

Synthesis of diphenylmethylene bridged fluorenyl cyclopentadienyl lanthanocene complexes with C_s symmetry and crystal structures of the ate complexes $[\text{Li}(\text{thf})_4][\text{LnCl}_2\{(\text{C}_{13}\text{H}_8)\text{CPh}_2(\text{C}_5\text{H}_4)\}]$ and $[\text{Li}(\text{thf})_4][\text{Ln}(\text{BH}_4)_2\{(\text{C}_{13}\text{H}_8)\text{CPh}_2(\text{C}_5\text{H}_4)\}]$ ($\text{Ln} = \text{Nd}$ or La)

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The reaction of anhydrous lanthanide chlorides LnCl_3 with the dilithium salt of $(\text{C}_{13}\text{H}_8)\text{CPh}_2(\text{C}_5\text{H}_5)$ in thf at ambient temperature led to the formation of the 'ate' complexes $[\text{Li}(\text{thf})_4][\text{LnCl}_2\{(\text{C}_{13}\text{H}_8)\text{CPh}_2(\text{C}_5\text{H}_4)\}]$ ($\text{Ln} = \text{Lu}$ **1** or **Y** **2**). Treatment of $[\text{Ln}(\text{BH}_4)_3(\text{thf})_3]$ with 3 equivalents of $(\text{C}_{13}\text{H}_8)\text{CPh}_2(\text{C}_5\text{H}_4)\text{Li}_2$ in thf solution gave the anionic complexes $[\text{Li}(\text{thf})_4][\text{Ln}(\text{BH}_4)_2\{(\text{C}_{13}\text{H}_8)\text{CPh}_2(\text{C}_5\text{H}_4)\}]$ ($\text{Ln} = \text{La}$ **3** or **Nd** **4**). The crystal structures of complexes **1**, **3**, **4** were determined and indicated that they existed as discrete cation and anion pairs, which showed two crystallographically independent molecules in the unit cell.

Introduction

Since the discovery of the first stereorigid chiral ansa metallocene complex¹ and the application of such compounds as homogeneous catalysts in stereospecific polymerization of α -olefins to polymers with stereoregular microstructures, a wide variety of metallocene catalysts from Groups 3 and 4 have now been prepared. The tacticity of polypropylene varies predictably with the structure of the ansa metallocene catalysts: C_2 symmetric metallocenes produce highly isotactic polypropylene; C_1 metallocenes also produce isotactic polypropylene, but generally with less stereospecificity; syndiotactic polypropylene has been produced using essentially a single type of C_s symmetric ansa-metallocene catalyst.² However, the chemistry of ansa-lanthanocene has been very limited, especially when compared with that of the Group 4 metallocenes. Since the metallocenes of the rare earth elements are isoelectronic in structure with Group 4 cationic alkyl metallocene complexes $d^0 \text{MCp}_2\text{R}^+$ ($\text{Cp} = \text{C}_5\text{H}_5$). This analogy has been used in the design of olefin polymerization catalysts. A potentially significant advantage of these catalysts is that they are single-component catalysts; no cocatalyst $(\text{MeAlO})_n$ (MAO) is needed. They can also catalyse the polymerization of ethylene and polar monomer without the cocatalyst MAO and exhibit high activity. Moreover, this fact facilitates significantly the study of the α -olefin polymerization mechanism and the influence of the metal-ligand environment on the structure and properties of the resultant polymer

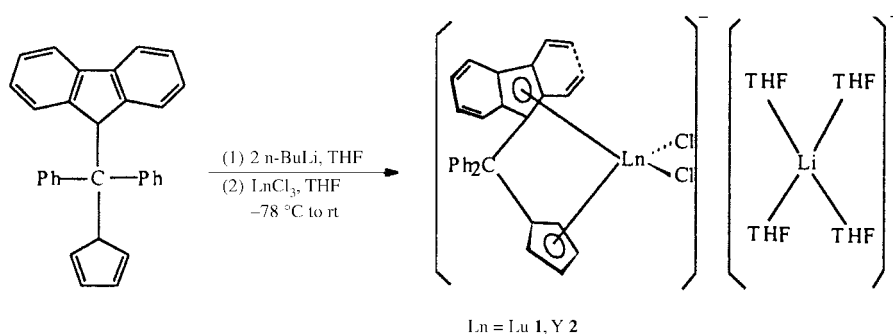
because the intermediates can be isolated more easily than in the case of the Group 4 metallocenes.³

Until now most of the work reported was on compounds stabilized by bis(pentamethylcyclopentadienyl) or closely related ligand systems.⁴ In our previous work, we have reported C_2 symmetric bis(indenyl) ansa-lanthanocene complexes.⁵ So far, no lanthanocene complexes with ansa-bonded fluorenyl ligands have been reported. In this paper we report the synthesis and structure of some representative 'ate' complexes: tetra(tetrahydrofuran) lithium dichloro(fluorene-9-ylidiphenylmethylcyclopentadienyl) lanthanidates and lithium (fluorene-9-ylidiphenylmethylcyclopentadienyl)bis(tetrahydroborato) lanthanidates which should prove useful as precursors to lanthanocene(III) complexes such as hydrides and alkyls.

Results and discussion

Synthesis

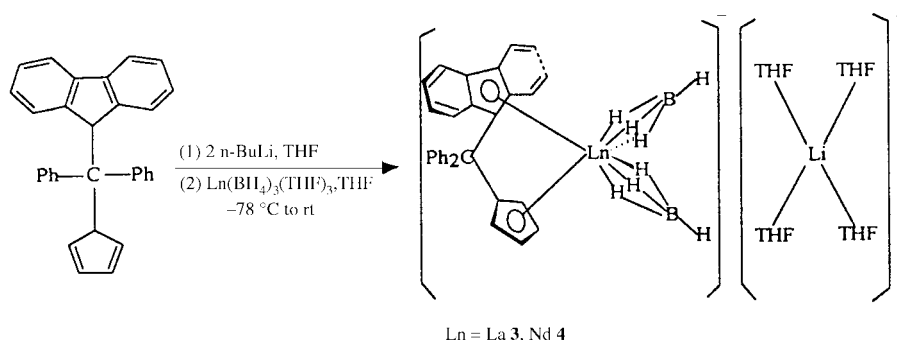
The ate complexes $[\text{Li}(\text{thf})_4][\text{LnCl}_2\{(\text{C}_{13}\text{H}_8)\text{CPh}_2(\text{C}_5\text{H}_4)\}]$ ($\text{Ln} = \text{Lu}$ **1** or **Y** **2**) were synthesized by using a reaction between a dilithio salt of an ansa ligand and an anhydrous lanthanide chloride (Scheme 1). These complexes are readily dissolved in thf, but just sparingly soluble in toluene at room temperature. They remain air and moisture sensitive, whether in the solid or solution phase. We attempted to extend this chemistry to light lanthanide elements, but failed. This can be explained by



Scheme 1

Table 1 The ^1H NMR data (δ , J/Hz) of complexes **1–3** in $[\text{D}_8]\text{thf}$ at 25 °C (300 MHz)

Complex	$\delta\text{CH}(\text{Ph})$	$\delta\text{CH}(\text{fluorene})$	$\delta\text{CH}(\text{Cp})$
1	6.98 (t, 2 H, $J = 7.1$)	6.52 (d, 2 H, $J = 8.69$)	
	7.09 (m, 4 H)	6.81 (t, 2 H)	5.81 (t, 2 H, $J = 2.6$)
	7.90 (d, 2 H, $J = 7.52$)	7.22 (t, 2 H)	5.90 (t, 2 H, $J = 2.6$)
	8.00 (d, 2 H, $J = 8.2$)	8.08 (d, 2 H, $J = 7.89$)	
2	6.97 (t, 2 H, $J = 7.1$)	6.48 (d, 2 H, $J = 8.7$)	
	7.09 (m, 4 H)	6.84 (t, 2 H)	5.82 (t, 2 H, $J = 2.6$)
	7.90 (d, 2 H, $J = 7.6$)	7.10 (t, 2 H)	5.92 (t, 2 H, $J = 2.6$)
	8.01 (d, 2 H, $J = 8.2$)	8.04 (d, 2 H, $J = 9.2$)	
3	7.30 (m, 2 H)	6.98 (t, 2 H)	
	7.15–7.32 (m, 2 H)	7.10 (t, 2 H)	6.31 (t, 2 H, $J = 2.6$)
	8.44 (m, 6 H)	7.95 (d, 2 H, $J = 8.0$)	6.74 (t, 2 H, $J = 2.6$)
		8.30 (d, 2 H, $J = 7.8$)	

**Scheme 2**

the steric considerations which determine the stability and structure of lanthanide complexes. The smaller radius of the Cl group could only match the steric demand of the heavy lanthanide elements.

The usual route to synthesis of organolanthanide tetrahydroborates is by the reaction of a halide precursor with LiBH_4 or NaBH_4 .⁶ Besides $[(\text{thf})_2(\text{BH}_4)_2\text{Nd}(\mu\text{-}\eta^7\text{:}\eta^7\text{-C}_7\text{H}_7)\text{Nd}(\text{BH}_4)_2(\text{thf})_2]$ ⁷ and $[\{\text{Nd}(\text{COT})(\text{BH}_4)(\text{thf})\}_2]$,⁸ which were obtained from the reaction of $\text{Nd}(\text{BH}_4)_3(\text{thf})_n$ ($n = 2$ or 3) with KC_7H_9 or $\text{K}_2\text{C}_8\text{H}_8$ respectively, no ansa-(cyclopentadienyl)-lanthanide tetrahydroborate complexes have been isolated directly by the reaction of $\text{Nd}(\text{BH}_4)_3(\text{thf})_n$ with cyclopentadienyl anionic reagents. Compounds $[\text{Li}(\text{thf})_4][\text{Ln}\{(\mu\text{-H})_3\text{BH}\}_2\text{-}\{(C_{13}H_8)\text{CPh}_2(C_5H_4)\}]$ ($\text{Ln} = \text{La}$ **3** or Nd **4**) were synthesized directly by the reaction of $[\text{Ln}(\text{BH}_4)_3(\text{thf})_3]$ with $(C_{13}H_8)\text{CPh}_2(C_5H_4)\text{Li}_2$ in thf (Scheme 2). By slow diffusion of hexane into the concentrated thf solution, we got single crystals suitable for X-ray diffraction. The crystal structures indicated that they belonged to the class of 'ate' complexes instead of the expected homometallic compounds or heterometallic ones. Taking into consideration the larger radius and the versatile bonding modes of the BH_4 group in comparison with chloride, it would be expected that the tetrahydroborate complexes of most of the rare earth elements should be obtainable. However in this series, we only isolated the light lanthanide tetrahydroborate complexes. Any attempt to obtain yttrium tetrahydroborate complex from the reaction of $[\text{Y}(\text{BH}_4)_3(\text{thf})_3]$ with the dilithium salt of the ligand failed and unfortunately a non-crystallizing oil formed which can not be purified or further characterized.

Spectroscopic properties

In the case of diamagnetic complexes, the ^1H NMR spectra of **1** and **2** were recorded in THF-d_8 , and that of **3** in C_6D_6 . The spectra show similar patterns for the four protons of the cyclopentadienyl. The two pseudotriplets lay in the range δ 5.8–6.7 with ^1H , ^1H coupling constants of 2.5–2.7 Hz. The protons of the fluorenyl ligands give rise to a doublet, triplet, triplet,

Table 2 Selected bond lengths (Å) and angles (°) for complex **1**

Lu–Cl(1)	2.496(2)	Cl(1)–Lu–Cl(2)	96.48(7)
Lu–Cl(2)	2.501(2)	Cl(1)–Lu–C(13)	126.3(1)
Lu–C(1)	2.631(5)	Cl(2)–Lu–C(13)	124.8(1)
Lu–C(6)	2.818(5)	Cl(1)–Lu–C(15)	126.6(1)
Lu–C(7)	2.841(5)	Cl(2)–Lu–C(15)	126.7(1)
Lu–C(12)	2.673(6)	C(1)–C(13)–C(14)	126.4(4)
Lu–C(13)	2.570(6)	C(12)–C(13)–C(14)	125.8(4)
Lu–C(15)	2.561(5)	C(1)–C(14)–C(15)	101.7(4)
Lu–C(16)	2.567(5)	C(14)–C(15)–C(16)	124.9(4)
Lu–C(17)	2.615(5)	C(14)–C(15)–C(19)	124.3(4)
Lu–C(18)	2.626(5)	C(20)–C(14)–C(26)	103.5(4)
Lu–C(19)	2.577(5)		

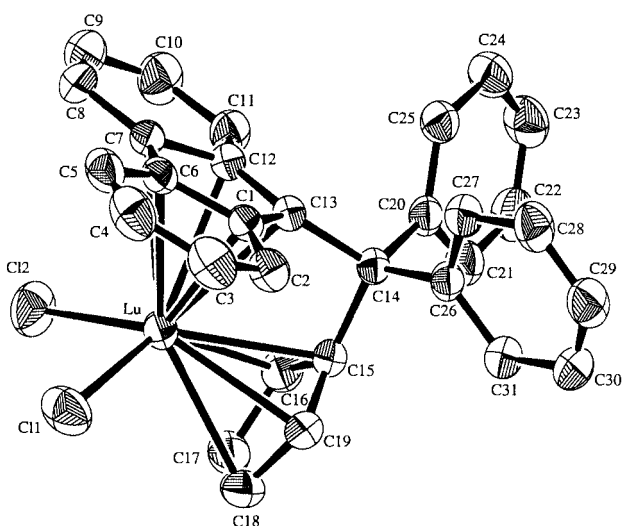
doublet pattern. Since the additional phenyl substituents show signals in the same region as the fluorenyl ligand, their spectra are too complicated accurately to calculate the ^1H , ^1H coupling constants. The data are collected in Table 1. Since compound **4** exhibits paramagnetic chemical shifts it is very difficult to assign its ^1H NMR spectrum.

Molecular structure

X-Ray diffraction quality crystals were grown from thf solution. All the crystal structures of these three ate complexes consist of isolated ion pairs. Selected bond lengths and internal angles are given in Tables 2 and 3. The molecular structures of **1** and **4** are shown in Figs. 1 and 2, respectively. In the anion the complexes adopt the pseudotetrahedral, bent metallocene motif commonly observed for $\text{Cp}_2\text{LnX}_2^-$ complexes.^{10,11} The Ln–C (Cp ring, fluorene-ring) bond distances display the dispersion pattern observed in other ring-bridged organolanthanide complexes with longer Ln–C (Cp ring, fluorene-ring) distances for carbon atoms (C(6), C(7), C(17), C(18)) distal to the Ph_2C bridge vs. proximal carbon atoms (C(13), C(15)).⁴ The Ln–C (Cp ring) distances in these three complexes are within the range expected for ansa-lanthanocene. However, for the Ln–C (fluorene-ring), the metal–carbon bond distances between Ln and C(6), C(7) are much longer than the proximal

Table 3 Selected bond lengths (Å) and angles (°) for complexes **3** and **4**

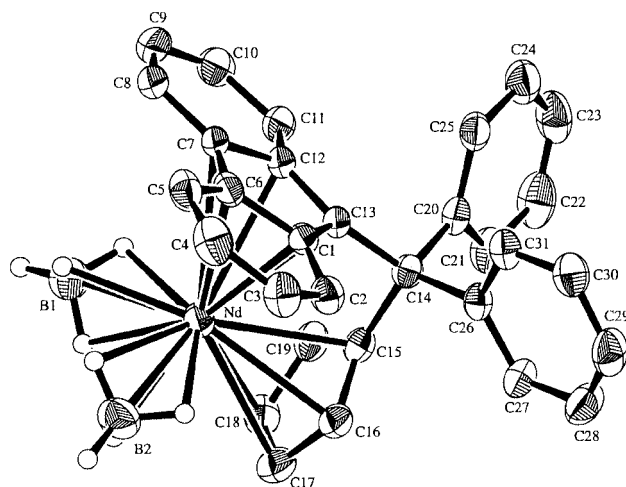
	3 (La)	4 (Nd)
Ln–B(1)	2.717(5)	2.642(7)
Ln–B(2)	2.713(5)	2.658(6)
Ln–H(23)	2.37(6)	2.53(4)
Ln–H(24)	2.43(4)	2.38(6)
Ln–H(25)	2.38(5)	2.38(4)
Ln–H(27)	2.52(5)	2.39(4)
Ln–H(28)	2.49(5)	2.45(5)
Ln–H(29)	2.40(4)	2.45(5)
Ln–C(1)	2.845(3)	2.793(4)
Ln–C(6)	3.001(3)	2.946(4)
Ln–C(7)	3.010(3)	2.954(4)
Ln–C(12)	2.861(3)	2.806(4)
Ln–C(13)	2.788(3)	2.725(4)
Ln–C(15)	2.763(3)	2.701(4)
Ln–C(16)	2.769(3)	2.699(4)
Ln–C(17)	2.828(4)	2.771(4)
Ln–C(18)	2.830(4)	2.767(4)
Ln–C(19)	2.769(3)	2.708(4)
B(1)–Ln–B(2)	99.5(2)	99.3(2)
C(1)–C(13)–C(14)	126.6(3)	126.8(3)
C(12)–C(13)–C(14)	125.6(3)	125.3(3)
C(13)–C(14)–C(15)	104.1(2)	102.4(3)
C(14)–C(15)–C(16)	125.9(3)	125.5(3)
C(14)–C(15)–C(19)	125.8(3)	125.9(4)
C(20)–C(14)–C(26)	102.7(2)	103.1(3)

**Fig. 1** An ORTEP⁹ drawing of the $[\text{LuCl}_2(\text{C}_{13}\text{H}_8)\text{CPh}_2(\text{C}_5\text{H}_4)]^-$ anion.

Ln–C(13) distance. This can be explained by the inclined stereorigid planar fluorenyl ligation.

In the crystal structure of complex **1** the central metal Lu is tetrahedrally co-ordinated to the bridging ligand and the two Cl atoms with angle Cl(1)–Lu–Cl(2) 96.48(7)° and the bond lengths Lu–Cl(1) 2.496(2) and Lu–Cl(2) 2.501(2) Å. Since the Nd³⁺ radius is 0.15 Å larger than that of Lu³⁺, this compound is comparable to the anion $[\text{Nd}(\text{Cp}')_2\text{Cl}_2]^-$ ¹¹ (Cp' = C₅Me₅) where the average Nd–Cl distance is 2.668(4) Å and Cl(1)–Nd–Cl(2) is 99.3(1)°. Since the chlorine atoms do not co-ordinate with the lithium in these ate compounds, these values depart somewhat from those found in other classes of lutetium metallocenes *e.g.* for $[(\text{R})\text{-Me}_2\text{SiCp}''[(+)\text{-neomenthylCp}]\text{Lu}(\mu\text{-Cl})_2\text{Li}(\text{OEt}_2)_2]$ ¹² (Cp'' = Me₄C₅) (86.9(1)°; 2.569(4) Å and 2.571(4) Å) and for achiral $[\text{Cp}'_2\text{Yb}(\mu\text{-Cl})_2\text{Li}(\text{OEt}_2)_2]$ ^{10b} (85.89°; Lu–Cl 2.586 and 2.584 Å), correcting for differences in Lu³⁺ and Yb³⁺ eight-co-ordinate ionic radii,¹³ in which the longer Ln–Cl distance (>0.06–0.07 Å) and smaller Cl(1)–Ln–Cl(2) angle (<10°) are caused by the bridging nature of the chlorides.

Complexes **3** and **4** have almost identical structures and so

**Fig. 2** An ORTEP drawing of the $[\text{Nd}(\text{BH}_4)_2(\text{C}_{13}\text{H}_8)\text{CPh}_2(\text{C}_5\text{H}_4)]^-$ anion.

only that of **4** is discussed. This compound exists as discrete cation and anion pairs, and shows two crystallographically independent molecules in the unit cell. The Nd is bonded to the cyclopentadienyl ring and fluorenyl ring in η⁵ fashion, and to two BH₄ ligands in symmetric geometry. The angle of B(1)–Nd–B(2) (99.3(2)°) is almost equal to the value of Cl(1)–Nd–Cl(2) in the anion $[\text{Nd}(\text{Cp}'')_2\text{Cl}_2]^-$, 99.3(1)°. The Nd–C (Cp ring) distances range from 2.699(4) to 2.767(4) Å, average 2.729 Å. The Nd–C (fluorene-ring) distances range from 2.725(4) to 2.954(4) Å, average 2.845 Å. The angle at the diphenylmethylene carbon C(13)–C(14)–C(15) 102.4(3)° is larger than in previously reported Group 4 metallocenes having a C₅H₄CR₂C₁₃H₈ (R = Me or Ph) chelating ligand system.¹⁴ We believe that the progressive increase in the Nd–C bond distances from the bridgehead carbon C(13)(2.725(4)) to C(1)(2.793(4)), C(12)(2.806(4)), C(6)(2.946(4)), C(7)(2.954(4)) Å is due to the non-bonding interaction between the two borate ligands. Similar reasoning applies to the Nd–C bond distances to the cyclopentadienyl moiety. The Nd–C(17) (2.771(4)) and Nd–C(18) (2.767(4) Å) distances which are on average about 0.1 Å larger than the other three are also due to the non-bonding interaction between the two borate ligands, and the (dorsal/distal)carbon and hydrogen atoms are responsible for the repulsion that gives rise to this bond lengthening. The most remarkable structural feature of the complex is the mode of attachment of the tetrahedral BH₄ ligands. The two boron atoms have almost the same ligation geometry. Each of them is linked to the metal centre *via* a μ₃-hydrogen bridging the B and the Nd atoms. This 'ate' co-ordination type of tetrahydroborate ligand has not been encountered in organolanthanide tetrahydroborate compounds, but is known in uranium compounds.¹⁵ The two Nd–B distances (Nd–B(1) 2.642(7), Nd–B(2) 2.658(6) Å) which may be compared with that of 2.664(25) Å in the monomeric neodymium complex $[\text{Nd}(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{OMe})_2(\text{BH}_4)]$ ^{16b} are shorter than that of dimeric neodymium complexes (*e.g.* 2.875(6) and 2.941(6) in $[\{\text{Nd}\{(\text{COT})(\text{BH}_4)(\text{thf})\}_2]^{8+}$). The short distances are characteristic of tridentate BH₄ ligands. The six Nd–H_b bond distances for the tridentate groups are not significantly different (2.53(4), 2.45(5), 2.39(4), 2.38(4) Å). In each Nd–μ-H moiety two of the Nd–H_b bond distances are equal (2.38(5) and 2.45(5) Å, respectively). The Nd–B–H_b angles are equal to 64(2) or 72(2)°, whereas the two Nd–B–H_t angles are almost linear (Nd–B(1)–H_t 173(3), Nd–B(2)–H_t 178(2)°). The tetrahedral BH₄ groups seem much more distorted than its ideal H–B–H angles of 109°28'. The bond distances of B–H_b and B–H_t are not significantly different, varying from 0.97(6) to 1.10(5) Å. In the FT-Raman spectrum the sharp singlet at 2421 and 2221 cm⁻¹ are characteristic of tridentate BH₄ groups.

Table 4 X-Ray diffraction data collection parameters for complexes **1**, **3** and **4**

	1	3	4
Formula	C ₄₇ H ₅₄ Cl ₂ LiLuO ₄	C ₄₇ H ₆₂ B ₂ LaLiO ₄	C ₄₇ H ₆₂ B ₂ LiNdO ₄
<i>M</i>	935.76	858.47	863.81
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P1</i> (no. 2)	<i>P1</i> (no. 2)	<i>P1</i> (no. 2)
<i>a</i> /Å	12.529(5)	12.422(3)	12.415(6)
<i>b</i> /Å	15.280(3)	16.343(4)	16.245(5)
<i>c</i> /Å	12.247(3)	12.337(4)	12.337(5)
<i>a</i> °	99.06(2)	110.50(2)	110.43(3)
<i>β</i> °	100.53(2)	103.16(2)	103.23(4)
<i>γ</i> °	76.02(2)	76.16(2)	76.13(3)
<i>V</i> /Å ³	2173(1)	2249(1)	2234(1)
<i>T</i> /K	293	293	293
<i>Z</i>	2	2	2
<i>μ</i> (Mo-Kα)/cm ⁻¹	24.35	9.85	12.01
Reflections collected	8051	7918	5026
Independent reflections	7659	7522	4707
<i>R</i> , <i>R'</i>	0.037, 0.052	0.032, 0.041	0.027, 0.036

The cation [Li(thf)₄]⁺ which exists in the three crystal structures is classical and quite similar to that in the complex [Li(thf)₄][Yb(t-BuCp)(NPh₂)₃].¹⁶ Each lithium is co-ordinated 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.

Since the single atom bridge of the Ph₂C 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 ‘opening’ of the wedge between the two planes where two BH₄ or Cl groups can be located on the metal to afford ate lanthanide complexes.

Conclusion

The synthesis, characterization and structure of several diphenylmethylene bridged cyclopentadienyl fluorenyl ‘ate’ lanthanocene chlorides and tetrahydroborates with C_s symmetry are reported. The crystal structures demonstrate that these exist as ate complexes in the solid state.

Experimental

All operations involving organometallics were carried out under an inert atmosphere of argon using standard Schlenk techniques. The thf was distilled under argon from sodium–benzophenone prior to use. Anhydrous lanthanide chlorides¹⁷ and lanthanide tetrahydroborate compounds^{8,18} were prepared according to the literature and the reactants *n*-butyllithium and fluorene were purchased from Aldrich. The compound (C₁₃H₈)CPh₂(C₅H₄)Li₂^{14b} was synthesized using the literature method for related compounds. The solvents C₆D₆ and thf-D₈ were degassed and dried over a Na/K alloy. Mass spectra were recorded on a Hp 5989A spectrometer (50–400 °C, 1.3 kV), ¹H NMR on IX-90Q (90 MHz) spectrometers. Elemental analyses were performed by the Analytical laboratory of the Shanghai Institute of Organic Chemistry.

Preparations

[Li(thf)₄][LnCl₂{(C₁₃H₈)CPh₂(C₅H₄)}]. *Complex 1*. A solution of (C₁₃H₈)CPh₂(C₅H₄)Li₂ (0.1 M, 42 ml in thf) was added dropwise to a stirred suspension of LuCl₃ (1.58 g, 5.6 mmol) in 20 ml thf at –78 °C under argon. The reaction mixture was then slowly warmed to room temperature and stirred for 2 d. The precipitate was filtered off. The filtrate was carefully concentrated to a slightly supersaturated solution and allowed to stand for several days at –20 °C to isolate yellow crystals of compound **1** (yield: 1.35 g, 63%) (Found: C, 57.40; H, 5.43. Calc. For C₃₁H₂₂Cl₂LiLu: C, 57.50; H, 3.40%). FT-Raman

(cm⁻¹): 3061m, 2986m, 2889m, 1595w, 1529m, 1436m, 1343s, 1327vs, 1002s, 667w, 438m and 286m.

Complex 2. A procedure similar to that for complex **1** was adopted for YCl₃ (1.40 g, 7.2 mmol), affording **2** as a yellow crystalline product (0.94 g, 41%) (Found: C, 65.52; H, 6.33. Calc. for C₄₇H₅₄Cl₂LiO₄Y: C, 66.38; H, 6.36%). FT-Raman (cm⁻¹): 3055m, 2888m, 2875m, 1530w, 1435m, 1326vs, 1003s, 668w, 438w and 286m.

[Li(thf)₄][Ln(BH₄)₂{(C₁₃H₈)CPh₂(C₅H₄)}]. *Complex 3*. To a suspension of [La(BH₄)₃(thf)₃] (0.85 g, 1.85 mmol) in 15 ml thf was added dropwise a solution of (C₁₃H₈)CPh₂(C₅H₄)Li₂ (0.05 M, 37 ml, in thf) with vigorous stirring at –78 °C under argon. The mixture was slowly warmed to room temperature and stirred for another 4 h. The precipitate was separated and resultant clear solution concentrated to 10 ml and slowly diluted with hexane. Orange crystals of complex **3** were formed after keeping overnight. (0.35 g, 22%) (Found: C, 64.77; H, 7.09. Calc. For C₄₇H₆₂B₂LaLiO₄: C, 65.70; H, 7.22%). EI mass spectrum (70 eV, 50–400 °C): *m/z* 764 (9.10, [M – LiBH₄ – thf]⁺) and 165 (100%). FT-Raman (cm⁻¹): 3064m, 3052m, 2984m, 2887m, 2413m, 2218m, 1585w, 1530w, 1436m, 1346m, 1326vs, 1004s, 667w, 437m and 289m.

Complex 4. Analogously to complex **3**, 0.89 g [Nd(BH₄)₃(thf)₃] (1.92 mmol) afforded **4** as green macrocrystals (0.79 g, 48%) (Found: C, 63.77; H, 6.88. Calc. For C₄₇H₆₂B₂LiNdO₄: C, 65.29; H, 7.18%). EI mass spectrum (70 eV, 50–400 °C): *m/z* 770 (12.03, [M – LiBH₄ – thf]⁺) and 165 (100%). FT-Raman (cm⁻¹): 3064m, 3052m, 2984m, 2887m, 2421m, 2221m, 1586w, 1530w, 1436m, 1347m, 1328vs, 1004s, 688w, 437m and 280m.

Crystallography

Single crystals were sealed in thin-walled glass capillaries under an atmosphere of argon. Crystal data and experimental details are given in Table 4. X-Ray diffraction data were collected at room temperature using the ω–2θ scan technique to a maximum 2θ value of 45.0°. The intensities of three representative reflections were measured after every 200. Over the course of data collection the standards decreased by 2.3%. A linear correction factor was applied to account for this. The data were corrected for Lorentz-polarization effects. The structure were solved by heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. All calculations were performed using TEXSAN.¹⁹

CCDC reference number 186/1592.

See <http://www.rsc.org/suppdata/dt/1999/3283/> for crystallographic files in .cif format.

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References

- 1 W. Kaminsky, K. Kulper, H. H. Brintzinger and F. R. P. Wild, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 507.
- 2 H. H. Brintzinger, D. Fishcher, R. Mulhaupt, B. Rieger and R. M. Waymouth, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1143; M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 1996, 255; A. Razavi and J. L. Atwood, *J. Organomet. Chem.*, 1993, **459**, 117; J. A. Ewen, R. L. Jones, A. Razavi and J. D. Ferrara, *J. Am. Chem. Soc.*, 1988, **110**, 6255.
- 3 E. B. Coughlin and J. E. Bercaw, *J. Am. Chem. Soc.*, 1992, **114**, 7606.
- 4 H. M. Christopher, L. S. Charlotte and T. J. Marks, *Organometallics*, 1996, **15**, 1765; P. W. Roesky, U. Denninger, C. L. Stern and T. J. Marks, *Organometallics*, 1997, **16**, 4486; D. Stern, M. Sabat and T. J. Marks, *J. Am. Chem. Soc.*, 1990, **112**, 9558.
- 5 C. Qian, G. Zou and J. Sun, *J. Chem. Soc., Dalton Trans.*, 1999, 519; 1998, 1607; *J. Organomet. Chem.*, 1998, **566**, 21; 1996, **525**, 53.
- 6 (a) M. F. Lappert, A. Singh, J. L. Atwood and W. E. Hunter, *J. Chem. Soc., Chem. Commun.*, 1983, 206; (b) D. Deng, X. Zheng, C. Qian, J. Sun and L. Zhang, *J. Organomet. Chem.*, 1994, **466**, 95; (c) T. J. Marks and G. W. Grynkewich, *Inorg. Chem.*, 1976, **15**, 1302.
- 7 T. Arliguie, M. Lance, M. Nierlich and M. Ephritikhine, *J. Chem. Soc., Dalton Trans.*, 1997, 2501.
- 8 S. M. Cendrowski-Guillaume, M. Nierlich, M. Lance and M. Ephritikhine, *Organometallics*, 1998, **17**, 786.
- 9 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
- 10 (a) P. L. Watson, J. F. Whitney and R. L. Harlow, *Inorg. Chem.*, 1981, 3271; (b) H. Schumann, I. Albrecht, J. Leobel, E. Hahn, B. Hossain and D. Van der Helm, *Organometallics*, 1986, **5**, 1296; (c) M. A. Giardello, V. P. Conticello, L. Brard and T. J. Marks, *J. Am. Chem. Soc.*, 1994, **116**, 10241; (d) M. D. Rausch, K. J. Moriarty, J. L. Atwood, J. A. Weeks, W. E. Hunter and H. G. Brittain, *Organometallics*, 1986, **5**, 1281.
- 11 M. F. Lappert, A. Singh, J. L. Atwood, W. E. Hunter and H. M. Zhang, *J. Chem. Soc., Chem. Commun.*, 1983, 69.
- 12 M. A. Giardello, M. Sabat, A. L. Rheingold and C. L. Stern, *J. Am. Chem. Soc.*, 1994, **116**, 10212.
- 13 R. E. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.
- 14 (a) A. Razavi and J. L. Atwood, *J. Organomet. Chem.*, 1993, **459**, 117; (b) A. Razavi and J. Ferrara, *J. Organomet. Chem.*, 1992, **435**, 299; (c) A. Razavi and J. L. Atwood, *J. Organomet. Chem.*, 1996, **520**, 115.
- 15 T. Arliguie, D. Baudry, J. C. Berthet, M. Ephritikhine, M. Nierlich, C. Lance and J. Viger, *J. Chem. Soc., Dalton Trans.*, 1992, 1019; P. C. Leverd, T. Arliguie, M. Lance, M. Nierlich, J. Vigner and M. Ephritikhine, *J. Chem. Soc., Dalton Trans.*, 1994, 501.
- 16 L. Mao, Q. Shen and S. Jin, *Polyhedron*, 1994, **13**, 1023.
- 17 J. H. Chapman and L. N. Owen, *J. Chem. Soc.*, 1950, 579.
- 18 U. Mirsaidov, T. G. Rotenberg and T. N. Dymova, *Chem. Abstr.*, 1976, 85, 136374; *Dokl. Akad. Nauk Tadzh. SSR*, 1976, **19**, 30.
- 19 TEXSAN, Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985.

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