Synthesis and Structure of 1-Cyclopentylindenyl Lanthanide(II) Complexes and Their Catalytic Behavior for Polymerization of Acrylonitrile

QI, Min-Hua[a,b](齐民华) SHEN, Qi*,[a,c](沈琪) GONG, Xin-Qiang[a](龚新强)
SHEN, Zhi-Quan[b](沈之荃) WENG, Lin-Hong[d](翁林红)

[a] *Department of Chemistry and Chemical Engineering, Suzhou University, Suzhou, Jiangsu 215006, China*
[b] *Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, Zhejiang 310027, China*
[c] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*
[d] *Institute of Elemento-organic Chemistry, Nankai University, Tianjin 300071, China*

The reaction between $K(1\text{-}C_5H_9C_9H_6)$ and anhydrous $LnCl_3$ (Ln = Sm, Yb) in the molar ratio of 2:1 in THF with subsequent treatment by Na-K alloy afforded $(1\text{-}C_5H_9C_9H_6)_2Ln(THF)_n$ (Ln = Sm, n = 1; Ln = Yb, n = 2), while the reaction of SmI_2 with $K(1\text{-}C_5H_9C_9H_6)$ in the molar ratio of 1:2 in THF gave the anionic complex $K(1\text{-}C_5H_9C_9H_6)_3Sm(THF)_3$. The X-ray structure of $(1\text{-}C_5H_9C_9H_6)_2Yb(THF)_2$ showed that central metal Yb is coordinated by two cyclopentadienyl rings of 1-cyclopentylindenyls and two oxygen atoms from two tetrahydrofuran molecules to form pseudo-tetrahedral coordinate geometry. All these complexes are active for the polymerization of acrylonitrile.

Keywords 1-cyclopentylindenyl complexes, crystal structure, acrylonitrile polymerization, divalent lanthanide complex

Introduction

Great progress has been made in the chemistry of divalent organolanthanide complexes. A variety of new classes of complexes have been synthesized and widely used in organic synthesis and polymer chemistry.[1-6] It was noticed that most of the work published is focused on the complexes with substituted cyclopentadienyl or aryloxide groups as the stabilizing and solubilizing moieties.

Indene can be easily modified in steric bulk and solubility by substitution, moreover its derivatives have not been widely applied in organolanthanide(II) chemistry. Up to now, there are only a few reports concerning the synthesis and catalysis of divalent indenyl complex of lanthanide, such as $(C_9H_7)_2Sm(THF)_x$,[7] $(C_9H_7)_2YbL$ [L = $(THF)_2$,[8] DME[9]], rac-$(CH_2)_2\{1\text{-}[4,7\text{-}(CH_3)_2(C_9H_4)]\}_2Yb(THF)_2$,[9] rac-$(CH_2)_2(1\text{-}C_9H_6)_2Yb(THF)_2$,[9] $[1\text{-}(Me_2NCH_2CH_2)C_9H_6]_2Ln$ (Ln = Sm, Yb)[10] and O-$[(CH_2CH_2)(1\text{-}C_9H_6)]_2Ln(THF)$ (Ln = Sm, Yb).[11] Among them, some complexes show good catalytic activity for polymerization of methyl methacrylate.[10,12] But studies on acrylonitrile polymerization with organolanthanide(II) complexes are limited.[13] Therefore, investigation on synthesis and reactivity of divalent organolanthanides with indene-derived ligand is expected to be interest. We started the program on the synthesis of substituted indenyl complexes of lanthanide(II), since such ligands would provide a sterically and electronically new environment, and here report the syntheses of bis(1-cyclopentylindenyl)lanthanide complexes $(1\text{-}C_5H_9C_9H_6)_2Yb(THF)_2$, $(1\text{-}C_5H_9C_9H_6)_2Sm(THF)$, $K(1\text{-}C_5H_9C_9H_6)_3Sm(THF)_3$, molecular structure of $(1\text{-}C_5H_9C_9H_6)_2Yb(THF)_2$ and the preliminary results on their catalytic activity in polymerization of acrylonitrile.

* E-mail: qshen@suda.edu.cn
Received July 16, 2001; revised and accepted March 4, 2002.
Project supported by the National Natural Science Foundation of China (No. 20072027).

Experimental

All manipulations of air- and moisture-sensitive materials were performed by the standard Schlenk technique under argon. THF and toluene were distilled from sodium benzophenone ketyl. Indene (Fluka) was dried over 0.4 nm molecular sieves and distilled before use. Acrylonitrile was distilled over fresh calcium hydride powder and stored over molecular sieves 0.3 nm under argon. Anhydrous $LnCl_3$ (Ln = Sm, Yb) was prepared by the published method.[14] SmI_2 was prepared by the literature method.[15] IR spectra were recorded on a Fourier infrared spectrometer as KBr pellet. Elemental analysis (C and H) was performed by direct combustion on a Carlo Erba 1110 instrument. The ^1H NMR spectra were recorded on a INOVA-400 instrument using $CDCl_3$ as solvent.

Preparation of 1-*cyclopentylindene*

To freshly distilled indene (23.2 g, 0.2 mol) in 200 mL of THF was added *n*-butyllithium (125 mL of a 1.60 mol/L solution in hexane) dropwise at 0 ℃ for 1 h with stirring. Until no gas gave off, a bromocyclopentane (30.0 g, 0.20 mol) solution in 30 mL of THF was added dropwise with stirring by an addition funnel over the course of 3 h at 0 ℃. After the reaction solution was stirred for another 3 h at room temperature, the resulting solution was quenched with water. The organic layer was washed thoroughly with water to remove LiBr, and the organic phase was dried over $CaCl_2$. The solvent was removed under reduced pressure. The residue was fractionally distilled at 115—120 ℃/0.7 kPa to afford 20.5 g (56%) of 1-cyclopentylindene as a yellow liquid. ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.15—7.48 (m, 4H, ArH), 6.82 (d, J = 4.4 Hz, 1H, sp^2 3-position), 6.52 (d, J = 5.2 Hz, 1H, sp^2 2-position), 3.45 (d, J = 7.2 Hz, 1H, sp^3 1-position), 1.1—2.1 (m, 9H, C_5H_9).

Synthesis of 1-*cyclopentylindenyl potassium*

To potassium (5.5 g) in THF (200 mL), 1-cyclopentylindene (20.5 g, 0.11 mol) in 30 mL of THF was added dropwise at 45—50 ℃ for a period of 1 h with rigorous stirring. The mixture was stirred for another 36 h at the same temperature to ensure the completion of the reaction. Then, the reaction mixture was centrifuged and transferred to a flask. After centrifugation a clear pale red solution was obtained and titrated before use.

Synthesis of $(1\text{-}C_5H_9C_9H_6)_2Yb(THF)_2$ (**1**)

$YbCl_3$ (1.26 g, 4.50 mmol) was placed in a Schlenk flask containing 15 mL of THF. After this mixture was stirred for 30 min, a solution of 1-cyclopentylindenyl potassium in THF (0.305 mol/L, 29.50 mL) was added with stirring for 48 h at ambient temperature. Into the reaction mixture Na-K alloy [K (0.2 g) and Na (0.05 g)] was added. The mixture was stirred for another 48 h and centrifuged to remove KCl. The solution was concentrated to about 15 mL under reduced pressure and 30 mL of toluene was added. The resulting solution was concentrated to about 30 mL and crystallized at −25 ℃. The purple crystals of **1** were obtained (1.62 g) in yield of 52.7%. The crystals decomposed at 170 ℃. IR (KBr) ν: 3070.9 (w), 2951.3 (s), 2866.4 (s), 2773.8 (w), 1635.8 (w), 1608.8 (m), 1539.3 (w), 1458.3 (s), 1396.6 (s), 1265.4 (w), 1051.5 (w), 1022.3 (m), 968.3 (m), 914.3 (m), 852.6 (w), 770.6 (s), 717.6 (s) cm^{-1}; Anal. calcd for $C_{36}H_{46}O_2Yb$: Yb 26.75, C 63.16, H 6.73; found Yb 26.50, C 62.98, H 6.49.

Synthesis of $K(1\text{-}C_5H_9C_9H_6)_3Sm(THF)_3$ (**2**)

Into the reaction flask containing 50 mL of solution of SmI_2 (0.082 mol/L, 4.1 mmol) in THF was added 40.32 mL (0.203 mol/L, 8.2 mmol) of solution of 1-cyclopentylindenyl potassium in THF. The mixture was stirred for 24 h at ambient temperature. After centrifugation to remove KI precipitate, the solution was concentrated to 15 mL and crystallized at room temperature. The black crystals of **2** were obtained (1.4 g, yield 35.7%). The crystals decomposed at 280 ℃. IR (KBr) ν: 3071.7 (m), 2955.9 (s), 2871.0 (s), 2778.4 (w), 1713.3 (w), 1628.4 (m), 1458.7 (s), 1396.9 (s), 1270.0 (w), 1540.1 (w), 1065.0 (m), 1018.7 (m), 972.4 (m), 918.4 (w), 864.4 (w), 771.8 (s), 717.7 (s) cm^{-1}; Anal. calcd for $C_{54}H_{69}KO_3Sm$: Sm 15.73, K 4.09, C 67.87, H 7.28; found Sm 16.02, K 3.95, C 67.35, H 7.13.

Synthesis of $(1\text{-}C_5H_9C_9H_6)_2Sm(THF)$ (**3**)

$SmCl_3$ (0.514 g, 2.00 mmol) was placed in a Schlenk flask containing 15 mL of THF. After the mixture was stirred for 30 min, a solution of 1-cyclopentylindenyl potassium in THF (0.305 mol/L, 13.10 mL) was added with stirring for 48 h at ambient temperature, then Na-K alloy [K (0.15 g) and Na (0.05 g)] was added. The

mixture was stirred for further 48 h and centrifuged to remove KCl. The solution was concentrated to dry under reduced pressure and the oily residue was extracted with 20 mL of toluene. After 15 mL of *n*-hexane was added, black precipitates were obtained and dried under reduced pressure. The black powder of **3** was obtained (0.65 g, yield 55.1%). The crystals decomposed at 169 ℃. IR (KBr) ν: 3070 (m), 2955.2 (s), 2851.0 (s), 2775.4 (m), 1597.2 (m), 1554.7 (s), 1496.9 (m), 1450.6 (s), 1381.1 (m), 1296.3 (s), 1199.8 (s), 1165.1 (w), 1095.7 (m), 1041.6 (s), 968.3 (m), 918.2 (w), 865.4 (w), 767.7 (s), 721.4 (m) cm^{-1}; Anal. calcd for $C_{32}H_{38}OSm$: Sm 25.53, C 65.25, H 6.50; found Sm 25.46, C 64.98, H 6.58.

Determination of crystal structure of $(1\text{-}C_5H_9C_9H_6)_2Yb(THF)_2$ (**1**)

A purple crystal with dimension of $0.20 \times 0.25 \times 0.35$ mm^3 was sealed in a thin walled lithium glass capillary. The intensity data were collected on a BRUKER SMART 1000 diffractometer with graphite-monochromated Mo Kα radiation $\lambda = 0.071073$ nm with $0° \leqslant \theta \leqslant 25.02°$, and 12554 reflections were collected. Independent reflections were 5458. The intensities were corrected for Lorentz-Polarization and absorption factors. A summary of data collection parameters is given in Table 1.

All calculations were carried out using SHELXS-97, SHELXL-97 program packages. The structure was solved by direct method and refined using the full-matrix least squares on F^2. Hydrogen atoms were located and refined from geometric considerations.

Polymerization of acrylonitrile

A preweighted catalyst was added into toluene at the requisite temperature with vigorous magnetic stirring. Into the catalyst solution was added 1.00 mL of acrylonitrile with a syringe, and the reaction was continuously stirred for 2 h. Polymerization was stopped by adding ethanol acidified with aqueous hydrochloric acid. The sample was washed well with ethanol and centrifuged to remove the upper layer liquid several times and dried *in vacuo* at room temperature for 6 h. Viscosity-number-average molecular weight (M_η) was determined with a typical Ubbelohde suspended-level dilution viscometer in DMF solution at (30 ± 0.05) ℃. Polymer microstructure was characterized by ^{13}C NMR spectra using standard analysis.[16]

Table 1 Crystallographic data of complex $(1\text{-}C_5H_9C_9H_6)_2Yb(THF)_2$ (**1**)

Formula	$C_{36}H_{46}O_2Yb$
Molecular weight	683.77
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimension	
a (nm)	1.27138 (15)
b (nm)	1.19203 (14)
c (nm)	2.0430 (2)
β (°)	92.077 (2)
V (nm^3)	3.0941 (6)
D_c (mg/mm^3)	1.468
Z	4
Scan range, θ (°)	1.60 to 25.02
μ (cm^{-1})	30.52
F (000)	1392
Reflections	12554
Independent reflections	5458
R	0.0276
R_w	0.0624

Results and discussion

Synthesis

1-Cyclopentylindene was synthesized by the reaction of indenyl lithium with bromocyclopentane. 1-Cyclopentylindene was deprotonated with potassium to give the corresponding indenyl potassium. It was attempted to synthesize the neutral divalent complex of samarium, $(1\text{-}C_5H_9C_9H_6)_2Sm$, via the transmetallation between $SmI_2(THF)_x$ and 2 equiv. of $K(1\text{-}C_5H_9C_9H_6)$ in THF. In fact, the anionic complex $K(1\text{-}C_5H_9C_9H_6)_3Sm(THF)_3$ (**2**) was isolated as shown in Eq. (1).

$$SmI_2 + 3K(1\text{-}C_5H_9C_9H_6) \xrightarrow{THF} K(1\text{-}C_5H_9C_9H_6)_3Sm(THF)_3 + KI \quad (1)$$

The reductive reaction of $(1\text{-}C_5H_9C_9H_6)_2LnCl(THF)_x$ (Ln = Yb, Sm), which was formed *in situ* from the reaction of $LnCl_3$ (Ln = Yb, Sm) with 2 equiv. of

$K(1\text{-}C_5H_9C_9H_6)$ in THF, by Na-K alloy gave the divalent complexes $(1\text{-}C_5H_9C_9H_6)_2Ln(THF)_x$ [Ln = Yb, $x = 2$, (**1**); Ln = Sm, $x = 1$, (**3**)] as shown in Eq. (2).

$$2K(1\text{-}C_5H_9C_9H_6) + LnCl_3 \xrightarrow[2)\ NaK]{1)\ THF} (1\text{-}C_5H_9C_9H_6)_2Ln(THF)_x + 2KI \qquad (2)$$

Complexes **1**, **2** and **3** are all sensitive to air and moisture. They have very good solubility in THF and DME. Their structures were confirmed by elemental analysis and IR.

Study on structure

The molecular structure of **1** was shown in Fig. 1. Central metal Yb lies in an approximate tetrahedral coordinate environment by the two centroids of cyclopentadienyl rings of 1-cyclopentylindenyls and two oxygen atoms from two tetrahydrofuran molecules. The 1-cyclopentylindenyl groups in complex **1** are located at opposite sides of the molecule and directed away from each other. Selected bond distances and bond angles were listed in Table 2. The angle cent(1)-Yb-cent(2) [125.2(1)°] is smaller than the angles for substituted cyclopentadienyl Yb(II) complexes: $(t\text{-}BuC_5H_4)_2Yb(THF)_2$ (134.4°),[17] $(C_5H_5)_2Yb(THF)_2$ (127.9°),[18] $[C_5H_4(CH_2)_3C_5H_4]Yb(THF)_2$ (127°)[19] and that in $Ind_2Yb(DME)$ (129.4°).[9] But it is greater than those for bridged indenyl Yb(II) complexes as follows: rac-$(CH_2)_2(1\text{-}C_9H_6)_2Yb(THF)_2$ (117.6°)[9] and rac-$(CH_2)_2\{1\text{-}[4,7\text{-}(CH_3)_2(C_9H_4)]\}_2Yb(THF)_2$ (118.1°).[9] The Yb—Cent distances in complex **1** [0.2460(1), 0.2472(0) nm] are comparable with those in $Ind_2Yb(DME)$ (0.243 nm),[9] $(CH_2)_2(1\text{-}C_9H_6)_2Yb(THF)_2$,[9] (0.243, 0.245, 0.246, 0.246 nm) and rac-$(CH_2)_2\{1\text{-}[4,7\text{-}(CH_3)_2(C_9H_4)]\}_2Yb(THF)_2$ (0.2431, 0.2437 nm).[9] The Yb—O distances in complex **1** (0.2422(3), 0.2431(3) nm) are almost equal to those in other ytterbocene(II) $(t\text{-}BuC_5H_4)_2Yb(THF)_2$ (0.243 nm), $(Cp)_2Yb(THF)_2$ (0.244 nm),[18] $(1,3\text{-}{}^tBu_2C_5H_3)_2Yb(OEt_2)$ (0.243 nm).[20] The O(1)-Yb-O(2) angle [79.62(12)°] is somewhat smaller than the angles in $Cp_2Yb(THF)_2$ (81.6°),[18] $[C_5H_4(CH_2)_3C_5H_4]Yb(THF)_2$ (82.4°)[19] and $(t\text{-}BuC_5H_4)_2Yb(THF)_2$ (83.3°).[17]

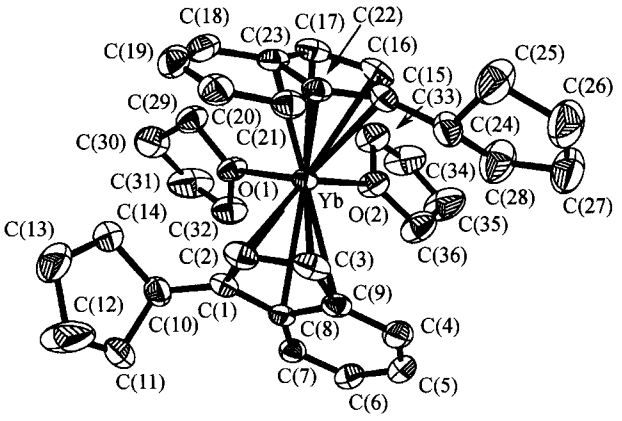

Fig. 1 Molecular structure of complex **1**.

The ytterbium-carbon distances range from 0.2652 nm to 0.2840 nm with the average values of 0.2749(2) and 0.2756(2) nm for Yb—C($ring_1$), Yb—C($ring_2$), respectively. Comparison of the Yb—C(2) distance [0.2652(4) nm] and the Yb—C(3) distance [0.2665(4) nm] with the other Yb—C distances in $ring_1$ 0.2775(4) nm for Yb—C(1); 0.2803(4) nm for Yb—C(9) and 0.2850(4) nm for Yb—C(8) suggests that the steric environment of carbon atom directly affect the value of Yb—C distance.

Polymerization of acrylonitrile with complex **1**, **2** *or* **3**

All the three new complexes **1**, **2** and **3** can catalyze the acrylonitrile polymerization. Without any cocatalyst, when acrylonitrile was added to the toluene solution of complex **1**, **2** or **3**, the yellow precipitates of polyacrylonitrile were produced immediately. The yields ranged from 20% to 30% at 30 ℃ for 2 h in the case of $[M]_0/[I] = 960$ in toluene. The microstruture of polyacrylonitrile is atactic, which is similar to those published by Shen *et al.*,[13, 21, 22] Yasuda *et al.*[23] and Okuda *et al.*[24] It was also observed that the yields would increase greatly when a little amount of $CH_3(CH_2)_{15}N(CH_3)_3Br$ was added into the polymerization systems. For example, the yield increased from 20.0% to 55.0% for complex **1**, 24.3% to 57.1% for complex **2** and 30.0% to 67.5% when 4 equiv. of $CH_3(CH_2)_{15}N(CH_3)_3Br$ was added as an additive, while $CH_3(CH_2)_{15}N(CH_3)_3Br$ itself did not show any catalytic activity at all in the polymerization. The reason needs further research.

Table 2 Selected bond lengths (nm) and angles (°) for complex $(1\text{-}C_5H_9C_9H_6)_2Yb(THF)_2$ (**1**)

Yb—O(1)	0.2431(3)	Yb—O(2)	0.2422(3)
Yb—C(1)	0.2775(4)	Yb—C(15)	0.2784(4)
Yb—C(2)	0.2652(4)	Yb—C(16)	0.2694(4)
Yb—C(3)	0.2665(4)	Yb—C(17)	0.2691(5)
Yb—C(8)	0.2850(4)	Yb—C(22)	0.2837(4)
Yb—C(9)	0.2803(4)	Yb—C(23)	0.2775(4)
C(15)—C(16)	0.1406(7)	C(16)—C(17)	0.1410(7)
C(17)—C(23)	0.1420(7)	C(23)—C(18)	0.1418(7)
C(22)—C(23)	0.1437(6)	C(18)—C(19)	0.1343(8)
C(19)—C(20)	0.1407(8)	C(20)—C(21)	0.1360(7)
C(21)—C(22)	0.1413(6)	C(22)—C(15)	0.1427(6)
C(15)—C(24)	0.1508(7)	C(24)—C(25)	0.1475(8)
C(24)—C(28)	0.1499(8)	C(25)—C(26)	0.1509(9)
C(26)—C(27)	0.1470(10)	C(27)—C(28)	0.1515(9)
Yb—Cent(1)[a]	0.2460(1)	Yb—Cent(2)[b]	0.2472(0)
Yb—C($ring_1$)[c]	0.2749(2)	Yb—C($ring_2$)[d]	0.2756(2)
Cent(1)-Yb-O(1)	107.0(2)	Cent(1)-Yb-O(2)	117.4(2)
Cent(2)-Yb-O(1)	114.2(2)	Cent(2)-Yb-O(2)	104.5(2)
O(1)-Yb-O(2)	79.62(12)	Cent(1)-Yb-Cent(2)	125.2(1)

[a] Cent(1) is the centroid of ring 1 defined by C(1), C(2), C(3), C(8) and C(9). [b] Cent(2) is the centroid of ring 2 defined by C(15), C(16), C(17), C(22) and C(23). [c] Yb—C($ring_1$) is the average distance of ytterbium-carbon of ring 1. [d] Yb—C($ring_2$) is the average distance of ytterbium-carbon of ring 2.

Table 3 Results of acrylonitrile polymerization catalyzed with 1-cyclopentylindenyl lanthanide(II) complexes[a]

Catalysts	$[CH_3(CH_2)_{15}N(CH_3)_3Br]/[cat.]$ (mol/mol)	Conversion (%)	M_η (10^4)	Tacticity (%)		
				rr	mm	mm
1	0	20.0	5.8	26	41	33
1	4	55.0	18.4	26	42	32
2	0	30.0	10.1	27	42	31
2	4	67.5	12.6	28	40	32
3	0	24.3	11.1	26	43	31
3	4	57.1	14.0	28	41	31
none[b]		0.0	–			

[a] Reaction conditions: $[M]_0/[cat.] = 960$; solvent, toluene; solvent/$[M]_0 = 2$ (*V*/*V*); reaction time, 2 h; temperature, 30 ℃. [b] Vacant experiment: $[M]_0/[CH_3(CH_2)_{15}N(CH_3)_3Br] = 240$.

References

1 Evans, W. J. *Polyhedron* **1987**, *6*, 803.

2 Evans, W. J.; Bloom, T. H.; Hunter, W. E.; Atwood, W. J. *J. Am. Chem. Soc* **1982**, *103*, 6507.

3 Gagne, M. R.; Nolan, S. P.; Marks, T. *J. Organometallics* **1990**, *9*, 1716.

4 Zhang, Y.; Hou, Z.; Wakatsuki, Y. *Macromolecules* **1999**, *32*, 939.

5 Kaita, S.; Hou, Z.; Wakatsuki, Y. *Macromolecules* **1999**, *32*, 9078.

6 Shen, Q.; Jiang, T. *Chin. Sci. Bull.* **1992**, *23*, 2157.

7 Evans, W. J.; Gummersheimer, T. S.; Boyle, T. J.; Ziller, J. W. *Organometallics* **1998**, *17*, 284.

8 Deacon, G. B.; Newham, R. H. *Aust. J. Chem.* **1985**, *38*, 1757.

9 Khvostov, A. V.; Bulychev, B. M.; Belsky, V. K.; Sizov, A. I. *J. Organomet. Chem.* **1999**, *584*, 164.

10 Qian, C.; Li, N.; Chen, Y.; Zou, G. In *the Proceedings of the 19th IUPAC International Conference of Organometallic Chemistry* (*Book of Abstract*) Shanghai, China, **2000**, p. 017C.

11 Qian, C.; Li, H.; Sun, J.; Nie, W. *J. Organomet. Chem.* **1999**, *585*, 59.

12 Yasuda, H.; Kokta, K.; Yamomoto, H.; Nakamura, A. In *the Proceedings of the 2nd International Conference on Rare Earth Development and Application*, Beijing, China, **1991**, p. 831.

13 Yao, Y.; Shen, Q.; Zhang, L. *Chin. Sci. Bull.* **2001**, *46*, 1443.

14 Taylor, M. D.; Carler, C. P. *J. Inorg. Nucl. Chem.* **1962**, *24*, 387.

15 Evans, W. J.; Grate, J. W.; Choi, H. W.; Bloom, I.; Hunter, W. E. *J. Am. Chem. Soc.* **1985**, *107*, 941.

16 Jenkins, A. D.; Lappert, M.; Srivastava. R. C. *Eur. Polym. J.* **1971**, *7*, 289.

17 Shen, Q.; Zheng, D.; Lin, L.; Lin, Y. *J. Organomet. Chem.* **1990**, *391*, 321.

18 Xia, J.; Wei, G.; Jin, Z.; Chen. W.; Xue, W. *Chin. J. Rare Earths* **1992**, *10*, 88.

19 Swamy, S. J.; Loebel, J.; Schumann, H. *J. Organomet. Chem.* **1989**, *379*, 51.

20 Khvostov, A. V.; Sizov, A. I.; Bulychev, B. M.; Khjazhanski, S. Yu.; Belsky, V. K. *J. Organomet. Chem.* **1998**, *559*, 97.

21 Ren, J.; Shen, Q. *Chin. J. Appl. Chem.* **1995**, *12*, 105.

22 Hu, J.; Qi, G.; Shen, Q. *J. Rare Earths* **1995**, *13*, 144.

23 Yasuda, H.; Ihara, E. *Adv. Polym. Sci.* **1977**, *133*, 72.

24 Hultzsch, K. C.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 227.

(E0107128 ZHAO, X. J.; HUANG, W. Q.)