ELSEVIER

Journal of Organometallic Chemistry 662 (2002) 144–149

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Synthesis, characterization of homoleptic lanthanide amidinate complexes and their catalytic activity for the ring-opening polymerization of ε-caprolactone

Yunjie Luo [a], Yingming Yao [a], Qi Shen [a,*], Jie Sun [b], Linhong Weng [c]

[a] *Department of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215006, China*

[b] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*

[c] *Department of Chemistry, Fudan University, Shanghai 200433, China*

Received 28 May 2002; received in revised form 2 September 2002; accepted 12 September 2002

Abstract

Addition of [CyNC(R)NCy]Lithium (Cy = cyclohexyl, R = methyl, phenyl) to anhydrous lanthanide trichlorides in 3:1 molar ratio yielded a series of homoleptic amidinate lanthanide complexes with the general formula $[CyNC(R)NCy]_3Ln\cdot nTHF$ (R = methyl, Ln = Nd (**1**), Gd (**2**), Yb (**3**), $n = 0$; R = phenyl, Ln = Nd (**4**), Y (**5**), Yb (**6**), $n = 2$). The X-ray crystal structural determination of **3** and **6** revealed that the ytterbium ions in both complexes are coordinated by three bidentate amidinate moieties with a trigonal planar geometry. These amidinate lanthanide complexes showed extremely high activity for the ring-opening polymerization of ε-caprolactone at room temperature.

Keywords: Organolanthanides; Amidinate ligands; Polymerization; ε-Caprolactone; Crystal structure

1. Introduction

Since Brookhart and his co-workers discovered that late transition metal diimine systems could efficiently suppress the β-H elimination and catalyze ethylene polymerization [1], the application of nitrogen-containing bidentate ancillary ligands, such as guanidinates [2], amidinates [3] and β-diketiminates [4] etc. in organometallic chemistry of main and transition metals have attracted much attention, and some of these complexes were reported to have fascinating reactivity. For example, copper (I) β-diketiminate ethylene complex can activate dioxygen [4e], Zn(II) β-diketiminate complexes are effective catalysts for alternating copolymerization of epoxide and CO_2 [4f], and Zr(IV) amidinate-based complexes are precatalysts for living cyclopolymerization of nonconjugated dienes [3f]. However, most of the studies on the utility of such ancillary ligands in organolanthanide chemistry are centered on the synthesis and characterization of the corresponding complexes [5–7]. Few papers reported in the literature describe the catalytic activity of this kind of complexes, and point out that some heteroleptic alkoxo or aryloxo lanthanide complexes supported by these ligands are active for the ring-opening polymerization of lactides [8,9]. Recently, Mashima et al. also reported that heteroleptic substituted pyrrolyl yttrium derivatives were able to initiate the polymerization of ε-caprolactone, while the homoleptic yttrium species exhibited no catalytic activity at all [10].

We have recently been interested in understanding the chemistry of organolanthanide complexes with nitrogen-based polydentate ligands, and have reported the synthesis, structure and reactivity of organolanthanide complexes with β-diketiminates [7b] and guanidinates [11], etc. As an extension of our continuous study in this area, we prepared a series of homoleptic amidinate lanthanide complexes, $[CyNC(R)NCy]_3Ln\cdot nTHF$ (R = methyl, Ln = Nd (**1**), Gd (**2**), Yb (**3**), $n = 0$; R = phenyl, Ln = Nd (**4**), Y (**5**), Yb (**6**), $n = 2$). Furthermore, we

* Corresponding author. Tel.: +86-512-6511-2513; fax: +86-512-6511-2371

E-mail address: qshen@suda.edu.cn (Q. Shen).

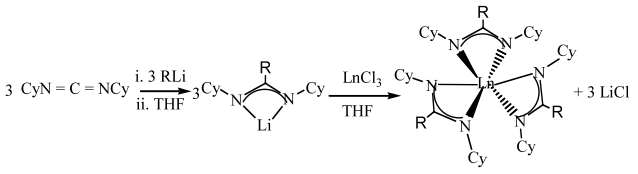
0022-328X/02/$ - see front matter © 2002 Published by Elsevier Science B.V.
PII: S0022-328X(02)01902-2

found that homoleptic amidinate lanthanide complexes could efficiently initiate the ring-opening polymerization of ε-caprolactone. Here, we report these results.

2. Results and discussion

2.1. Synthesis and characterization of the amidinate lanthanide complexes

The reaction of *N*,*N*′-dicyclohexylcarbodiimide with an equivalent molar amount of MeLi (or PhLi) in THF gives quantitative yield of *N*,*N*′-bis(cyclohexyl)methylamidinate lithium, so in most cases freshly prepared solution of amidinate lithium is directly used in the following metathesis reactions. Thus, after *N*,*N*′-dicyclohexylcarbodiimide reacted with MeLi (or PhLi) in THF for 30 min at room temperature, the resulting solution was slowly added into a slurry of $LnCl_3$ in 3:1 molar ratio. After workup, the expected complexes $[CyNC(R)NCy]_3Ln\cdot nTHF$ (R = methyl, Ln = Nd (**1**), Gd (**2**), Yb (**3**), $n = 0$; R = phenyl, Ln = Nd (**4**), Y (**5**), Yb (**6**), $n = 2$) were isolated as shown in Eq. (1):



(1)

The formulation of these homoleptic amidinate lanthanide species is supported by elemental analysis and IR spectroscopy. In the IR spectra, there are strong absorptions of C=N stretch at approximate 1640 cm^{-1}, which are consistent with the delocalized double bond of the N–C–N linkage [12]. Because these amidinate lanthanide complexes are paramagnetic except for **5**, therefore, it is difficult to obtain acceptable NMR spectra.

All these lanthanide complexes are air- and moisture-sensitive, they are soluble in toluene, THF and diethyl ether, but not soluble in hexane.

X-ray crystallographic analyses of **3** and **6** reveal that the two complexes are both monomeric in the solid state. The molecular structures of **3** and **6** are presented in Figs. 1 and 2, respectively. Tables 1 and 2 give partial lists of bond distances and angles of **3** and **6**, respectively. Details of the crystallographic analyses of **3** and **6** are listed in Table 3. The structures of **3** and **6** are analogous, but they crystallize in different space groups (**3** in triclinic, **6** in orthorhombic). There is a plane of symmetry along the line of Yb–C20–C21–C24 in **6**. The average bond distances of Yb to C on N–C–N in

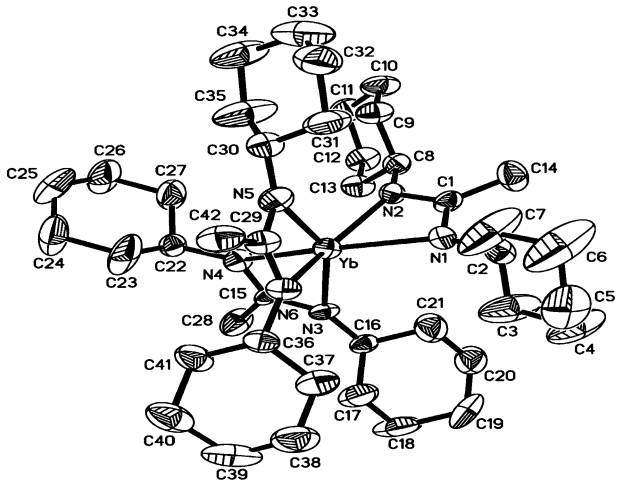


Fig. 1. The molecular structure of **3**.

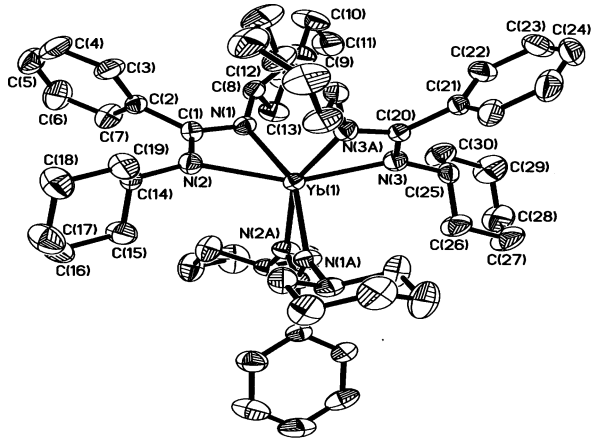


Fig. 2. The molecular structure of **6**.

Table 1
Selected bond distances (Å) and angles (°) for **3**

Bond distances			
Yb–N2	2.300(8)	Yb–N1	2.340(8)
Yb–N6	2.346(8)	Yb–N5	2.349(9)
Yb–N3	2.355(8)	Yb–N4	2.361(7)
Yb–C15	2.741(9)	Yb–C29	2.764(10)
Yb–C1	2.769(10)	N1–C1	1.318(12)
N3–C15	1.353(10)	N2–C1	1.331(11)
N6–C29	1.351(13)	N5–C29	1.348(13)
N4–C15	1.286(11)		
Bond angles			
N2–Yb–N	56.9(3)	N6–Yb–N5	58.3(3)
N3–Yb–N4	57.5(3)	C15–Yb–C29	119.8(3)
C29–Yb–C1	118.9(3)	C1–N2–Yb	95.7(6)
C1–N1–Yb	94.2(6)	C15–N3–Yb	91.2(6)
C15–N4–Yb	92.7(5)	C29–N5–Yb	92.8(7)
N4–C15–N3	118.6(8)	C29–N6–Yb	92.8(6)
N5–C29–N6	116.0(9)	N1–C1–N2	113.1(9)

Table 2
Selected bond distances (Å) and angles (°) for **6**

Bond distances			
Yb–N1	2.333(5)	Yb–N2	2.323(5)
Yb–N3	2.321(5)	Yb–C1	2.739(6)
Yb–C	202.748(7)	N1–C1	1.330(7)
N2–C1	1.329(7)	N3–C20	1.337(6)
C1–C2	1.515(8)	C20–N3	1.337(6)
C20–C21	1.504(9)		
Bond angles			
N3–Yb–N3(A)	58.1(2)	N2–Yb–N1	57.98(17)
C1–Yb–C20	119.44(13)	N2–C1–N1	116.2(5)
N3–C20–N3(A)	114.9(6)	C1–N2–Yb	93.1(4)
C20–N3–Yb	93.5(4)	C1–N1–Yb	92.7(4)

Table 3
Experimental data for the X-ray diffraction study of **3** and **6**

	3	**6**
Empirical formula	$C_{42}H_{75}N_6Yb$	$C_{65}H_{97}N_6O_2Yb$
Formula weight	837.12	1167.53
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	*Pbcn*
Unit cell dimensions		
a (Å)	11.354(3)	19.792(6)
b (Å)	13.132(3)	17.467(5)
c (Å)	16.942(4)	18.071(5)
α (°)	76.957(4)	90.00
β (°)	89.411(4)	90.00
γ (°)	64.959(4)	90.00
V (Å^3)	2219.1(9)	6247(3)
Z	2	4
D_{calc} (g cm^{-3})	1.253	1.241
Absorption coefficient (mm^{-1})	2.140	1.542
F(000)	878	2460
Theta range for data collection (°)	1.77–25.50	1.55–26.01
Reflections collected	11 536	25 739
Independent reflections	8128 [$R_{int} = 0.2140$]	6160 [$R_{int} = 0.0474$]
Data/restraints/parameters	8128/0/445	6160/0/336
Goodness-of-fit on F^2	0.870	1.316
Final R indices [$I > 2\sigma(I)$]	0.0710	0.0433
Rw	0.1627	0.0819

amidinate moiety are 2.76 Å for **1** and 2.74 Å for **6**, which indicate an η^3-allyl structure [13]. The ytterbium ions are both ligated by three bidentate amidinate moieties through nitrogen atoms with the Yb–N–C–N units only deviating slightly from planarity (torsion angles $< 2.3°$). The geometries about the ytterbium ions for the two complexes are best described as trigonal planars with each chelating bidentate amidinate ligand to occupy one coordination vertex (in **3**, C1–Yb–C29 = 118.9(3)°, C1–Yb–C15 = 121.2(3)°, C15–Yb–C29 = 119.8(3)°, sum of the angles, 359.9°; in **6**, C1–Yb–C20 = 119.44(3)°, C1–Yb–C1′ = 121.1(3)°, sum of the angles, 359.9°). The C–N bond distances within the chelating NCN unit are nearly equal and the average value is 1.33 Å for both complexes, which reflect the delocalization of the π bond in the N–C–N unit [5b]. Taking into account the difference in ionic radii of the metals, the Yb–N distances, which range from 2.300(8) to 2.361(7) Å (average 2.34 Å) in **3** and 2.321(5) to 2.333(5) Å (average 2.33 Å) in **6**, are comparable with those of the analogous homoleptic complexes, [4-$MeOC_6H_4C(NSiMe_3)_2]_3Pr$ (2.48 Å) [6g], [Ph-$C(NSiMe_3)_2]_2Yb\cdot 2THF$ (2.48 Å) [6j].

2.2. The ring-opening polymerization of ε-caprolactone

The catalytic behavior of $[CyNC(Me)NCy]_3Ln$ for the ring-opening polymerization of ε-caprolactone in toluene was tested. The preliminary results are listed in Table 4. The high catalytic activity of such kind of homoleptic amidinate lanthanide complexes for the ring-opening polymerization of ε-caprolactone has never been reported in the literature, and it is quite different to that of the structural analogous homoleptic pyrrolyl yttrium species, which exhibit no catalytic activity at all [10]. For examples, [CL]:[I] = 500:1 at 25 °C in the case of **1**, 100% of conversion is obtained in 15 min; even the catalytic amount decreases to [CL]:[I] = 1000:1, the polymerization still gives the conversion as high as 96.1%. When the polymerization takes place at −5 °C, **1** also exhibits quite good activity (entry 4). The effect of the central metals on the activity can be observed. The active order under the present polymerization conditions is Nd > Gd > Yb (entries 2, 5 and 6), which is consistent with that in the system with the metallocene-based organolanthanide catalysts [14]. The catalytic activity of $[CyNC(Ph)NCy]_3Ln$ is somewhat lower than that of $[CyN(Me)NCy]_3Ln$ under the same polymerization conditions; the lower activity might be attributed to the fact that $[CyNC(Ph)NCy]_3Ln$ have a less open coordination environment around the metals. The moderate polydispersities are identical to those for the ring-opening polymerization of ε-caprolactone by homoleptic $Y[N(SiMe_3)_2]_3$ as an initiator [15], indicating that the number of Ln–N bonds significantly affects molecular weight distributions.

3. Conclusion

Homoleptic amidinate lanthanide complexes, $[CyNC(R)NCy]_3Ln\cdot nTHF$, can be easily prepared in good yield by the reaction of [CyNC(R)NCy]Li (R = methyl or phenyl) with anhydrous lanthanide trichlorides in 3:1 molar ratio. Moreover, the homoleptic amidinate lanthanide complexes were found to be able to initiate

Table 4
Polymerization of ε-caprolactone initiated by $[CyNC(R)NCy]_3Ln \cdot nTHF$ [a]

Entry	Initiator	Temperature (°C)	[M]/[I]	Yield [b] (%)	M_n ($\times 10^4$)	M_w/M_n [c]
1	1	25	500	100	4.41	1.81
2	1	25	1000	96.1	4.67	1.71
3	1	40	1000	100	3.34	1.81
4	1	−5	1000	64	3.47	1.79
5	2	25	1000	85.6	3.86	1.74
6	3	25	1000	78.8	3.97	1.79
7	4	25	500	94.2	21.74	1.90
8	4	25	1000	89.3	20.48	2.18
9	6	25	300	53.4	17.63	2.09
10	6	25	700	27.2	18.08	2.29

[a] General polymerization conditions: in toluene; 15 min; solvent/monomer = 25 v/v.
[b] Yield = weight of polymer obtained/weight of monomer used.
[c] Measured by GPC calibrated with standard polystyrene samples.

the ring-opening polymerization of ε-caprolactone with high activity to give moderate polydispersities polymers.

4. Experimental

All manipulations were performed under pure Ar with rigorous exclusion of air and moisture using standard Schlenk techniques. Solvents were distilled from Na/benzophenone ketyl prior to use. Anhydrous $LnCl_3$ were prepared according to the literature procedures [16]. *N*,*N*′-Dicyclohexylcarbodiimide was purchased from Aldrich and used as received without further purification. ε-Caprolactone was purchased from Acros, dried by stirring with CaH_2 for 48 h, then distilled under reduced pressure. Melting points were determined in sealed Ar-filled capillary tubes and are uncorrected. Metal analyses were carried out by complexometric titration. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion on a Carlo-Erba EA-1110 instrument. The IR spectra were recorded on a Magna-IR 550 spectrometer. Molecular weight and molecular weight distributions were determined against polystyrene standard by gel permeation chromatography (GPC) on a Waters 1515 apparatus with three HR columns (HR-1, HR-2 and HR-4); THF was used as an eluent at 30 °C. ^{1}H-NMR and ^{13}C-NMR spectra were measured on a Unity Inova-400 spectrometer.

4.1. Synthesis of $[CyNC(Me)NCy]_3Nd$ (1)

A Schlenk flask was charged with *N*,*N*′-dicyclohexylcarbodiimide (2.44 g, 11.8 mmol), THF (30 ml), and a stir bar. To this solution was added MeLi (11.2 ml, 11.8 mmol, 1.05 M in Et_2O) dropwise via syringe at room temperature. The solution was stirred for 30 min and then added slowly to a pale-gray slurry of $NdCl_3$ (0.99 g, 3.93 mmol) in THF (60 ml). The color of the solution immediately changed to blue–purple. The resulting solution was then stirred for another 24 h and evaporated to dry in vacuo. The residue was extracted with Et_2O and LiCl was removed by centrifugation. When the extracts were concentrated and cooled to −20 °C for crystallization, blue–purple crystals were formed. Yield: 2.5 g (79%). M.p. 175–178 °C. Anal. Calc. for $C_{42}H_{75}N_6Nd$: C, 62.35; H, 9.37; N, 10.39; Nd, 17.85. Found: C, 61.87; H, 9.47; N, 10.4; Nd, 18.27%. IR (KBr pellet, cm^{-1}): 3445(s), 3290(s), 2932(s), 2854(s), 2588(s), 1643(s), 1452(s), 1103(m), 956(m), 891(s), 794(m), 659(s).

4.2. Synthesis of $[CyNC(Me)NCy]_3Gd$ (2)

Following the procedure similar to the synthesis of **1**, using 20.7 mmol of [CyNC(Me)NCy]Li, 1.80 g of $GdCl_3$ (6.90 mmol), and 60 ml of THF following by crystallization from toluene yielded colorless cubic crystals of **2** (4.8 g, 85%). Anal. Calc. for $C_{42}H_{75}GdN_6$: C, 61.42; H, 9.22; N, 10.23. Found: C, 60.68; H, 9.29; N, 9.87%. IR (KBr pellet, cm^{-1}) 3446(s), 3290(s), 2934(s), 2857(s), 2589(s), 1642(s), 1454(s), 1103(m), 958(m), 889(s), 795(m), 657(s).

4.3. Synthesis of $[CyNC(Me)NCy]_3Yb$ (3)

This complex was prepared from 1.74 g of $YbCl_3$ (6.2 mmol), 18.6 mmol of [CyNC(Me)NCy]Li in 60 ml of THF using the procedure described above. Bright yellow crystals were collected from THF–toluene mixed solution. Yield: 4.3 g (83%). M.p. 161–164 °C. Anal. Calc. for $C_{42}H_{75}N_6Yb$: C, 60.26; H, 9.05; N, 10.04. Found: C, 59.94; H, 8.81; N, 10.17%. IR (KBr pellet, cm^{-1}) 3447(s), 3291(s), 2935(s), 2858(s), 2583(s), 1647(s), 1451(s), 1102(m), 956(m), 891(s), 795(m), 658(s).

4.4. Synthesis of [CyNC(Ph)NCy]$_3$Nd·2THF (**4**)

A Schlenk flask was charged with *N*,*N*′-dicyclohexylcarbodiimide (3.42 g, 16.58 mmol), THF (30 ml), and a stir bar. To this solution was added PhLi (11.4 ml, 16.58 mmol, 1.45 M in Et_2O) dropwise via syringe at ambient temperature. The solution was stirred for 30 min and then added slowly to a pale-gray slurry of $NdCl_3$ (1.35 g, 5.39 mmol) in THF (60 ml). The color of the solution immediately changed to blue–purple. The resulting solution was then stirred for 8 h and removed the solvent in vacuo. The residue was extracted with toluene and LiCl was removed by centrifugation. After the extracts were concentrated and cooled to −20 °C for a day, blue–purple crystals formed. Yield: 4.4 g (82%). M.p. 145 °C. Anal. Calc. for $C_{65}H_{97}N_6NdO_2$: C, 68.55; H, 8.60; N, 7.38; Nd, 12.67. Found: C, 68.06; H, 8.59; N, 7.34; Nd, 13.08%. IR (KBr pellet, cm^{-1}): 2924(s), 2851(s), 2665(w), 1636(s), 1601(m), 1481(s), 1447(s), 1346(m), 1315(m), 1257(m), 1072(m), 1026(m), 983(m), 891(m), 771(m), 762(s), 659(m).

4.5. Synthesis of [CyNC(Ph)NCy]$_3$Y·2THF (**5**)

This complex was prepared from 0.98 g of YCl_3 (5.01 mmol), 15.05 mmol of [CyNC(Ph)NCy]Li in 60 ml of THF using the procedure described above. Colorless crystals were collected from THF. Yield: 4.3 g (80%). M.p. 153 °C. ^{1}H-NMR (C_6D_6, δ): 7.18 (m, 15H, Ar), 3.72 (m, 8H, THF-α-CH_2), 3.19 (m, 6H, unique Cy-*H*), 2.15–1.14 (m, 60H, C_6H_{10}), 1.11 (m, 8H, THF-β-CH_2). ^{13}C-NMR (C_6D_6, δ): 177.75 (s, N*C*(Ph)N), 128.50 (m, C_6H_5), 68.84 (s, THF-α-*C*H_2), 57.46, 36.70, 26.73, 26.10 (4s, C_6H_{11}), 25.85 (s, THF-β-*C*H_2). Anal. Calc. for $C_{65}H_{97}N_6O_2Y$: C, 72.06; H, 9.04; N, 7.76. Found: C, 71.68; H, 8.81; N, 7.52. IR (KBr pellet, cm^{-1}): 2928(s), 2854(s), 1635(s), 1574(m), 1450(m), 1361(m), 1211(s), 1153(s), 1068(m), 891(m), 775(m), 706(m), 669(m), 501(m).

4.6. Synthesis of [CyNC(Ph)NCy]$_3$Yb·2THF (**6**)

This complex was prepared from 1.60 g of $YbCl_3$ (5.73 mmol), 17.01 mmol of [CyNC(Ph)NCy]Li in 60 ml of THF using the procedure described above. Bright yellow crystals were collected from toluene solution. Yield: 5.2 g (78%). M.p. 138 °C. Anal. Calc. for $C_{65}H_{97}N_6O_2Yb$: C, 66.86; H, 8.39; N, 7.20. Found: C, 66.94; H, 8.61; N, 7.17%. IR (KBr pellet, cm^{-1}): 2989(s), 2851(s), 1639(s), 1481(m), 1153(m), 891(m), 789(m), 702(m), 501(w).

4.7. A typical procedure for polymerization reactions

The procedures for the polymerization of ε-caprolactone are the same (Table 4), and a typical polymerization reaction is given below (entry 1, Table 4). A 50 ml Schlenk flask equipped with a magnetic stir bar was charged with a 4.5 mM solution of initiator in toluene. To this solution was added 1 ml of ε-caprolactone using rubber septum and syringe. The contents of the flask were then vigorous stirred for 15 min at 25 °C. The magnetic stirring was ceased within a few minutes due to the viscosity. The reaction mixture was quenched by the addition of 1 M HCl solution and then poured into a cold petroleum ether to precipitate the polymer, which was dried under vacuum and weighed.

4.8. X-ray structural determination of **3** and **6**

A suitable crystal was mounted in a thin-walled glass capillary for X-ray structural analysis. Diffraction data were collected on a Bruker SMART CCD area detector using phi and omega scans. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. The structures were solved and refined using SHELXS-97 and SHELXL-97 programs, respectively.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 186583 for complex **3**, and 186584 for complex **6**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We are indebted to the Chinese National Natural Science Foundation and the Department of Education of Jingsu Province for financial support.

References

[1] (a) L.K. Johnson, C.M. Killian, M. Brookhart, J. Am. Chem. Soc. 117 (1995) 6414;
(b) L.K. Johnson, S. Mecking, M. Brookhart, J. Am. Chem. Soc. 118 (1996) 267.
[2] (a) P.J. Bailey, S. Pace, Coord. Chem. Rev. 214 (2001) 91;
(b) A.P. Duncan, S.M. Mullins, J. Arnold, R.G. Bergman, Organometallics 20 (2001) 1808.
[3] (a) F. Edelmann, Coord. Chem. Rev. 137 (1994) 403;
(b) J. Barker, M. Kilner, Coord. Chem. Rev. 133 (1994) 219;
(c) M.P. Coles, R.F. Jordan, J. Am. Chem. Soc. 119 (1997) 8125;

(d) C. Averbuj, M.S. Eisen, J. Am. Chem. Soc. 121 (1999) 8755;
(e) S.R. Foley, Y.L. Zhou, G.P.A. Yap, D.S. Richeson, Inorg. Chem. 39 (2000) 924;
(f) K.C. Jayaratne, R.J. Keaton, D.A. Henningsen, L.R. Sita, J. Am. Chem. Soc. 122 (2000) 10490.

[4] (a) C.E. Radzewich, M.P. Coles, R.F. Jordan, J. Am. Chem. Soc. 120 (1998) 9384;
(b) P.H.M. Budzelaar, R.D. Gelder, A.W. Gal, Organometallics 17 (1998) 4121;
(c) W.K. Kim, M.J. Fevola, L.M. Liable-Sands, A.L. Rheingold, K.H. Theopold, Organometallics 17 (1998) 4541;
(d) R. Vollmerhaus, M. Rahim, R. Tomaszewski, S. Xin, N.J. Taylor, S. Collins, Organometallics 19 (2000) 2161;
(e) X.L. Dai, T.H. Warren, Chem. Commun. (2001) 1998;
(f) M. Cheng, D.R. Moore, J.J. Reczek, B.M. Chamberlain, E.B. Lobkovsky, G.W. Coates, J. Am. Chem. Soc. 123 (2001) 8738;
(g) A.P. Dove, V.C. Gibson, E.D. Marsall, A.J.P. White, D.J. Williams, Chem. Commun. (2001) 283.

[5] (a) Y.L. Zhou, G.P.A. Yap, D.S. Richeson, Organometallics 17 (1998) 4387;
(b) Z.P. Lu, G.P.A. Yap, D.S. Richeson, Organometallics 20 (2001) 706.

[6] (a) S. Bambirra, A. Meetsma, B. Hessen, J.H. Teuben, Organometallics 20 (2001) 782;
(b) R. Duchateau, C.T. van Wee, A. Meetsma, P.T. van Duijnen, J.H. Teuben, Organometallics 15 (1996) 2279;
(c) R. Ducyateau, A. Meetsma, J.H. Teuben, Organometallics 15 (1996) 1656;
(d) R. Duchateau, C.T. van Wee, J.H. Teuben, Organometallics 15 (1996) 2291;
(e) R. Duchateau, C.T. van Wee, A. Meetsma, J.H. Teuben, J. Am. Chem. Soc. 115 (1993) 4931;
(f) C. Hagen, H. Reddmann, H.D. Amberger, F.T. Edelmann, U. Pegelow, G.V. Shalimoff, J. Organomet. Chem. 462 (1993) 69;
(g) M. Wedler, F. Knosel, U. Pieper, D. Stalke, F.T. Edelmann, H.D. Amberger, Chem. Ber. 125 (1992) 2171;
(h) M. Wedler, A. Recknagel, J.W. Gilje, M. Noltemeyer, F.T. Edelmann, J. Organomet. Chem. 426 (1992) 295;
(i) A. Recknagel, F. Knosel, H. Gornitzka, M. Noltemeyer, F.T. Edelmann, U. Behrens, J. Organomet. Chem. 417 (1991) 363;
(j) M. Wedler, M. Noltemeyer, U. Pieper, H.G. Schmidt, D. Stalke, F.T. Edelmann, Angew. Chem. Int. Ed. Engl. 29 (1990) 894.

[7] (a) P.G. Hayes, W.E. Piers, L.W.M. Lee, L.K. Knight, M. Parvez, M.R.J. Elsegood, W. Clegg, Organometallics 20 (2001) 2533;
(b) Y.M. Yao, Y. Zhang, Q. Shen, K.B. Yu, Organometallics 21 (2002) 819.

[8] K.B. Aubrecht, K. Chang, M.A. Hillmyer, W.B. Tolman, J. Polym. Sci. Part A: Polym. Chem. 39 (2001) 284.

[9] G.R. Giesbrecht, G.D. Whitener, J. Arnold, J. Chem. Soc. Dalton Trans. (2001) 923.

[10] Y. Matsuo, K. Mashima, K. Tani, Organometallics 20 (2001) 3510.

[11] Y.J. Luo, Y.M. Yao, Q. Shen, K.B. Yu, L.H. Weng, Eur. J. Inorg. Chem., in press.

[12] G.R. Giesbrecht, A. Shafir, J. Arnold, J. Chem. Soc. Dalton Trans. (1999) 3601.

[13] W.J. Evans, T.A. Ulibarri, J.W. Ziller, J. Am. Chem. Soc. 112 (1990) 2314.

[14] M. Yamashita, Y. Takemoto, E. Ihara, H. Yasuda, Macromolecules 29 (1996) 1798.

[15] K.C. Hultzsch, T.P. Spaniol, J. Okuda, Organometallics 16 (1997) 4845.

[16] M.D. Taylor, C.P. Carter, J. Inorg. Nucl. Chem. 24 (1962) 387.