

# (Diphenylphosphinoethyl)cyclopentadienyl complexes of yttrium and lutetium: synthesis and structure\*

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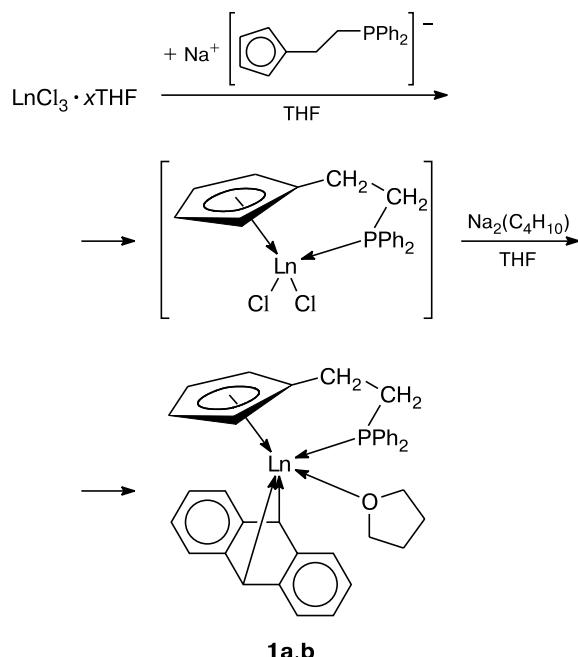
The reaction of  $\text{LnCl}_3 \cdot x\text{THF}$  with  $\text{Na}(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PPh}_2)$  followed by the *in situ* reaction with  $\text{Na}_2(\text{C}_{14}\text{H}_{10})$  afforded the  $(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PPh}_2)\text{Ln}(\text{C}_{14}\text{H}_{10})\text{L}$  complexes ( $\text{Ln} = \text{Y}$  or  $\text{Lu}$  and  $\text{L} = \text{THF}$  or  $\text{DME}$ ). The structure of  $(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PPh}_2)\text{Lu}(\text{C}_{14}\text{H}_{10})(\text{DME})$  was established by X-ray diffraction. In solution, there is an equilibrium between the complexes with the coordinated and uncoordinated phosphorus atom.

**Key words:** organolanthanide compounds, yttrium, lutetium, dianion, anthracene, substituted cyclopentadienyl anion.

Lanthanide complexes with substituted cyclopentadienyl anions are of considerable interest.<sup>1</sup> Earlier,<sup>2</sup> we have synthesized the lutetium complexes  $(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PPh}_2)_2\text{LuCl}$  by the reaction of  $\text{LuCl}_3 \cdot 3\text{THF}$  with  $\text{Na}(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PPh}_2)$ . However, an attempt to apply this method to the synthesis of the mono-substituted derivative failed due to the redistribution of the ligands in the monosubstituted complex, which gives rise to  $(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PPh}_2)_2\text{LuCl}$  and  $\text{LuCl}_3 \cdot 3\text{THF}$ . We succeeded in stabilizing the monocyclopentadienyl derivative by introducing the anthracene dianion as the ligand.

The mono(diphenylphosphinoethyl)cyclopentadienyl complexes  $(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PPh}_2)\text{Ln}(\text{C}_{14}\text{H}_{10})(\text{THF})$  (**1a,b**:  $\text{Ln} = \text{Y}$  (**a**) and  $\text{Lu}$  (**b**)) were synthesized by the successive addition of solutions of (diphenylphosphinoethyl)cyclopentadienylsodium and disodium anthracene to lanthanide chloride tetrahydrofuranates (Scheme 1). The complex with dimethoxyethane  $(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PPh}_2)\text{Lu}(\text{C}_{14}\text{H}_{10})(\text{DME})$  (**2**) was prepared

Scheme 1



\* Dedicated to Academician G. A. Abakumov on the occasion of his 70th birthday.

by recrystallization of complex **1b** from dimethoxyethane. The  $^1\text{H}$  NMR spectra of all complexes show a singlet at  $\delta$  3.50–3.75 corresponding to the signal for the H(9) and H(10) atoms of anthracene. The downfield shift of the signal compared to the signal of disodium anthracene ( $\delta$  1.55)<sup>3</sup> is indicative of the coordination of the anthracene dianion to the Lu<sup>3+</sup> cation.<sup>4</sup> The  $^{31}\text{P}$  NMR spectrum of the complex with THF (**1b**) shows an intense signal at  $\delta$  –12.0 and a weaker signal at  $\delta$  –18.5. The downfield shift of the signal with respect to the signal of the free ligand ( $\delta$  –15) gives evidence for the coordination of the phosphorus atom to the lanthanide atom.<sup>2</sup> Apparently, the complex with the coordinated phosphorus atom is characterized by the signal at  $\delta$  –12.0. The signal at  $\delta$  –18.5 is assigned to the complex with uncoordinated phosphorus, in which the vacant site in the coordination sphere is occupied by the second tetrahydrofuran molecule (Scheme 2). The spectrum of the complex with DME (**2**) also shows two signals at  $\delta$  –12.0 and –18.7, but the intensity ratio is inverse. Therefore, the complex with the uncoordinated phosphorus atom prevails in dimethoxyethane. This can be attributed to the stronger coordination of dimethoxyethane to the lanthanide atoms compared to tetrahydrofuran. To confirm this assumption, compound **2** was studied by X-ray diffraction. According to the X-ray diffraction data, the lutetium cation is coordinated by the cyclopentadienyl fragment of the (C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sup>–</sup> anion, the anthracene dianion, and one dimethoxyethane molecule (Fig. 1). The second DME molecule is included in the crystal lattice. There are no short contacts between the phosphine fragment of the (C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sup>–</sup> anion and the lutetium atom. The average Lu–C distance in the anthracene dianion is 2.417 Å; in the cyclopentadienyl fragment, these distances are in the range of 2.576–2.620 Å (Table 1). The Lu–C<sub>antr</sub> distances are shorter, on the average, by 0.03 Å, and the Lu–C<sub>Cp</sub> distances are longer, on the average, by 0.15 Å compared to the corresponding distances in (C<sub>5</sub>H<sub>5</sub>)Lu(C<sub>14</sub>H<sub>10</sub>)(THF)<sub>2</sub>.<sup>4</sup> Presumably, this may be partially associated with a weakening of the coordination of the cyclopentadienyl fragment due to the presence of the bulky CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> substituent.

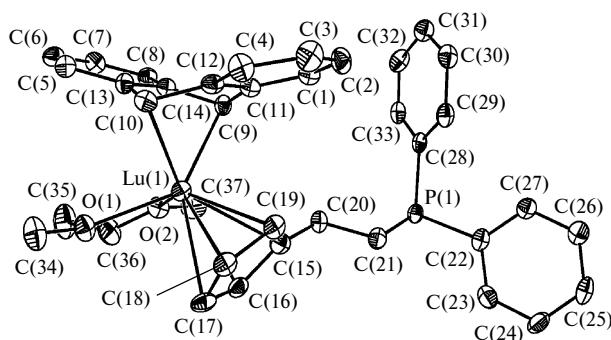
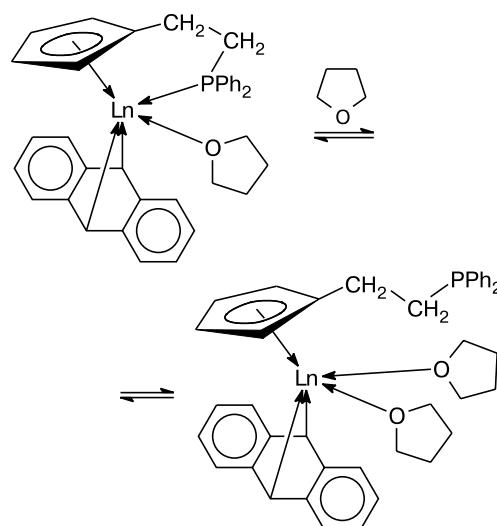


Fig. 1. Structure of complex **2** (hydrogen atoms are omitted).

Table 1. Selected geometric parameters of molecule **2**

Bond length	<i>d</i> /Å	Bond angle	$\omega$ /deg
Lu(1)–O(2)	2.316(5)	C(9)–Lu(1)–C(10)	70.5(2)
Lu(1)–O(1)	2.348(5)	C(11)–C(9)–C(14)	116.0(6)
Lu(1)–C(9)	2.399(6)	C(13)–C(10)–C(12)	115.7(6)
Lu(1)–C(10)	2.436(7)	C(12)–C(11)–C(9)	116.9(6)
Lu(1)–C(15)	2.620(7)	C(11)–C(12)–C(10)	117.7(6)
Lu(1)–C(16)	2.609(7)	C(14)–C(13)–C(10)	116.7(6)
Lu(1)–C(17)	2.599(7)	C(13)–C(14)–C(9)	118.1(6)
Lu(1)–C(18)	2.576(7)	O(2)–Lu(1)–O(1)	68.51(17)
Lu(1)–C(19)	2.579(7)	O(1)–Lu(1)–C(9)	132.0(2)
C(9)–C(11)	1.466(9)	O(2)–Lu(1)–C(9)	87.6(2)
C(9)–C(14)	1.470(9)	O(1)–Lu(1)–C(10)	90.8(2)
C(10)–C(13)	1.472(9)	O(2)–Lu(1)–C(10)	126.7(2)
C(10)–C(12)	1.480(9)		
C(11)–C(12)	1.438(9)		
C(13)–C(14)	1.436(9)		

Scheme 2



To summarize, we synthesized and characterized the (C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)Ln(C<sub>14</sub>H<sub>10</sub>)L complexes (Ln = Y or Lu and L = THF or DME). Studies of their reactivity and the dynamic processes in solutions of complexes **1a,b** and **2** are presently underway.

## Experimental

Since the compounds under study are highly sensitive to atmospheric oxygen and moisture, all synthetic operations were carried out in sealed evacuated apparatus. The solvents were purified according to known procedures.<sup>4</sup> Lanthanide chloride tetrahydrofuranates were synthesized according to a known procedure.<sup>5</sup> The  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra were recorded on Bruker WM-250, Bruker AM-300, and Bruker DRX-500 instruments. The metal content in samples was determined by the direct complexometric titration with Trilon B using the Xylenol Orange indicator.

**Sodium diphenylphosphinoethylcyclopentadienide.** The synthesis was performed according to the procedure described earlier for the preparation of  $KC_5H_4CH_2CH_2PPh_2$ (THF).<sup>6</sup> A mixture (5.2 mL) of diphenylphosphine (5.62 g, 30.2 mmol) and anhydrous THF (5 mL) was gradually added to a suspension of sodium hydride (1.45 g, 60 mmol) in anhydrous THF (50 mL) cooled to  $-10^{\circ}\text{C}$  under purified argon. The reaction mixture was stirred at room temperature for 1 day until evolution of hydrogen ceased. The resulting orange solution of sodium diphenylphosphide was decanted and cooled to  $0^{\circ}\text{C}$ . A solution of spiro[2,4]hepta-4,6-diene (3.33 g, 36.2 mmol) in anhydrous THF (20 mL) was added. The reaction mixture was stirred at room temperature for 2 h. The solvent was removed *in vacuo*. The product was washed with anhydrous petroleum ether and recrystallized from THF. The yield of  $NaC_5H_4CH_2CH_2PPh_2$ (THF) was 3.24 g (35.8%).  $^1\text{H}$  NMR (THF-d<sub>8</sub>),  $\delta$ : 2.40 (m, 2 H,  $\text{CH}_2\text{P}$ ); 2.75 (m, 2 H,  $\text{CH}_2\text{CH}_2\text{P}$ ); 5.66 (m, 4 H, H(2), H(3), H(4), H(5),  $C_5\text{H}_4$ ); 7.30 (m, 6 H,  $H_m$ ,  $H_p$ , Ph); 7.50 (m, 4 H,  $H_o$ , Ph).  $^{31}\text{P}$  NMR (THF-d<sub>8</sub>),  $\delta$ : -15.9 (s).

**(Diphenylphosphinoethyl)cyclopentadienyllutetium anthracenide tetrahydrofuranate (1b).** A 0.80 M solution of sodium diphenylphosphinoethylcyclopentadienide (1.64 mmol) in THF (20.5 mL) was added to a suspension of  $LuCl_3 \cdot 3\text{THF}$  (0.815 g, 1.64 mmol) in anhydrous THF (70 mL). The reaction mixture was stirred for 10 min. Then a solution of disodium anthracenide (70 mL), which was prepared according to a known procedure<sup>5</sup> from anthracene (0.292 g, 1.4 mmol), was added, and then the mixture was vigorously stirred for 6 h. The solution was separated from the precipitate and evaporated to dryness. The residue was washed with petroleum ether and recrystallized from THF. The yield of compound **1b** was 0.873 g (75.8%). Found (%): Lu, 24.51. Calculated (%): Lu, 24.93.  $^1\text{H}$  NMR (THF-d<sub>8</sub>),  $\delta$ : 2.53 (m, 2 H,  $\text{CH}_2\text{P}$ ); 2.58 (m, 2 H,  $\text{CH}_2\text{CH}_2\text{P}$ ); 3.50 (s, 2 H, H(9), H(10),  $C_14\text{H}_{10}$ ); 5.41 (m, 2 H, H(3), H(4),  $C_5\text{H}_4$ ); 5.69 (m, 2 H, H(2), H(5),  $C_5\text{H}_4$ ); 6.02 (dd, 4 H, H(1), H(4), H(5), H(8),  $C_{14}\text{H}_{10}$ ); 6.30 (dd, 4 H, H(2), H(3), H(6), H(7),  $C_{14}\text{H}_{10}$ ); 7.36 (m, 6 H,  $H_m$ ,  $H_p$ , Ph); 7.65 (m, 4 H,  $H_o$ , Ph).  $^{31}\text{P}$  NMR (THF-d<sub>8</sub>),  $\delta$ : 12.0 (br.s), -18.5 (br.s).

**(Diphenylphosphinoethyl)cyclopentadienylyttrium anthracenide tetrahydrofuranate (1a)** was synthesized analogously to the corresponding lutetium complex. Compound **1a** was obtained in a yield of 0.759 g (63.5%) from  $YCl_3 \cdot 2.7\text{THF}$  (0.754 g, 1.94 mmol). Found (%): Y, 22.73. Calculated (%): Y, 22.82.  $^1\text{H}$  NMR (THF-d<sub>8</sub>),  $\delta$ : 2.35 (m, 2 H,  $\text{CH}_2\text{P}$ ); 2.62 (m, 2 H,  $\text{CH}_2\text{CH}_2\text{P}$ ); 3.72 (s, 2 H, H(9), H(10),  $C_{14}\text{H}_{10}$ ); 5.61 (m, 2 H, H(3), H(4),  $C_5\text{H}_4$ ); 5.82 (m, 2 H, H(2), H(5),  $C_5\text{H}_4$ ); 6.10 (dd, 4 H, H(1), H(4), H(5), H(8),  $C_{14}\text{H}_{10}$ ); 6.32 (dd, 4 H, H(2), H(3), H(6), H(7),  $C_{14}\text{H}_{10}$ ); 7.30 (m, 6 H,  $H_m$ ,  $H_p$ , Ph); 7.48 (m, 4 H,  $H_o$ , Ph).

**(Diphenylphosphinoethyl)cyclopentadienyllutetium anthracenide dimethoxyethoxide (2)** was prepared by recrystallization of **1b** from dimethoxyethane. Found (%): Lu, 21.85. Calculated (%): Lu, 21.60.  $^1\text{H}$  NMR (THF-d<sub>8</sub>),  $\delta$ : 2.57 (m, 2 H,  $\text{CH}_2\text{P}$ ); 2.70 (m, 2 H,  $\text{CH}_2\text{CH}_2\text{P}$ ); 3.60 (s, 2 H, H(9); H(10),

$C_{14}\text{H}_{10}$ ); 5.42 (m, 2 H, H(3), H(4),  $C_5\text{H}_4$ ); 5.65 (m, 2 H, H(2), H(5),  $C_5\text{H}_4$ ); 6.02 (dd, 4 H, H(1), H(4), H(5), H(8),  $C_{14}\text{H}_{10}$ ); 6.31 (dd, 4 H, H(2), H(3), H(6), H(7),  $C_{14}\text{H}_{10}$ ); 7.33 (m, 6 H,  $H_m$ ,  $H_p$ , Ph); 7.50 (m, 4 H,  $H_o$ , Ph).  $^{31}\text{P}$  NMR (THF-d<sub>8</sub>),  $\delta$ : -12.0 (br.s), -18.7 (br.m).

**X-ray diffraction study of complex 2.** Crystals of **2** ( $C_{37}H_{38}\text{LuO}_2\text{P} \cdot C_4\text{H}_{10}\text{O}_2$ ) are monoclinic, at  $110\text{ K}$ , space group  $P2_1/c$ ,  $a = 13.969(7)\text{ \AA}$ ,  $b = 19.356(10)\text{ \AA}$ ,  $c = 14.648(6)\text{ \AA}$ ,  $\beta = 116.688(13)^{\circ}$ ,  $V = 3539(3)\text{ \AA}^3$ ,  $Z = 4$ ,  $d_{\text{calc}} = 1.522\text{ g cm}^{-3}$ ,  $\mu(\text{MoK}\alpha) = 28.76\text{ cm}^{-1}$ ,  $F(000) = 1648$ . The intensities of 23057 reflections were measured at  $110\text{ K}$  on a Smart 1000 CCD diffractometer ( $\lambda(\text{MoK}\alpha) = 0.71072\text{ \AA}$ ,  $\omega$ -scanning technique, the scan step was  $0.3^{\circ}$ ,  $2\theta < 54^{\circ}$ ), and 7718 independent reflections were used in the refinement. The experimental data were processed and merged and the absorption correction was applied with the use of the SAINT Plus and SADABS programs. The structure was solved by direct methods and the inspection of successive electron density maps. The hydrogen atoms were positioned geometrically. The refinement was carried out based on  $F^2_{hkl}$  with anisotropic displacement parameters for nonhydrogen atoms and isotropic displacement parameters for hydrogen atoms. The final  $R$  factors for **2** were  $R_1 = 0.0464$  (based on  $F_{hkl}$  for 4812 reflections with  $I > 2\sigma(I)$ ) and  $wR_2 = 0.1153$  (based  $F^2_{hkl}$  for all 7718 reflections), the number of variables was 428, GOOF = 1.001. The calculations were carried out with the use of the SHELXTL 5.10 program package.

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