization result. [Ph$_2$C(Fluo)(Cp)]ZrCl$_2$ (**6**) was used for comparison. T_g data were determined on a second heating at a heating rate of 15 °C/min.

Supporting Information Available: Tables of crystallographic data, atomic coordinates, bond lengths, bond angles, anisotropic displacement parameters, and H atom coordinates of **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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