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Synthesis and molecular structure of $(CH_3Cp)_2Yb \cdot DME$ and its catalytic activity for the polymerization of methyl methacrylate

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Abstract

The complex of $(CH_3Cp)_2Yb \cdot DME$ (DME = dimethoxyethane) has been synthesized by the reduction with metallic sodium of the corresponding chloride $(CH_3Cp)_2YbCl$. $(CH_3Cp)_2Yb \cdot DME$ crystallized from DME in the monoclinic space group *Cm*, with cell constants $a = 11.068(3)$, $b = 12.338(4)$, $c = 12.479(4)$ Å; $\beta = 100.51(2)°$, $V = 1675(1)$ Å^3, and $D_0 = 1.66$ g/cm^3 for $Z = 4$. Least-squares refinement of 1420 unique observed reflections led to final *R* of 0.0487. This complex can be used as a catalyst for the polymerization of methyl methacrylate (MMA).

1. Introduction

The organometallic chemistry of lanthanide metals in low oxidation states is currently undergoing rapid development. Study of divalent metal-complex chemistry has led to a variety of new classes of complexes and reactivity patterns [10–13]. We have recently synthesized and characterized structurally divalent complexes of $(^tBuCp)_2Ln \cdot 2THF$ (Ln = Sm, Yb) [14] and had examined their catalytic activity for the polymerization of styrene [15]. It was found that the activity changed depending upon the size of the metallocene [16]. Divalent complexes $(C_5Me_5)_2Yb \cdot 2THF$, $(C_5Me_5)_2Sm \cdot 2THF$, $(C_5Me_5)_2Yb \cdot (pyridine)_2$ and $(indenyl)_2Yb \cdot 2THF$ were recently reported to be good catalysts for syndiotactic polymerization of MMA [17]. In order to explore further the effect of the size of cyclopentadienyl ligand on the reactivity of divalent complexes, $(CH_3Cp)_2Yb \cdot DME$ was synthesized and structurally characterized and its catalytic activity for polymerization of MMA was tested *. It was found that the polymerization activity of the title complex is more active than that of $(C_5Me_5)Yb \cdot 2THF$ reported by Yasuda [17].

2. Experimental section

The complex described below is extremely air- and moisture-sensitive. All the experiments were conducted under pure argon by Schlenk techniques. THF, DME, hexane and toluene were predried with $CaCl_2$ and distilled from sodium benzophenone ketyl. Anhydrous $YbCl_3$ was prepared by Taylor's method [19]. MMA was distilled under vacuum before use. Analysis of rare earth metal was by direct complexometric titration. Infrared spectra were obtained on a Digilab-FST-20E spectrometer (KBr pellet). ^{13}C-NMR spectra of polyMMA were determined on a Varian Unity-400 NMR spectrometer.

2.1. Synthesis of $(CH_3Cp)_2Yb \cdot DME$

Anhydrous $YbCl_3$ (7.0 mmol) and THF (40 ml) were placed into a Schlenk flask and stirred overnight, then a solution of $(CH_3Cp)Na$ (14.0 mmol) in THF (11 ml) was added. The mixture was stirred continuously for 72 h at 60°C. After centrifugation to remove NaCl, metallic sodium (0.164 g, 7.1 mmol) was added to the resulting orange solution. 48 h reaction at 60°C with stirring gave a red-brown suspension. After centrifugation, the

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* Since the submission of this manuscript, decrease of catalytic activity for MMA polymerization with the increase of steric bulk of the ligand ($C_5H_5 > C_5Me_5$) was reported by Yasuda and Nakamura *J. Am. Chem. Soc.*, *114* (1992) 4908.

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red-brown solution was concentrated under vacuum and DME (5 ml) and hexane (1 ml) were added. The mixture was cooled to −10°C for crystallization. Blue crystals of $(CH_3Cp)_2Yb \cdot DME$ were obtained some days later (yield: 38%). Anal. Found: Yb, 40.82; $C_{16}H_{24}O_2Yb$ calcd.: 41.05%; IR(KBr): 3067w, 2925s, 2898m, 2732w, 1661w, 1611m, 1542m, 1513m, 1450m, 1367m, 1306m, 1245w, 1192m, 1078s, 1036m, 978w, 932w, 896w, 822m, 765s, 624m, 563w.

2.2. Polymerization

MMA was added to a solution in toluene of the complex described above at the desired temperature and the polymerization was carried out at the same temperature for 3 h, then terminated by ethanol containing 1wt% antioxidant. The polymer was precipitated by hexane, washed with ethanol/H_2O/HCl and dried under vacuum.

2.3. Crystal structure determination of $(CH_3Cp)_2Yb \cdot DME$

A single crystal of 0.48 × 0.40 × 0.40 mm was sealed in a thin-walled glass capillary under argon and placed in a Nicolet R_3M/E four-circle diffractometer with Mo Kα radiation and a scan range $3 \leqslant 2\theta \leqslant 58°$. Of the 2391 reflections collected, 1420 reflections with $I > 3\sigma(I)$ were considered to have been observed. The structure was solved by the heavy-atom method and refined by block-diagonal least-squares by the use of the SHELXTL program. The position of the heavy atom Yb was found from a Patterson map and the positions of other non-hydrogen atoms were found by Fourier techniques. The coordinates of hydrogen atoms were added according to theoretical models. The final agreement factors were $R = 0.0487$, $R_w = 0.0476$. The function minimised in the refinement was $\Sigma w(|F_o| - |F_c|)^2$ where $W = [\sigma^2(F_o) + 0.0002F_o^2]^{-1}$. The crystallographic data and atomic coordinates and thermal parameters are listed in Tables 1 and 2 respectively.

3. Results and discussion

3.1. Synthesis and molecular structure

The reduction of $(CH_3Cp)_2YbCl$ by metallic sodium in THF (reactions 1 and 2) gives the red-brown solution of $(CH_3Cp)_2Yb \cdot 2THF$. The solution was dried under vacuum to give a green-yellow powder containing solvated THF. The powder dissolved in DME to form a blue solution, from which blue crystals of $(CH_3Cp)_2Yb \cdot DME$ were isolated.

$$YbCl_3 + 2(CH_3Cp)Na \xrightarrow{THF} (CH_3Cp)_2YbCl + 2NaCl \quad (1)$$

TABLE 1. Crystal data

Compound	$(CH_3Cp)_2Yb \cdot DME$
mol wt	421.44
crystal size (mm)	0.48 × 0.40 × 0.40
cell constants	
a Å	11.068(3)
b Å	12.338(4)
c Å	12.479(4)
β deg	100.51(2)
V Å^3	1675(1)
scan range 2θ	3–58
reflections	2391
reflections for $I > 3\sigma(I)$	1420
space group	Cm
Z	4
D_c g/cm^3	1.66
R	0.0487
R_w	0.0476
$F(000)$	808
radiation	MoKα ($\lambda = 0.7107$ Å)

$$(CH_3Cp)_2YbCl + Na \xrightarrow{THF} (CH_3Cp)_2Yb \cdot 2THF + NaCl \quad (2)$$

$$\downarrow DME$$

$$(CH_3Cp)_2Yb \cdot DME$$

It was reported that $(CH_3Cp)_2Yb \cdot THF$ is a polymer in the solid state, in which the monomeric $(\mu\text{-}CH_3Cp)(CH_3Cp)Yb \cdot THF$ units are linked by bridging

TABLE 2. Atomic coordinates (× 10^4) and isotropic thermal parameters (× 10^3 Å^2)

	x	y	z	U_{eq} [a]
Yb(1)	0	163	5000	72(1)
Yb(2)	0	3020	0	73(1)
C(11)	−2322(19)	544(22)	4879(29)	136(15)
C(12)	−1926(16)	1558(15)	4809(17)	68(7)
C(13)	−1387(27)	1691(19)	3937(18)	107(12)
C(14)	−1650(27)	651(25)	3240(26)	112(14)
C(15)	−2311(25)	−3(27)	3920(30)	218(26)
C(16)	−3121(54)	210(44)	5338(47)	2218(110)
C(21)	2485(14)	2762(15)	395(17)	85(8)
C(22)	1996(32)	1704(26)	−150(26)	235(30)
C(23)	1418(33)	1250(31)	693(31)	280(35)
C(24)	1467(24)	1893(27)	1596(21)	110(15)
C(25)	2168(26)	2864(34)	1391(20)	125(17)
C(26)	3193(20)	3308(17)	−300(24)	146(16)
O(1)	401(14)	−1424(11)	4039(13)	67(6)
O(2)	−488(22)	4834(24)	902(16)	147(12)
C(1)	469(23)	−1301(23)	2955(20)	138(16)
C(2)	−132(46)	−2530(26)	4375(25)	301(33)
C(3)	75(15)	5644(12)	522(14)	73(6)
C(4)	−737(26)	4895(23)	1992(17)	111(12)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

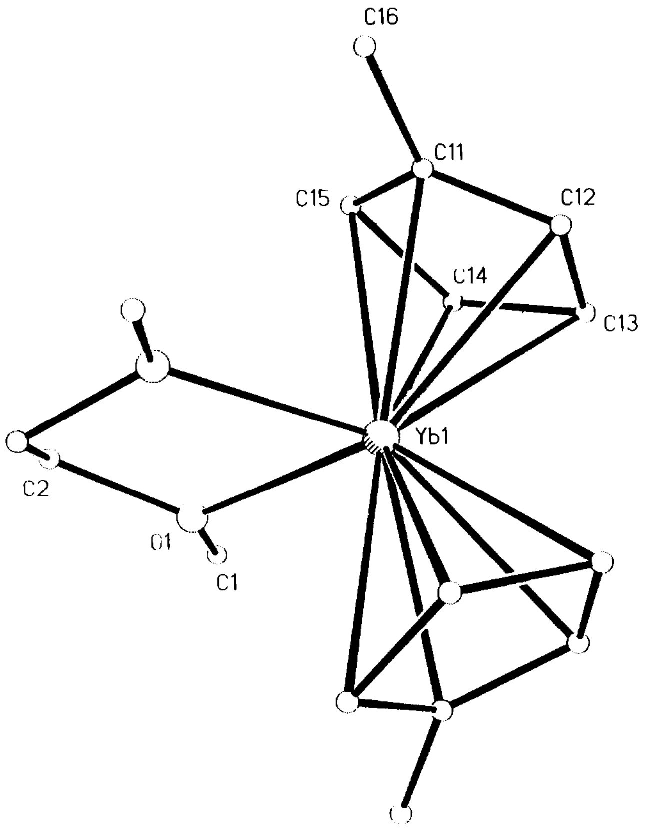

Fig. 1. Molecular structure of $(CH_3Cp)_2Yb \cdot DME$.

TABLE 3. Bond lengths (Å)

Yb(1)–C(11)	2.590(22)	Yb(1)–C(12)	2.716(18)
Yb(1)–C(13)	2.631(24)	Yb(1)–C(14)	2.656(29)
Yb(1)–C(15)	2.573(27)	Yb(1)–O(1)	2.379(15)
Yb(2)–C(21)	2.724(16)	Yb(2)–C(22)	2.776(35)
Yb(2)–C(23)	2.736(37)	Yb(2)–C(24)	2.711(27)
Yb(2)–C(25)	2.699(24)	Yb(2)–O(2)	2.606(28)
Yb(1)–Cen(1)	2.376 (1)	Yb(1)–Cen(2)	2.376 (1)
Yb(2)–Cen(3)	2.442 (1)	Yb(2)–Cen(4)	2.442 (1)
Yb(1)–C(ring)$_{av}$	2.663	Yb(2)–C(ring)$_{av}$	2.729

Cen is the centroid of cyclopentadienyl ring.

methylcyclopentadienyl group for increasing coordinative saturation. However, the molecular structure of the DME-solvated complex $(CH_3Cp)_2Yb \cdot DME$ consists of discrete monomer units as shown in Figs. 1 and 2. The geometry around the ytterbium ion can be described as a pseudo-tetrahedron with the centroids of the two methylcyclopentadienyl rings and oxygens of the bidentate DME at the apices of the tetrahedron. The methyl groups on the cyclopentadienyl rings are located at opposite sides. The angles around the ytterbium atom are displaced from the perfect tetrahedron in keeping with the steric requirement of the methylcyclopentadienyl ligands. Selected bond lengths and angles are listed in Tables 3 and 4 respectively. The centroid–Yb–centroid angles range from 124.3(1)° to 135.6(1)° which are similar to the relevant angles reported for $(^tBuCp)_2Yb \cdot 2THF$ (134°) [14], $(C_5H_5)_2Yb \cdot DME$ (133.9°) [18], $(Me_3SiCp)_2Yb \cdot 2THF$ (133°) [12], but larger than 114.6° to 118.0° in $(CH_3Cp)_2Yb \cdot THF$ [1]. This may be because $(CH_3Cp)_2Yb \cdot THF$ forms a chain structure in which ytterbium centres have a crowded coordinate environment. The angles O–Yb–O from 61.6° to 69.3° are considerably small, but comparable with the corresponding angles of 69.3(4)° for $(C_5H_5)_2Yb \cdot DME$ and 60.8(2)° for $[(Me_3Si)_2N]_2Eu \cdot 2DME$ [20].

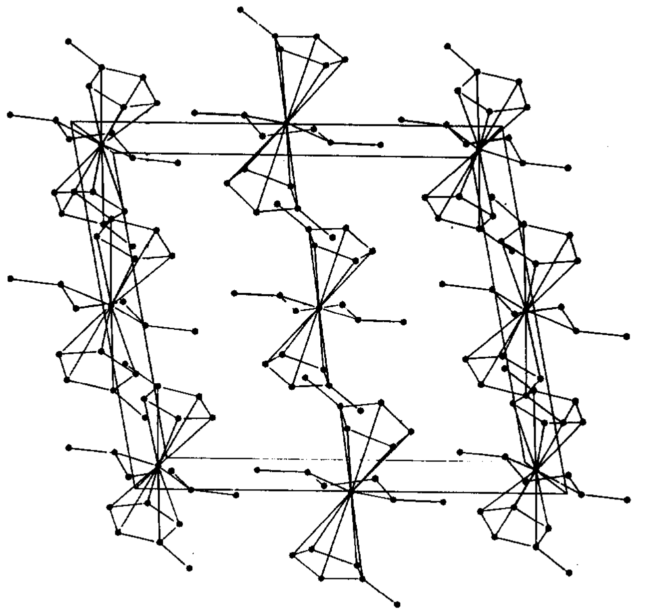

Fig. 2. Unit cell of $(CH_3Cp)_2Yb \cdot DME$.

The average ytterbium–carbon distances 2.633 Å for Yb(1)–C(ring)$_{av}$ and 2.729 Å for Yb(2)–C (ring)$_{av}$ are comparable with the corresponding average distances of 2.658 Å in $(C_5H_5)_2Yb \cdot DME$, 2.732 Å in $(CpCH_2CH_2CH_2Cp)$ $Yb \cdot 2THF$ [3]. As expected, these distances are shorter than those found in $(CH_3Cp)_2Yb \cdot THF$ which has ytterbium–C(ring) distances of 2.76 Å (terminal cyclopentadienyl ring), 2.91 Å and 2.87 Å (bridging cyclopentadienyl ring).

TABLE 4. Bond angles (°)

O(1)–Yb(1)–Cen(2)	107.05(1)	Cen(1)–Yb(1)–Cen(2)	135.6 (1)
Cen(1)–Yb(1)–O(1a)	107.05(1)	Cen(2)–Yb(1)–O(1a)	108.8 (1)
O(2)–Yb(2)–Cen(3)	117.4 (1)	Cen(3)–Yb(2)–Cen(4)	124.3 (1)
O(2)–Yb(2)–Cen(4)	110.0 (1)	Cen(4)–Yb(2)–O(2a)	117.4 (1)
Cen(3)–Yb(2)–O(2a)	110.0 (1)	Cen(1)–Yb(1)–O(1)	108.8 (1)
O(1)–Yb(1)–O(1a)	69.3 (8)	O(2)–Yb(2)–O(2a)	61.6(11)

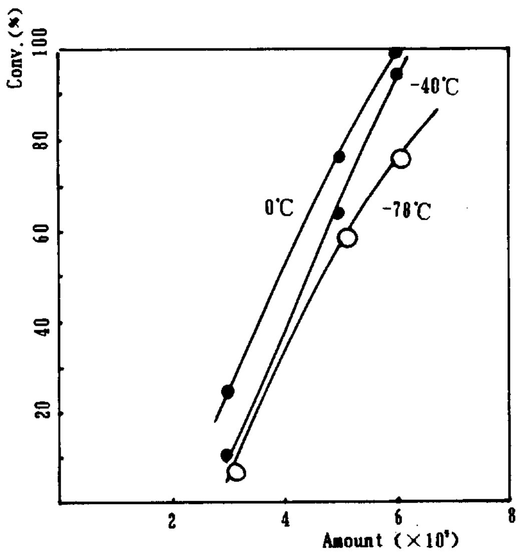

Fig. 3. Relationship between conversion and amount of catalyst at different temperatures ($(CH_3Cp)_2Yb \cdot DME$, 3 h, [MMA] = 1.9 M (toluene)).

3.2. Catalytic activity for the polymerization of MMA

The relationship between the conversion and the amount of catalyst at different temperatures is shown in Fig. 3. The results indicated that $(CH_3Cp)_2Yb \cdot DME$ is an excellent catalyst for the polymerization of MMA, showing high activity even at −78°C and the catalytic activity increases with increasing amount of catalyst used. $(C_5Me_5)_2Yb \cdot 2THF$ was reported to be used as a catalyst for MMA polymerization at above −50°C, however shows little catalytic action below −50°C [17]. Thus, the catalytic activity of $(CH_3Cp)_2Yb \cdot DME$ is higher than that of $(C_5Me_5)Yb \cdot 2THF$. This may be because the more crowded cyclopentadienyl ligand makes insertion of MMA more difficult and the catalytic activity lower. However there is almost no difference between C_5H_5 and C_5H_4Me in catalytic activity for the polymerization of MMA. The tacticity of polymers determined as based on the ^{13}C NMR measurement depends upon the temperature of polymerization. The syndiotactic content increases from 70.1% to 90.5% when the temperature of polymerization decreases from 0°C to −78°C as shown in Fig. 4. Further investigations of the copolymerization of MMA and other olefins such as styrene are currently under way.

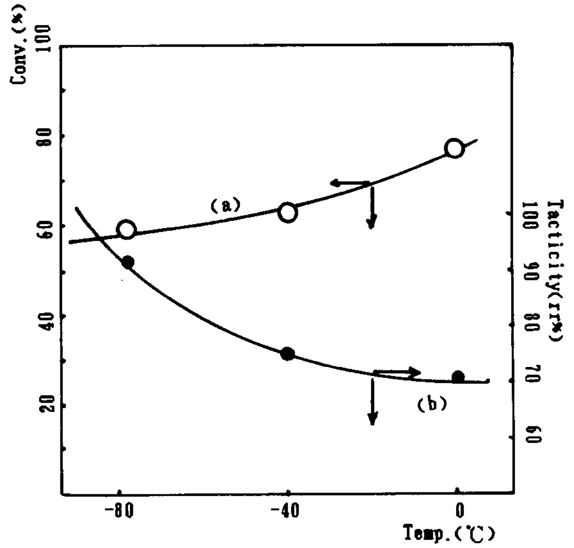

Fig. 4. Conversion *vs.* polymerization temperature (a) and syndiotacticity *vs.* temperature (b) (amount: 5×10^{-5} mol cat./ml MMA, [MMA] = 1.9 M (toluene), $(CH_3Cp)_2Yb \cdot DME$).

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