ELSEVIER

Journal of Organometallic Chemistry 647 (2002) 114–122

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Synthesis, structural characterization and catalytic behavior of one-atom bridged fluorenyl cyclopentadienyl lanthanocene complexes with C_s- or C_1-symmetry

Wanli Nie, Changtao Qian *, Yaofeng Chen, Sun Jie

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, People's Republic of China

Received 2 August 2001; accepted 10 December 2001

Abstract

A series of silylene- and methylene-bridged fluorenyl cyclopentadienyl *ansa*-lanthanocene chlorides, hydrocarbyls, amides and tetrahydroborates with C_s- or C_1-symmetry have been synthesized successfully. X-ray structural studies have been carried out for these complexes. The hydrocarbyls and amides were applied for catalyzing the polymerization of methyl methacrylate and lactones. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Lanthanide; Fluorenyl cyclopentadienyl; Lanthanocene

1. Introduction

Lanthanocene complexes have demonstrated catalytic ability for the polymerization of olefins [1,2], polar monomers [2–4] and many organic transformations, including cyclic hydroamination of both alkynes and alkenes [5], and hydrogenation [6]. The catalytic activity and stereoselectivity of the lanthanocene complexes are profoundly influenced by the nature of π-ancillary ligands and central metal ions. Until now, most of the works reported focused on the complexes bearing cyclopentadienyl, permethylated cyclopentadienyl, indenyl or their analogues [7]. The synthesis, structure and catalytic behavior of the fluorenyl lanthanocenes, which in turn has played a unique role in Group 4 metallocene catalyst systems in α-olefin polymerization, has been rarely explored [8]. Recently, we synthesized several new types of C_s- and C_1-symmetric silylene- or methylene-bridged fluorenyl cyclopentadienyl organolanthanide halide, amide, hydrocarbyl and tetrahydroborate complexes, and investigated their catalytic activity toward methyl methacrylate (MMA) and lactones.

2. Synthesis and structural characterization of C_s- and C_1-symmetric *ansa*-lanthanocene complexes

2.1. Synthesis and structural characterization of dimethylsilyl- and diphenylsilyl-bridged fluorenyl cyclopentadienyl neutral ansa-lanthanocene chlorides, amides and hydrocarbyls [9]

Reactions between a dilithio salt of the ligand $[Me_2Si(C_5H_5)(C_{13}H_9)]$ [10] and anhydrous lanthanide chlorides provide solvent-free dimeric chlorides $[Me_2Si(C_5H_4)(C_{13}H_8)LnCl]_2$ [Ln = Y (**1**), Lu (**2**), Er (**3**), Dy (**4**)] (Scheme 1) with C_s-symmetry. Organometallic complexes containing two cyclopentadienyl or two tetramethylcyclopentadienyl ligands bridged by silylene units are generally known to assume a metal-chelating structure [1c,11], and only a rare example of bridging structure has been reported [12]. However, mass spectra indicate that all complexes we obtained assume the Flu–SiR$_2$–Cp bridging structure instead of the normal chelating structure, which is further confirmed by X-ray analysis of **1**. In order to understand the substitution effects on the coordination modes, we further synthesized two solvent-free dimeric chlorides $[Ph_2Si(^tBuC_5H_3)(C_{13}H_8)LnCl]_2$ [Ln = Y (**5**), Dy (**6**)] with C_1-symmetry. X-ray analysis of **5** reveals that this C_1-symmetric

---

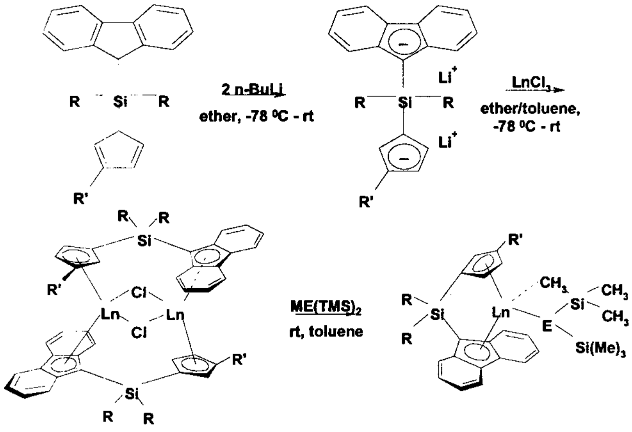
* Corresponding author. Tel.: + 86-21-64163300; fax: + 86-21-64166128.

E-mail address: qianct@pub.sioc.ac.cn (C. Qian).

0022-328X/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0022-328X(02)01121-X

complex also exhibits the bridging structure. This observation indicates that the bulkier substituents on the Cp ring and on the silylene-bridged atom do not hamper the formation of the bridging coordination structure.

The X-ray crystal structures of **1** and **5** are shown in Figs. 1 and 2. In the crystal structure of complex **1**, the Y_2Cl_2 skeleton is almost a square. The angles of Cl–Y–Cl′ and Y–Cl–Y′ are 88.18 and 91.82°, respectively. The Y–Y′ distance of 3.797 Å is shorter than that of the chelating isomer (3.987 Å) $[(C_5H_5)_2Yb(\mu\text{-}Cl)]_2$ [13], but it is in agreement with that of the bridging isomer (3.750 Å) $[Me_2Si(C_5H_4)_2Yb(\mu\text{-}Cl)]_2$ [12] (ionic radius of Y^{3+} is only 0.03 Å larger than that of Yb^{3+}). The Y_2Cl_2 skeleton in C_1 complex **5** is somewhat different from that in C_s-symmetric compounds. It has a rhombic arrangement. The angles of Cl–Y–Cl′ and Y–Cl–Y′ are 88.0 and 102.4°, respectively. The Y–Y′ distance of 3.659 Å is shorter than that of the analogous C_s-symmetric complex **1** (3.797 Å). In these binuclear complexes, the Y–Cl distances for **1** (2.645 Å) and for **5** (2.641 Å) are somewhat longer than those in the mononuclear complexes (e.g. 2.610 Å in $Me_2Si(Flu)(Cp')YCl_2Li(Et_2O)_2$ ($Cp' = C_5Me_4$) [8c], and 2.627 Å in $Me_2Si[(SiMe_3Cp)(CMe_3Cp)]YCl_2LiEt_2O$ [14]).



Chlorides (C_S): R=Me, R'=H; Ln = Y (**1**), Lu (**2**), Er (**3**), Dy (**4**) 15-20%

Chlorides (C_1): R=Ph, R'=t-Bu; Ln=Y (**5**) 37%, Dy (**6**) 72%

Amides (C_S): R=Me, R'=H, E=N; Ln=Dy (**7**) 39%, Ln=Er(**9**) 12%

Hydrocarbyls (C_S): R=Me, R'=H, E=CH; Ln=Dy (**8**) 13%, Ln=Er(**10**) 8%

Scheme 1.

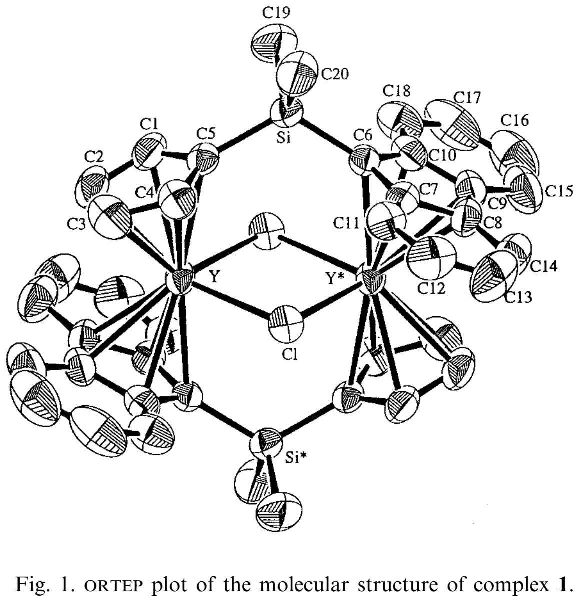


Fig. 1. ORTEP plot of the molecular structure of complex **1**.

A remarkable difference exists between the C_s-symmetric complex **1** and the C_1-symmetric **5** in the bonding mode of the Ln atom to the two π-rings. In **1**, the distances of Y–C (Cp, Flu ring) bonds, ranging from 2.599 to 2.699 Å, show the typical pattern of normal η^5-bonding. However, in complex **5**, the Y–C (Cp, Flu ring) distances [2.604(6)–2.825(6) Å] do not display the typical η^5-dispersion pattern. The longer Y–C [8–10] [2.732(6)–2.825(6) Å] distances originate from the repulsive interaction between the ^{t}Bu group and the fluorenyl group of the other coordinated ligand.

The monomeric salt-free and solvent-free amido and hydrocarbyl complexes $[Me_2Si(C_5H_4)(C_{13}H_8)]LnE(TMS)_2$ [E = N, Ln = Dy (**7**), Er (**9**); E = CH, Ln = Dy (**8**), Er (**10**)] were synthesized by reacting anhydrous $LnCl_3$ with the dilithio salt of the silylene-bridged ligand in ether, followed by the treatment with the $ME(TMS)_2$ (M = K or Li; E = N, CH) in toluene in a one-pot manner (Scheme 1).

The X-ray crystal structures of **7** and **8** are shown in Figs. 3 and 4. The structures of amide **7** and hydrocarbyl **8** display the γ-agostic interaction between the Ln^{3+} center and the methyl group. One of the trimethylsilyl substituents is close to the Ln^{3+} center, with a more acute $\angle Ln–C_\alpha–Si_\beta$ (1) angle. In the amide **7**, one of the Dy–N–Si angles is 106.8° and the other is 124.8°. In the hydrocarbyl **8**, the two Dy–C(27)–Si angles are 96.8(3) and 129.8(5)°, respectively. The Dy–N bond (2.207(5) Å) in **7** is shorter than the Dy–C(27) (2.364(9) Å) bond in **8**, which is due to the strong donation of the lone pair of nitrogen to the electron-deficient lanthanide metal center.

2.2. Synthesis and structural characterization of diphenylmethylene-bridged fluorenyl cyclopentadienyl ate ansa-lanthanocene chlorides, tetrahydroborates and neutral amides [15]

We selected the methylene instead of the silylene as the bridging unit. Two chlorides $[(C_{13}H_8)CPh_2(C_5H_4)Ln(Cl)_2][Li(THF)_4]$ [Ln = Y (**11**), Lu (**12**)] were prepared by reacting the dilithio salt of an *ansa*-ligand with anhydrous lanthanide chlorides (Scheme 2). These chlorides are different from the silylene-bridged ones.

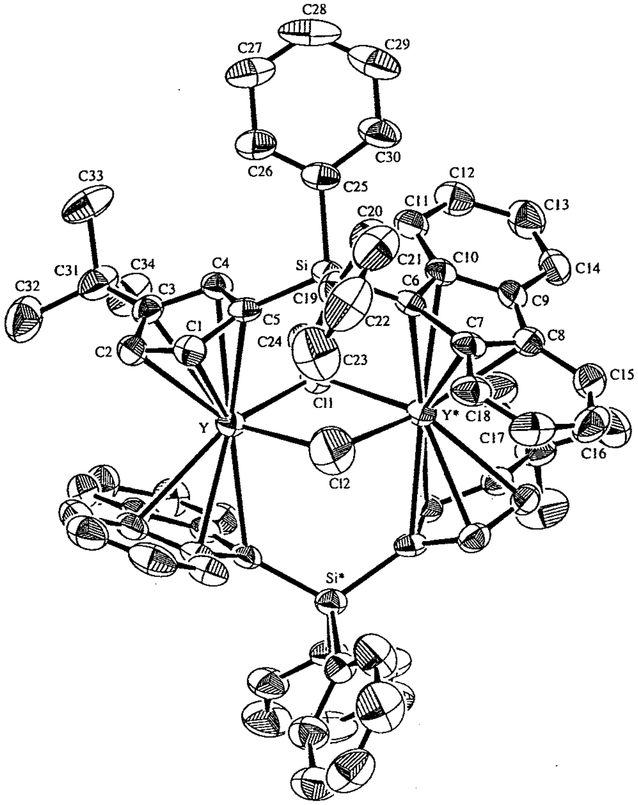


Fig. 2. ORTEP plot of the molecular structure of complex **5**.

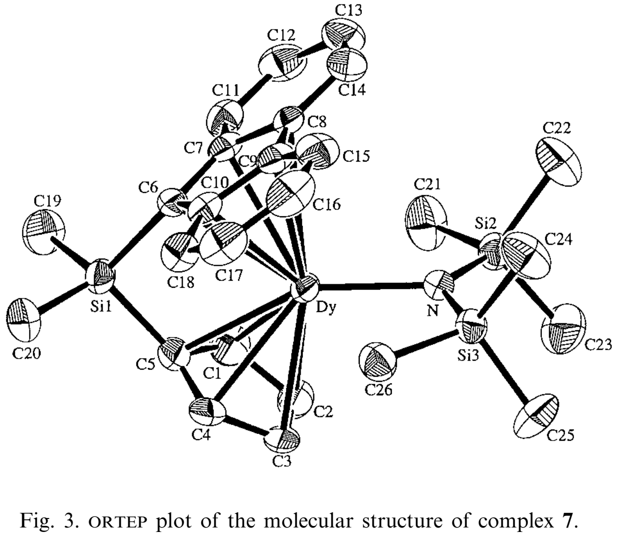


Fig. 3. ORTEP plot of the molecular structure of complex **7**.

They are ate- lanthanide complexes and have a chelating coordination structure. We attempted to extend this chemistry to light lanthanide elements, but failed. This can be explained by steric consideration, which determines the stability and structure of lanthanide complexes. The smaller radius of the Cl group could only match the smaller steric demand of the heavy lanthanide elements. The chloride complexes of the light lanthanides are not stable enough to be obtained under our reaction conditions.

The common route to synthesis of organolanthanide tetrahydroborates is by the reaction of a halide precursor with $LiBH_4$ or $NaBH_4$ [16]. However, the ate-compounds $\{(C_{13}H_8)CPh_2(C_5H_4)Ln((\mu\text{-H})_3BH)_2\}\{Li(THF)_4\}$ [Ln = La (**13**), Nd (**14**)] were synthesized directly by the reaction of $Ln(BH_4)_3(THF)_3$ with $(C_{13}H_8)CPh_2(C_5H_4)Li_2$ in THF (Scheme 3). Taking into consideration the larger radius and the versatile bonding modes of the BH_4^- ion in comparison with the chlorine ion, it would be expected that the borohydride complexes of most of the rare earth elements should be obtainable. However, in this series, we only isolated the light lanthanide borohydrides. Any attempt to obtain yttrium borohydride complex failed.

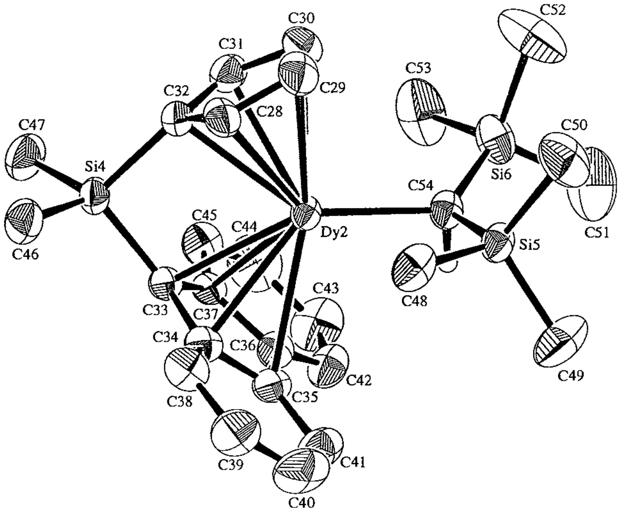
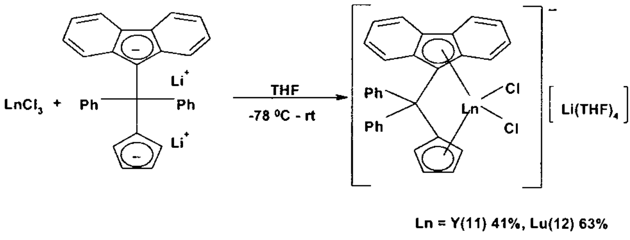
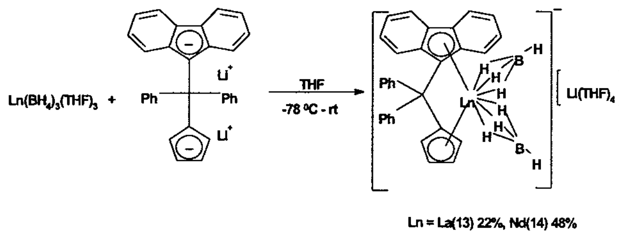


Fig. 4. ORTEP plot of the molecular structure of complex **8**.



Scheme 2.



Scheme 3.

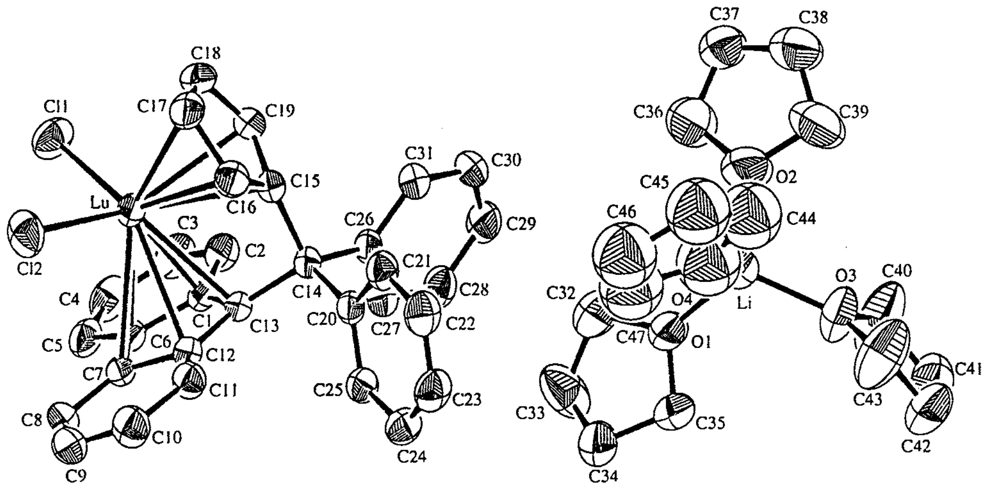


Fig. 5. ORTEP plot of the molecular structure of complex **12**.

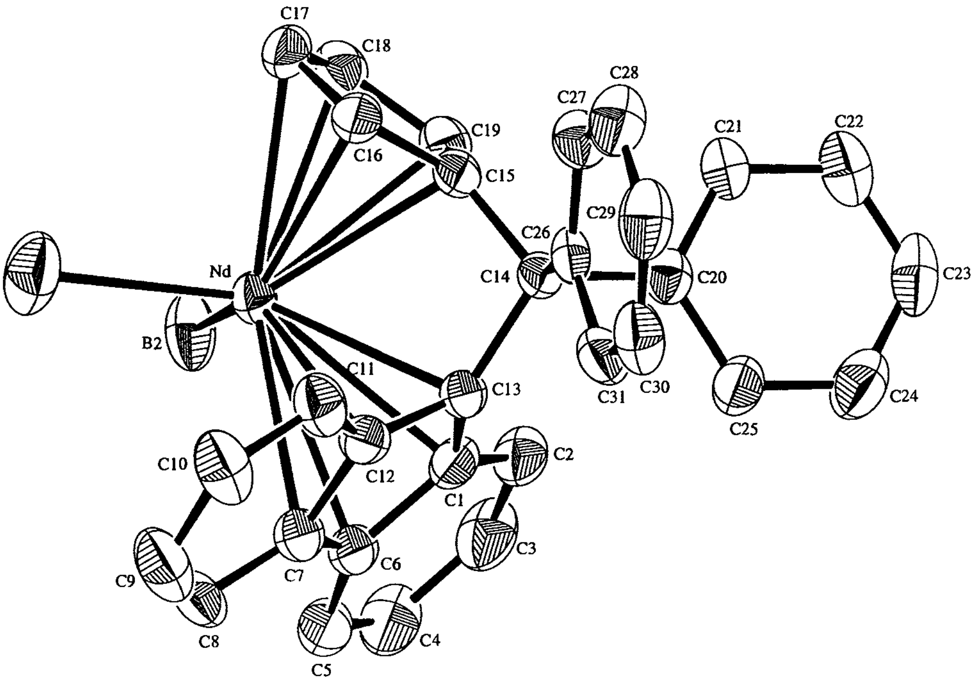
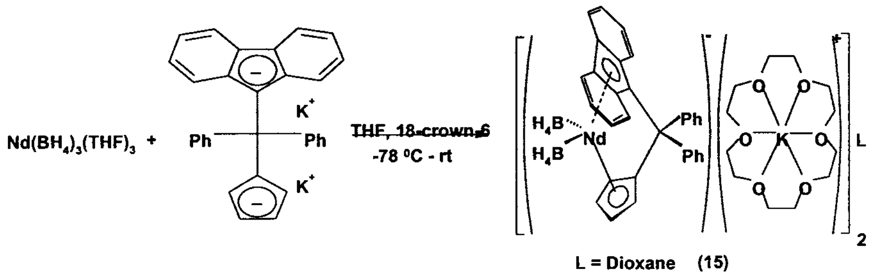


Fig. 6. ORTEP plot of the $\{FluCPh_2CpNd(BH_4)_2\}^-$ anion structure of complex **14**.

The crystal structures of complexes **12**, **13** and **14** indicate that they exist as discrete cation and anion pairs and belong to the ate complexes. In the anion moieties, all complexes adopt the pseudotetrahedral, bent metallocene motif commonly observed for $Cp_2LnX_2^-$ complexes [17] (Fig. 5).

In chloride **12**, the central metal Lu^{3+} is coordinated by the bridging ligand and two Cl atoms. The Cp ring is η^5-bonded to the Lu^{3+} [Lu–C (Cp ring) = 2.561(5)–2.626(5) Å], while the fluorene ring should be considered η^3- rather than η^5-bonded to the Lu^{3+} [Lu–C (fluorene ring) = 2.570(6), 2.631(5), 2.673(6) Å and 2.818(5), 2. 841(5) Å]. The angle of Cl(1)–Lu–Cl(2) is 96.48(7)°, and the bond lengths of Lu–Cl are 2.501(2) and 2.496(2) Å, respectively. Since the Nd^{3+} radius is 0.15 Å larger than that of Lu^{3+}, this compound is comparable to the anion $[Nd(Cp')_2Cl_2]^-$ ($Cp' = C_5Me_5$) [17e], where the average Nd–Cl distance is 2.668(4) Å and ∠Cl(1)–Lu–Cl(2) is 99.3(1)°.

Tetrahydroborates **13** and **14** have almost identical structures. The central metal ions are bonded to the cyclopentadienyl ring and fluorenyl ring in a η^5-fashion, and are coordinated by two BH_4 ligands in symmetric geometry. The B(1)–La–B(2) and B(1)–Nd–B(2) angles are 99.5(2) and 99.3(2)°, respectively. The most remarkable structural feature of these complexes is the attachment mode of the tetrahedral BH_4 ligands. The two boron atoms have almost the same ligation geome-



Scheme 4.

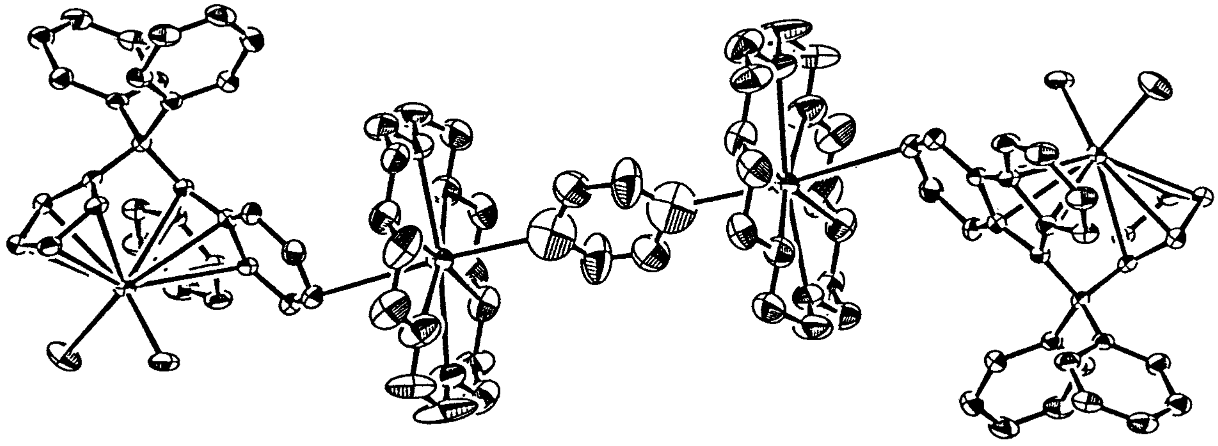


Fig. 7. ORTEP plot of the molecular structure of complex **15**.

try. Each of them is linked to the metal center via a μ^3-hydrogen bridging the B and the metal atoms (Fig. 6).

The cation $[Li(THF)_4]^+$, which exists in the three crystal structures, is classical [18]. Each lithium is coordinated by four oxygen atoms from four THF molecules, forming a tetrahedral structure, with Li–O distances ranging from 1.907(9) to 1.934(9) Å.

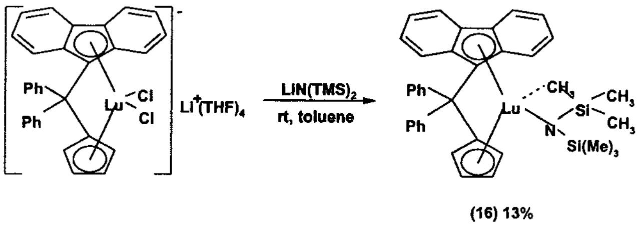
The single atom bridge of the $[Ph_2C]$ linker provides a relatively rigid *ansa*-metallocene ligand framework and serves to increase the dihedral angle between the cyclopentadienyl and fluorenyl planes. This leads to the opening of a wedge between the two planes, where two BH_4 or Cl groups can be located on the metal to afford ate- lanthanide complexes instead of homometallic complexes or heterometallic ones.

In the presence of 18-crown-6 ether, the reaction between $[Nd(BH_4)_3(THF)_3]$ [19] and $K_2[FluCPh_2Cp]$ [20] in THF affords an anionic complex $[K(18\text{-crown-}6)\{(C_{13}H_8)CPh_2(C_5H_4)Nd(BH_4)_2\}]_2{\cdot}C_4H_8O_2$ (**15**) in 20% yield (Scheme 4).

The crystal structure of complex **15** reveals that it is built up by the unit $[K(18\text{-crown-}6)\{(C_{13}H_8)CPh_2(C_5H_4)Nd(BH_4)_2\}]$ as the fundamental group, while two units are bridged by the bidentate ligand 1,4-dioxane (Fig. 7). The discrete tetrahedral anion $\{FluCPh_2CpNd(BH_4)_2\}^-$ moiety is almost identical to those in complexes **13** and **14**. The K^+ ion is coordinated by six oxygen atoms of the 18-crown-6 ether and one oxygen atom of 1,4-dioxane. Close contacts between the K^+ ion and two carbon atoms [$K–C_3 = 3.322(7)$ Å, $K–C_4 = 3.403(7)$ Å] of the six-membered ring of the fluorenyl moiety were observed; other K–C (1, 2, 5, 6) distances are much longer (out of 4.00 Å). There is a weak η^2 interaction of the K^+ ion with the fluorenyl moiety.

The monomeric salt-free and solvent-free amido complex $[Ph_2C(C_5H_4)(C_{13}H_8)]LuN(TMS)_2$ (**16**) was synthesized by the reaction of anhydrous $LuCl_3$ with dilithio salt of the methylene-bridged ligand in ether, followed by the treatment with the $LiN(TMS)_2$ in toluene in the one-pot manner (Scheme 5).

The X-ray crystal structure of **16** (Fig. 8) displays γ-agostic interaction between Lu^{3+} and the methyl group. The Δangle ($\angle Ln–N–Si - \angle Ln–N–Si = 29°$) in



(16) 13%

Scheme 5.

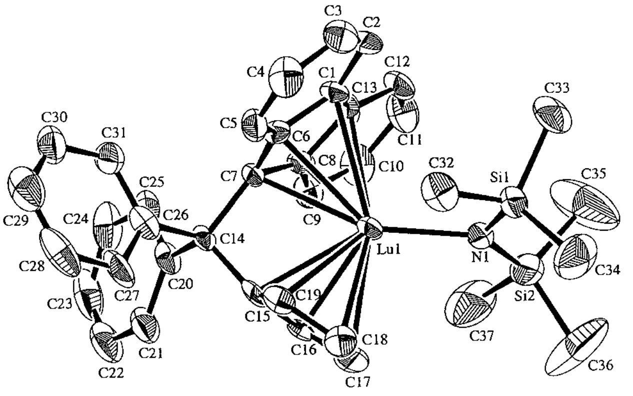
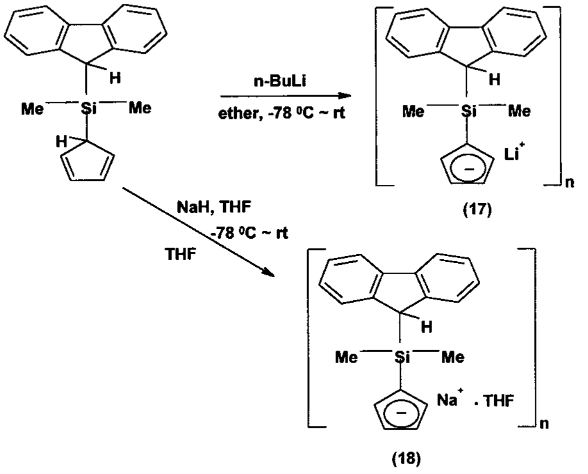


Fig. 8. ORTEP plot of the molecular structure of complex **16**.



Scheme 6.

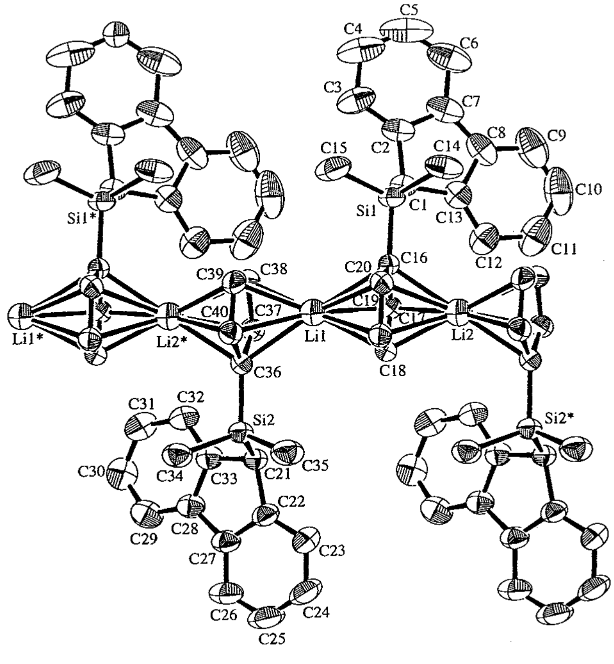


Fig. 9. ORTEP plot of the molecular structure of complex **17**.

the methylene-bridged complex **16** is larger than that ($\angle$Ln–N–Si − $\angle$Ln–N–Si = 18°) in the silylene-bridged complex **7** (18°) [9], indicating that the metal–methyl interaction in complex **16** is more sterically accessible than in complex **7**, presumably caused by the larger C(7)–C(14)–C(15) (101.1(7)°) angle and dihedral angle (74.38°) of complex **16** compared with the corresponding values of complex **7** (99.7(3) and 65.87°), which make the metal center more open so that one of the trimethylsilyl substituents of the amide ligand can closely approach the Ln^{3+} center.

2.3. Preparation and structure of the monoalkali-metal derivates of dimethylsilylene-bridged fluorenyl cyclopentadienyl systems [21]

In the recent years, there has been a great interest in the synthesis of transition metal compounds containing a bridged dicyclopentadienyl-type ligand with only one of its rings linked to the metal in penta-hapto coordination. These types of complexes are usually considered as potential precursors for the synthesis of binuclear complexes [22]. However, until now, no crystal structure of the monoalkali-metal salt was reported for *ansa*-metallocenes. In the course of our studies of silylated dicyclopentadienyl metallocenes, we obtained polymeric dimethylsilylene fluorenylsilyl cyclopentadienyl metallic compounds of the alkali metals of lithium and sodium.

Monoalkali-metal salts $\{[(C_{13}H_9Me_2Si)C_5H_4]Li\}_n$ (**17**) and $\{[(C_{13}H_9Me_2Si)C_5H_4]Na\cdot THF\}_n$ (**18**) were synthesized by the reaction of the dimethylsilyl-bridged fluorene cyclopentadiene ligand with one equivalent of *n*-butyl lithium or sodium hydride, respectively (Scheme 6). Any attempt to isolate the mono-potassium salt failed. $\{[(C_{13}H_9)Me_2Si(C_5H_4)]Li\}$ (**17**) was first observed as a by-product of the reaction of $\{[(C_{13}H_8)Me_2Si(C_5H_4)]Li_2\}$ with $NdCl_3$ in Et_2O. The X-ray structural analyses indicate that both the monoalkali-metal salts **17** and **18** (Figs. 9 and 10, respectively) possess similar polymeric structural features, with a parallel oriented high linear infinite unit in the solid state. Each of these units contains a super-sandwich complex, which consists of a repeating sequence of alkali-metal atoms on both sides of the cyclopentadienyl rings. In mono-lithium salt **17**, the lithium ion coordinated with the cyclopentadienyl ring in η^5-fashion, but in the corresponding sodium salt **18**, the coordination mode is in η^3-fashion.

3. Catalytic behavior toward polar monomers

3.1. Catalytic activity for polymerization of MMA

Poly(methyl methacrylate) (PMMA) is an important polymer in materials and surface-coating industries.

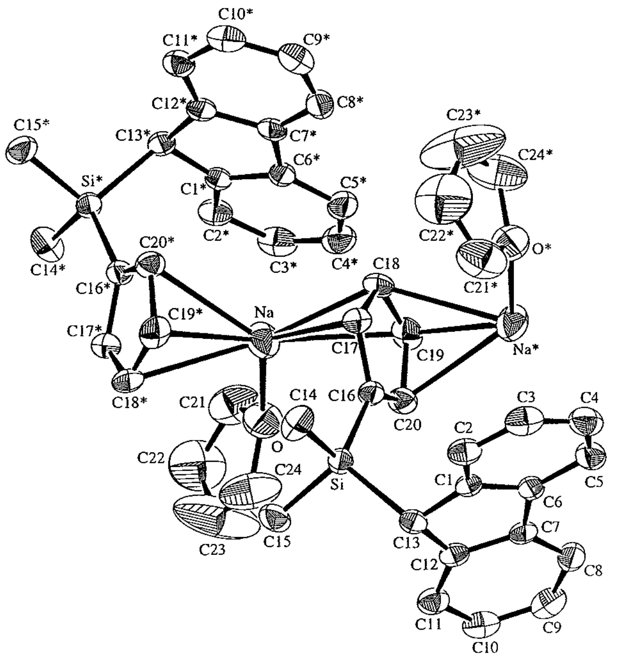


Fig. 10. ORTEP plot of the molecular structure of complex **18**.

Recently, lanthanocenes have been found to efficiently catalyze the living highly stereospecific polymerization of MMA. Yasuda et al. and Marks and co-workers have studied the activity of the C_{2v}- and C_1-symmetric lanthanocenes for MMA polymerization [3].

The catalytic activities of compounds **7**–**10** and **16** toward MMA polymerization have been examined. All of these C_s-symmetric complexes show comparably high activity (60–100%) and high stereoselectivity (rr = 60–83%). On lowering the temperature, the conversion and stereoregulation of the polymerization by amide complexes increased, while those by hydrocarbyls decreased. It can also be seen that erbium complexes show higher stereoselectivity than the dysprosium ones in this case. Solvent effects have also been tested. The polymers obtained in THF or DME remain *syn*-rich (about 50–60%), while **9** was used as a catalyst (entries 14 and 15 in Table 1).

3.2. Catalytic activity for ring-opening polymerization of lactones

The amides **7**, **9** and **16** also catalyze the ring-opening polymerization of ε-caprolactone (CL) and δ-valerolactone (VL). The results of polymerization are summarized in Table 2. The dimethylsilyl-bridged amides **7** and **9** show high activity toward CL polymerization in toluene. While in CH_2Cl_2, the activity of **7** decreased sharply. The activity of **16** toward lactone polymerization is lower than those of **7** and **9**. The polymers formed are of high molecular weight ($M_w > 3 \times 10^4$) and show narrow polydispersities ($M_w/M_n < 2.0$).

4. Conclusions

In summary, a series of new one-atom bridged fluorenyl cyclopentadienyl *ansa*-lanthanocene chlorides, hydrocarbyls, amides and tetrahydroborates with C_1- or C_s-symmetry have been synthesized successfully. The

Table 1
Data for the polymerization of methyl methacrylate [a]

Entry	Catalyst	T (h)	T_p (°C)	Conversion (%)	Stereoselectivity (%)		
					rr	rm	mm
1	**7**	1	20	80.5	61	31	8
2	**7**	1	0	81.7	64	27	9
3	**7**	0.5	−20	98.2	59	26	4
4	**7**	0.5	−78	90.1	73	21	6
5	**7**	1	−95	100	80	20	0
6	**8**	1	20	100	60	33	7
7	**8**	0.5	0	88.6	59	34	7
8	**8**	1	−78	61.4	52	36	12
9	**9**	2	0	67.5	67	26	7
10	**9**	0.5	−78	100	82	18	0
11	**9**	1	−95	82.7	83	17	0
12	**10**	0.5	0	100	56	29	15
13	**10**	0.5	−78	48.3	68	26	4
14 [b]	**9**	3	12	56.3	55	–	–
15 [c]	**9**	3	12	28.5	60	–	–
16	**16**	2	0	12.3	59	23	18
17	**16**	2	−78	0	–	–	–

[a] Reaction conditions: catalyst concentration, 0.5 mol% monomer; solvent, toluene; Solv/$[M_0]$ = 1 vol/vol.

[b] Solvent, THF; solvent/monomer = 2 vol/vol.

[c] Solvent, DME; solvent/monomer = 2 vol/vol.

Table 2
Data for the ring-opening polymerization of lactones

Entry	Catalyst	Solvent	Monomer	[mon]/[cat]	T_p (°C)	Yield (%)	M_w ($\times 10^{-4}$)	M_n ($\times 10^{-4}$)	M_w/M_n
1	**7**	Toluene	CL	180	0	76	3.21	1.76	1.81
2	**7**	Toluene	CL	225	0	85	4.91	2.70	1.81
3	**7**	Toluene	CL	450	0	83	8.10	5.00	1.62
4	**7**	Toluene	CL	675	0	88	9.79	5.85	1.67
5	**7**	Toluene	CL	675	25	90	2.95	1.36	2.16
6	**7**	CH_2Cl_2	CL	675	25	57	0.88	0.51	1.72
7	**7**	Toluene	VL	600	25	25	2.79	1.93	1.45
8	**9**	Toluene	CL	130	0	100	3.52	1.98	1.77
9	**16**	Toluene	CL	600	25	53	8.15	4.38	1.85
10	**16**	Toluene	VL	600	25	17	3.90	2.32	1.68

Reaction conditions: time, 2 h; solvent/monomer = 2 vol/vol.

silylene-bridged lanthanidocene chlorides assume the Flu–SiR_2–Cp bridging structure instead of the normal chelating structure, while the methylene-bridged lanthanidocene chlorides and tetrahydroborates are ate-type complexes, with chelating coordination mode.

Reactions between dimethylsilyl-bridged fluorene cyclopentadiene and one equivalent of n-butyl lithium or sodium hydride smoothly afford the corresponding monoalkali-metal salts. X-ray crystal structural analyses reveal that both complexes possess similar linear polymeric structural aggregate types in the solid state.

The C_s-symmetric organolanthanide hydrocarbyl and amide complexes are efficient single-component catalysts for the syndiospecific polymerization of methyl methacrylate. The amide complexes also show comparably high activity for the ring-opening polymerization of lactones. The polymers formed are of high molecular weight and show narrow polydispersities.

Acknowledgements

The authors are grateful to the National Nature Science Foundation of China and the State Key Project of Basic Research (Project 973) (No. G2000048007) for their financial support.

References

[1] (a) P.L. Watson, J. Am. Chem. Soc. 104 (1982) 337;
(b) G. Jeske, H. Lauke, H. Mauermann, P.N. Swepstone, H. Schumann, T.J. Marks, J. Am. Chem. Soc. 107 (1985) 8091;
(c) G. Jeske, L.E. Schock, P.N. Swepstone, H. Schumann, T.J. Marks, J. Am. Chem. Soc. 107 (1985) 8103;
(d) P.J. Shapiro, W.D. Cotter, W.P. Schaefer, J.A. Labinger, J.E. Bercaw, J. Am. Chem. Soc. 116 (1994) 4623;
(e) E.B. Coughlin, J.E. Bercaw, J. Am. Chem. Soc. 114 (1992) 7606.

[2] (a) H. Yasuda, E. Ihara, Macromol. Chem. Phys. 196 (1995) 2417;
(b) H. Yasuda, E. Ihara, Bull. Chem. Soc. Jpn. 70 (1997) 1745.

[3] (a) H. Yasuda, H. Yamamoto, K. Yokota, S. Miyake, A. Nakamura, J. Am. Chem. Soc. 114 (1992) 4908;
(b) H. Yasuda, H. Yamamoto, M. Yamashita, K. Yokota, A. Nakamura, S. Miyake, Y. Kai, N. Kanehisa, Macromolecules 26 (1993) 7134;
(c) M.A. Giardello, Y. Yamamoto, L. Brard, T.J. Marks, J. Am. Chem. Soc. 117 (1995) 3276.

[4] (a) M. Yamashita, E. Ihara, H. Yasuda, Macromolecules 29 (1996) 1798;
(b) K.C. Hultzsch, T.P. Spaniol, J. Okuda, Organometallics 16 (1997) 4847.

[5] (a) Y. Li, T.J. Marks, J. Am. Chem. Soc. 118 (1996) 707;
(b) Y. Li, T.J. Marks, J. Am. Chem. Soc. 118 (1996) 9295;
(c) M.R. Gagne, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 114 (1992) 275.

[6] (a) W.J. Evans, I. Bloom, W.E. Hunter, J.L. Atwood, J. Am. Chem. Soc. 103 (1981) 6507;
(b) G.A. Molander, J. Winterfeld, J. Organomet. Chem. 524 (1996) 275.

[7] H. Schumann, J.A. Meese-Marktscheffel, L. Esser, Chem. Rev. 95 (1995) 865.

[8] (a) W.J. Evans, T.S. Gummersheimer, T.J. Boyle, J.W. Ziller, Organometallics 13 (1994) 1281;
(b) R.K. Sharma, C.P. Sharma, J. Indian Chem. Soc. 64 (1987) 506;
(c) M.H. Lee, J.-E. Hwang, Y. Kim, J. Kim, Y. Do, Organometallics 18 (1999) 5124.

[9] C. Qian, W. Nie, J. Sun, Organometallics 19 (2000) 4134.

[10] (a) K. Patsidis, H.G. Alt, W. Milius, S.J. Palackal, J. Organomet. Chem. 509 (1996) 63;
(b) Y. Chen, M.D. Rausch, J.C.W. Chien, J. Organomet. Chem. 497 (1995) 1.

[11] (a) W. Abriel, J. Heck, J. Organomet. Chem. 302 (1986) 363;
(b) C.M. Fendrick, E.A. Mintz, L.D. Schertz, T.J. Marks, V.W. Day, Organometallics 3 (1984) 819.

[12] N. Hock, W. Oroschin, G. Paolucci, R.D. Fisher, Angew. Chem. Int. Ed. Engl. 25 (1986) 738.

[13] H. Lueken, J. Schmitz, W. Lambert, P. Hannibal, K. Handrick, Inorg. Chim. Acta 156 (1989) 119.

[14] R.E. Marsh, W.P. Schaefer, E.B. Coughlin, J.E. Bercaw, Acta Crystallogr. Sect. C 48 (1992) 1773.

[15] (a) C. Qian, W. Nie, J. Sun, J. Chem. Soc. Dalton Trans. (1999) 3283;
(b) C. Qian, W. Nie, J. Sun, J. Organomet. Chem. 626 (2001) 171;
(c) C. Qian, W. Nie, Y. Chen, J. Sun, J. Organomet. Chem. 645 (2002) 82.

[16] (a) M.F. Lappert, A. Singh, J.L. Atwood, W.E. Hunter, J. Chem. Soc. Chem. Commun. (1983) 206;

(b) D. Deng, X. Zheng, C. Qian, J. Sun, L. Zhang, J. Organomet. Chem. 466 (1994) 95;

(c) T.J. Marks, G.W. Grynkewich, Inorg. Chem. 15 (1976) 1302.

[17] (a) P.L. Watson, J.F. Whitney, R.L. Harlow, Inorg. Chem. (1981) 3271;

(b) H. Schumann, I. Albrecht, J. Leobel, E. Hahn, B. Hossain, D. Van der Helm, Organometallics 5 (1986) 1296;

(c) M.A. Giardello, V.P. Conticello, L. Brard, T.J. Marks, J. Am. Chem. Soc. 116 (1994) 10241;

(d) M.D. Rausch, K.J. Moriarty, J.L. Atwood, J.A. Weeks, W.E. Hunter, H.G. Brittain, Organometallics 5 (1986) 1281;

(e) M.F. Lappert, A. Singh, J.L. Atwood, W.E. Hunter, H.M. Zhang, J. Chem. Soc. Chem. Commun. (1983) 69.

[18] L. Mao, Q. Shen, S. Jin, Polyhedron 13 (1994) 1023.

[19] M.C. Cassani, D.J. Duncalf, M.F. Lappert, J. Am. Chem. Soc. 120 (1998) 12958.

[20] H. Viecrock, T. Panther, U. Behrens, E. Weiss, J. Organomet. Chem. 491 (1995) 19.

[21] W. Nie, C. Qian, Y. Chen, J. Sun, Organometallics 20 (2001) 5780.

[22] I. Dorado, J.C. Flores, M. Galakhov, P.G. Sal, A. Martin, P. Royo, J. Organomet. Chem. 563 (1998) 7.