Novel zirconacyclopentadiene complex; 8,8-bis(cyclopentadienyl)-7,9-bis(trimethylstannyl)-8-zirconabicyclo-[4.3.0]nona-1(9),6(7)-diene: synthesis, X-ray analysis, and catalytic activity for ethylene polymerization

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Abstract

Zirconacyclopentadiene complex 2c containing *gem*-dimetallated carbon atoms by zirconium and tin was prepared by the oxidative coupling reaction of 'Cp$_2$Zr' with distannyldiyne compounds. Complex 2c having trimethylstannyl groups was characterized by X-ray diffraction and its structure was compared with zirconacyclopentadiene analogues having *tert*-butyl groups (2a) or trimethylsilyl groups (3). The five-membered zirconacycle ring of 2c has a planar conformation whereas it is twisted in complexes 2a and 3. The C–Zr–C angle in 2c is smaller than those of the corresponding 2a and 3. The polymerization of ethylene proceeded when these complexes were used in combination with methylaluminoxane and it was found that the catalytic activities of these complexes were remarkably influenced by the substituents on the α-carbon atoms.

Keywords: Zirconium; Tin; Silicon; Crystal structure; Ethylene polymerization; Metallacycle

1. Introduction

These days, zirconocene complexes containing *gem*-dimetallated carbon with zirconium and other metals have attracted much attention because they are expected to show interesting chemical and physical properties. Several zirconocene complexes containing aluminum [1], gallium [2], and boron [3] were recently prepared, isolated and characterized by X-ray analysis. Those complexes are prepared either by the hydrozirconation reaction using Schwartz's reagent (Cp$_2$Zr(H)Cl) or the oxidative coupling reaction of 'Cp$_2$Zr' with the corresponding alkenyl- or alkynyl-metal. To our knowledge, zirconocene complexes containing *gem*-dimetallated carbon with zirconium and tin [4] or zirconium and zinc [5] had only been prepared in situ by the hydrozirconation.

Here, we would like to describe the synthesis and structural characterization of stable zirconocene com-

plex containing *gem*-dimetallated carbon with zirconium and tin. The catalytic activity of this complex for ethylene polymerization was also examined.

2. Experimental details

2.1. General procedure

All operations were carried out under dry nitrogen or argon atmosphere. ^{1}H NMR measurements were performed on a JEOL Model FX-270 spectrometer. C$_6$D$_6$ solvent for NMR measurements was distilled from sodium–benzophenone ketyl under nitrogen atmosphere.

2.2. Preparation of 1,8-bis(trimethylstannyl)-1,7-octadiyne (1c)

To a solution of 1,7-octadiyne (1.03 g, 9.37 mmol) in tetrahydrofuran (THF) (20 ml) at 0°C was added drop-

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wise a solution of n-butyllithium in hexane (11.4 ml, 18.7 mmol). After the reaction mixture was stirred at 0°C for 1 h, trimethylstannyl chloride (3.73 g, 18.7 mmol) in THF (5 ml) was added at 0°C. The mixture was stirred for 2 h at room temperature and was quenched with saturated ammonium chloride. The crude product was extracted with ether, washed with water, and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure. Distillation of the residue afforded the product (3.72 g, 92% yield) as a white solid: b.p. 160°C (0.1 Torr). ^{1}H NMR (CDCl$_3$): $\delta = 0.27$ (18H, s), 1.62 (4H, m), 2.28 (4H, m).

2.3. Preparation of 8,8-bis(cyclopentadienyl)-7,9-bis(trimethylstannyl)-8-zirconabicyclo[4.3.0]nona-1(9), 6(7)-diene (2c)

To a solution of bis(cyclopentadienyl) zirconium dichloride (585 mg, 2.00 mmol) in THF (10 ml) at −78°C was added dropwise a solution of n-butyllithium in hexane (2.4 ml, 4.00 mmol) [6]. After the reaction mixture was stirred at −78°C for 1 h, 1,8-bis(trimethylstannyl)-1,7-octadiyne (863 mg, 2.00 mmol) in THF (2 ml) was added at −78°C. The temperature was allowed to rise to room temperature, and the mixture was stirred for another 3 h. The solvent was removed under reduced pressure and the product was extracted with toluene. A solid part was removed by filtration. The clear filtrate was concentrated and kept at 0°C to afford the product (723 mg, 55% yield). ^{1}H NMR (C$_6$D$_6$): $\delta = 0.19$ (18H, s), 1.52 (4H, m), 2.17 (4H, m), 6.00 (10H, s).

2.4. Preparation of zirconacyclopentadienes 2a, 2b and 2d

In a similar manner, zirconacyclopentadienes 2a, 2b and 2d were prepared. 2a; ^{1}H NMR (C$_6$D$_6$): $\delta = 1.21$ (18H, s), 1.50 (4H, m), 2.22 (4H, m), 5.88 (10H, s). 2b; ^{1}H NMR (C$_6$D$_6$): $\delta = 0.17$ (18H, s), 1.52 (4H, m), 2.18 (4H, m), 5.97 (10H, s). 2d; ^{1}H NMR (C$_6$D$_6$): $\delta = 1.60$ (4H, m), 1.70 (6H, s), 2.30 (4H, m), 5.90 (10H, s).

2.5. X-ray diffraction analysis of 2c

A pale prismatic crystal of C$_{24}$H$_{36}$Sn$_2$Zr having approximate dimension of 0.50 × 0.40 × 0.30 mm^3 was mounted in a glass capillary. All measurements were made on a Rigaku AFC5S diffractometer with graphite monochromated Mo Kα radiation. Crystal data: space group P1 (No. 2), triclinic, $a = 10.623(6)$ Å, $b = 12.35(1)$ Å, $c = 10.373(6)$ Å, $\alpha = 100.79(5)°$, $\beta = 105.71(5)°$, $\gamma = 83.04(6)°$, $V = 1282(1)$ Å^3, $Z = 2$, $d_{calcd} = 1.69$ g cm^{-3}, $F(000) = 640.00$, $R = 0.040$, $R_w = 0.035$.

2.6. Ethylene polymerization

A five-necked flask (500 ml) equipped with a thermometer, gas inlet and outlet tubes, and an agitator was flushed with dry nitrogen. Dry toluene (200 ml) was placed in the flask and ethylene was introduced and saturated into toluene solution at ambient temperature. After 10 min, temperature was raised up to 60°C, and a prescribed amount of methylaluminoxane (MAO) was added and the solution was agitated for 1 min. Then, polymerization was initiated by addition of the catalyst solution to the reaction vessel. During the polymerization, ethylene was continuously fed and the temperature was kept at 60°C. The polymerization was quenched by adding methanol–HCl. The solution was poured into a large amount of methanol to precipitate the polymer. The polymer obtained was isolated and dried in vacuo.
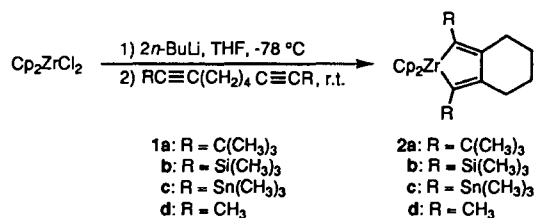
3. Results and discussion

3.1. Preparation of zirconacyclopentadienes 2a–d

Several zirconacyclopentadienes 2a–d were prepared by the oxidative coupling reaction of 'Cp$_2$Zr' with diynes 1a–d (Scheme 1). The intermediate 'Cp$_2$Zr' was generated in situ from the reaction of bis(cyclopentadienyl)zirconium dichloride with two equivalents of n-butyllithium [6]. The zirconacyclopentadienes 2a–d were obtained in moderate yield and were stable in the air for a few days.

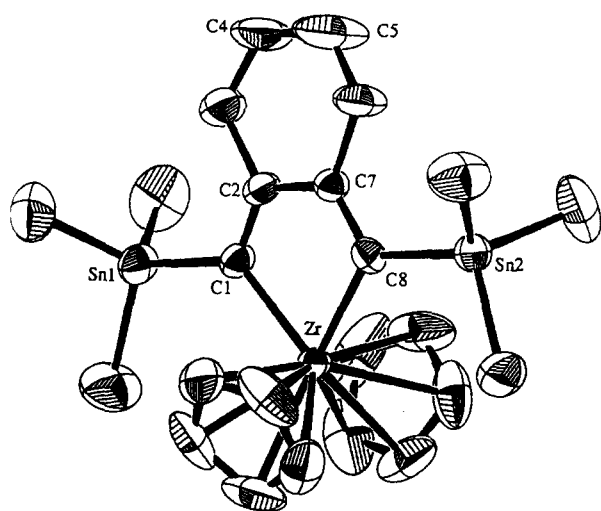### 3.2. Structural features of zirconacyclopentadiene 2c

For X-ray diffraction, suitable single crystals of zirconocene complex (2c) containing gem-dimetallated carbon with zirconium and tin were obtained upon cooling a toluene solution of 2c to 0°C. The crystal structure of 2c were determined by X-ray diffraction. An ORTEP view of 2c is shown in Fig. 1. Disorder at C(4) and C(5) is observed as the cyclohexyl ring flips between chair and boat conformations.

The X-ray crystal structure analysis and a detailed comparison with tert-butyl analogue 2a [7] and trimethylsilyl analogue 3 [8] revealed two interesting structural features of zirconacyclopentadiene 2c. One of them is

Cp$_2$ZrCl$_2$ $\xrightarrow{\begin{array}{c}1)\ 2n\text{-BuLi, THF, -78 °C}\\2)\ RC\equiv C(CH_2)_4 C\equiv CR,\ r.t.\end{array}}$

1a: R = C(CH$_3$)$_3$
b: R = Si(CH$_3$)$_3$
c: R = Sn(CH$_3$)$_3$
d: R = CH$_3$

2a: R = C(CH$_3$)$_3$
b: R = Si(CH$_3$)$_3$
c: R = Sn(CH$_3$)$_3$
d: R = CH$_3$

Scheme 1.

Fig. 1. An ORTEP drawing of 2c.

the metallacyclic framework of zirconacyclopentadiene 2c. Zirconacycle ring of 2a having *tert*-butyl groups at α-carbon (C(1) and C(8)) are twisted and the torsion angles Zr–C(1)–C(2)–C(7) and C(1)–C(2)–C(7)–C(8) in 2a are −20.6° and +33.6° respectively (Table 1). In the case of zirconacyclopentadiene 3 having trimethylsilyl groups at α-carbon, the conformation of the zirconacycle ring was less puckered than 2a. The zirconacyclopentadiene 2c having trimethylstannyl groups at α-carbon has a planar conformation, which is indicated by the observed torsion angles Zr–C(1)–C(2)–C(7)

(−1.3°) and C(1)–C(2)–C(7)–C(8) (+1°). These observations could be explained by the C(1)–M bond length (Table 1). The complex 2a has the short C(1)–M bond (1.54 Å) which causes the steric repulsion between the Cp ring and *tert*-butyl group leading to the twisted zirconacycle ring. In contrast, the long C(1)–M bond in 2c (2.15 Å) reduces the extent of steric repulsion between the Cp ring and trimethylstannyl group. Also zirconacyclopentadiene 2c exists in the planar conformation.

Another feature is the C(1)–Zr–C(8) angle of the five-membered zirconacycle ring; that is, the C(1)–Zr–C(8) angle in 2c is quite acute (79.4°), and is smaller than 3 (85.5°) and 2a (92.2°) (Table 1).

3.3. Catalytic activities of zirconacyclopentadienes 2a–d for ethylene polymerization

Since dialkylzirconocenes are the precursors of a homogeneous Ziegler–Natta catalyst in olefin polymerization [9], the catalytic activities of zirconacyclopentadienes 2a–d for ethylene polymerization in the presence of MAO were examined (Table 2). The catalytic activities of zirconacyclopentadienes 2 were remarkably influenced by the substituents at the α-carbon atoms. Of these four complexes 2a–d, zirconacyclopentadiene 2c having a trimethylstannyl group at the α-carbon exhibited the highest activity. The activity of 2c is ca. 2.5 times higher than that of 2b and ca. 5 times higher than that of 2a. Interestingly, it was found that the catalyst

Table 1
Comparison of the structures of zirconacyclopentadienes

2a: M = C, R^1 = R^2 = –(CH$_2$)$_4$–
3: M = Si, R^1 = R^2 = Ph
2c: M = Sn, R^1 = R^2 = –(CH$_2$)$_4$–
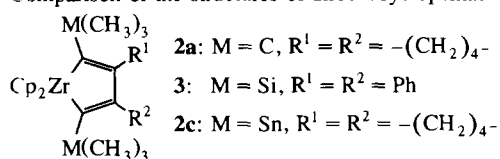
Entry	Complex	M	Bond length (Å) C(1)–M	Torsion angle (deg)		Angle (deg) C(1)–Zr–C(8)
				Zr–C(1)–C(2)–C(7)	C(1)–C(2)–C(7)–C(8)	
1	2a	C	1.54	−20.6	+33.6	92.2
2	3	Si	1.88	−2.8	+4.3	85.5
3	2c	Sn	2.15	−1.3	+1	79.4

Table 2
Polymerizations of ethylene in the presence of different zirconacyclopentadienes and MAO [a]

Entry	Catalyst	R	Activity (kg(PE) mol^{-1} (Zr) h^{-1})	[η] [b] (dl g^{-1})
1	2a	C(CH$_3$)$_3$	4900	4.86
2	2b	Si(CH$_3$)$_3$	9800	4.71
3	2c	Sn(CH$_3$)$_3$	25300	4.23
4	2d	CH$_3$	14100	4.75

[a] Conditions: Zr 5.0 μmol l^{-1}, Al 3.75 mmol l^{-1}, toluene 200 ml, 60°C.
[b] Viscosity measurements were performed in decahydronaphthalene at 135°C.

with the longer C(1)–M bond showed the higher catalytic activity. From the other experimental result that the complex **2d**, containing a smaller substituent, exhibited remarkably higher activity than **2a**, the sterical hindrance around the zirconium center appears to be the primary factor in determining the catalytic activity of the complexes.

Generally, the active species of zirconocene-catalyzed polymerization has been regarded to be a cationic zirconocene alkyl complex $(Cp_2Zr(R)^+)$, which is generated by the transfer of one of the two alkyl groups (R^-) from the dialkylzirconocene (Cp_2ZrR_2) to MAO [10]. It is also reasonable to consider, in the present case, that one of the C–Zr bonds of complexes **2** would be cleaved at the initiation step by the attack of the aluminum compound (MAO) to generate the cationic zirconocene complex $(Cp_2Zr(R)^+)$. The complex **2c** containing the longer C(1)–M(Sn) bond or the complex **2d** containing the smaller substituent allows the zirconium center to be less crowded. These complexes, therefore, could be preferably attacked by the aluminum compounds at the initiation step to form the active species more efficiently.

4. Conclusion

Stable zirconacyclopentadiene containing *gem*-dimetallated carbon with zirconium and tin can be synthesized by the oxidative coupling reaction of 'Cp₂Zr' with distannyldiyne. The five-membered zirconacycle ring of this complex is characterized by X-ray analysis as a planar conformation with the acute C–Zr–C angle. The catalytic activities of zirconacyclopentadienes for ethylene polymerization are influenced by the substituents at the α-carbon atoms.

Acknowledgement

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