Organometallic Chemistry

Reaction of cyclopentadienyllutetium anthracenide with azobenzene. Synthesis and molecular and crystal structure of the binuclear complex $[C_5H_5(THF)Lu(\mu\text{-}\eta^2:\eta^2\text{-}PhN{-}NPh)]_2(THF)_2$ and its dynamic behavior in solution

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The reaction of the cyclopentadienyllutetium anthracenide, $C_5H_5Lu(C_{14}H_{10})^{2-}(THF)_2$ (**1**), with azobenzene yielded the $[C_5H_5(THF)Lu(\mu\text{-}\eta^2:\eta^2\text{-}PhN{-}NPh)]_2(THF)_2$ (**2**) binuclear complex. The structure of the reaction product was established by X-ray structural analysis. The dynamic behavior of complex **2** in a THF-d_8 solution was studied by ^1H NMR spectroscopy in the temperature range of 265—330 K.

Key words: organolanthanide compounds; lutetium, azobenzene, complex, molecular and crystal structure.

One of the most interesting fields of the chemistry of organic derivatives of lanthanides involves redox reactions. Unfortunately, application of these reactions for organolanthanide compounds is restricted by derivatives of cerium, ytterbium, samarium, and europium, *i.e.*, by derivatives of 4f metals, which can form stable organometallic compounds in different oxidation states.[1]

Previously, anthracenide complexes of lutetium containing an anthracene dianion as a ligand, which is an efficient two-electron reducing agent, have been synthesized.[2,3] The use of these complexes make it possible to carry out redox reactions of organolanthanide compounds without changing the oxidation state of the metal atom.

In this work, we studied the reaction of cyclopentadienyllutetium anthracenide with azobenzene as well as the structure of the resulting new complex of lutetium with the azobenzene dianion and its dynamic behavior in solution.

Results and Discussion

We found that the anthracenide complex of lutetium, $(\eta^5\text{-}C_5H_5)Lu(C_{14}H_{10})^{2-}(THF)_2$ (**1**), reacts with azobenzene to form the binuclear organolutetium compound $[C_5H_5(THF)Lu(\mu\text{-}\eta^2:\eta^2\text{-}PhN{-}NPh)]_2(THF)_2$ (**2**). The structure of complex **2** was established by X-ray

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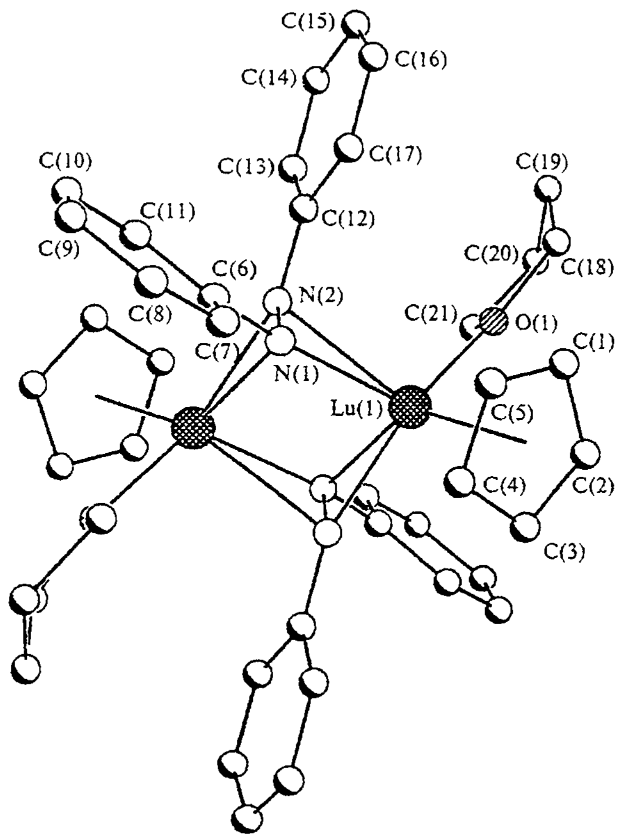
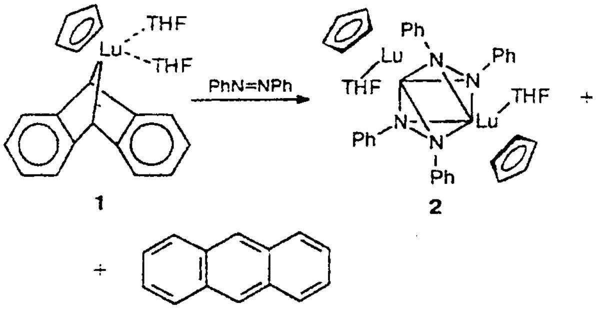


Fig. 1. Overall view of molecule **2** and the atomic numbering scheme.

structural analysis (Fig. 1, Tables 1 and 2). After addition of an equimolar amount of azobenzene to a solution of complex **1** in THF at ~20 °C, the color of the reaction mixture changed from dark-orange to greenish-yellow in several minutes, and a colorless precipitate formed. When the resulting mixture was heated to 55 °C and then cooled slowly to room temperature, colorless needle-like crystals of complex **2**, which are poorly soluble in THF at room temperature, were formed.



Previously, the complexes of Yb and Sm with the azobenzene dianions, $[C_5H_5(THF)Yb(\mu\text{-}\eta^2{:}\eta^2\text{-}PhN{-}NPh)]_2$

Table 1. Coordinates of nonhydrogen atoms (×10^4) and equivalent thermal parameters (U_{eq}×10^3) in the structure of **2**

Atom	x	y	z	U_{eq}/Å^2
Lu(1)	−554(1)	8528(1)	10415(1)	28(1)
O(1)	1491(9)	69655(13)	12267(10)	29(3)
N(1)	−949(10)	10390(10)	11176(7)	24(2)
N(2)	690(11)	10230(12)	11199(9)	39(2)
C(1)	−1928(17)	6634(15)	11488(12)	47(3)
C(2)	−1817(16)	6298(15)	10420(13)	45(3)
C(3)	−2695(14)	7316(14)	9751(12)	40(3)
C(4)	−3333(15)	8310(15)	10417(13)	42(3)
C(5)	−2911(15)	7820(15)	11460(12)	42(3)
C(6)	−1648(14)	11308(13)	11792(10)	28(3)
C(7)	−3183(14)	11348(14)	11946(11)	37(3)
C(8)	−3971(16)	12278(14)	12518(11)	41(3)
C(9)	−3281(16)	13211(14)	12963(12)	43(3)
C(10)	−1814(16)	13180(14)	12872(12)	42(3)
C(11)	−991(14)	12255(13)	12267(10)	42(3)
C(12)	1346(14)	9742(12)	12193(10)	26(3)
C(13)	2885(14)	9709(14)	12313(11)	35(3)
C(14)	3590(16)	9242(15)	13284(12)	45(4)
C(15)	2791(17)	8741(16)	14158(13)	54(4)
C(16)	1297(16)	8716(15)	14079(13)	50(4)
C(17)	581(15)	9184(14)	13138(11)	37(3)
C(18)	1566(15)	6023(14)	12041(11)	40(3)
C(19)	3199(16)	5820(16)	12314(13)	50(4)
C(20)	3948(16)	5850(15)	11198(13)	49(4)
C(21)	2953(15)	6986(15)	10506(12)	43(3)
O(1S)	1279(13)	3753(12)	4200(10)	74(4)
C(1S)	1889(19)	4281(20)	5095(14)	70(5)
C(2S)	3375(18)	3471(17)	5340(13)	59(4)
C(3S)	3134(19)	2106(17)	5025(12)	59(4)
C(4S)	2040(16)	2473(16)	4117(12)	48(4)

Table 2. Principal bond lengths (*d*) and bond angles (ω) in the structure of **2**

Bond	d/Å	Bond	d/Å
Lu(1)—N(1)	2.20(1)	Lu(1)—C(3)	2.63(1)
Lu(1)—N(1)*	2.58(1)	Lu(1)—C(4)	2.58(1)
Lu(1)—N(2)	2.48(1)	Lu(1)—C(5)	2.62(1)
Lu(1)—N(2)*	2.21(1)	N(1)—N(2)	1.49(1)
Lu(1)—O(1)	2.351(8)	N(1)—C(6)	1.37(2)
Lu(1)—C(1)	2.61(1)	N(2)—C(12)	1.39(2)
Lu(1)—C(2)	2.64(1)		

Angle	ω/deg	Angle	ω/deg
N(1)—Lu(1)—N(2)*	89.5(4)	N(1)*—Lu(1)—Lu(1)*	42.1(2)
N(1)—Lu(1)—N(2)	36.5(4)	C(6)—N(1)—N(2)	115.9(9)
N(1)—Lu(1)—N(1)*	94.1(3)	C(6)—N(1)—Lu(1)	158.1(8)
N(2)—Lu(1)—N(1)*	75.6(3)	N(2)—N(1)—Lu(1)	82.2(6)
N(2)*—Lu(1)—N(2)	91.9(4)	C(6)—N(1)—Lu(1)*	113.6(8)
N(1)—Lu(1)—O(1)	117.8(3)	N(2)—N(1)—Lu(1)*	58.8(5)
N(2)*—Lu(1)—O(1)	123.5(4)	Lu(1)—N(1)—Lu(1)*	85.9(3)
O(1)—Lu(1)—N(2)	86.6(3)	C(12)—N(2)—N(1)	116.6(10)
O(1)—Lu(1)—N(1)*	91.1(3)	C(12)—N(2)—Lu(1)*	153.8(8)
N(1)—Lu(1)—Lu(1)*	51.9(3)	N(1)—N(2)—Lu(1)*	86.1(6)
N(2)*—Lu(1)—Lu(1)*	49.4(3)	C(12)—N(2)—Lu(1)	113.7(8)
O(1)—Lu(1)—Lu(1)*	109.2(2)	N(1)—N(2)—Lu(1)	61.4(5)
N(2)—Lu(1)—Lu(1)*	42.5(3)	Lu(1)*—N(2)—Lu(1)	88.1(4)

* The atom is generated from the basis atom by the symmetry transformation $-x$, $-y + 2$, $-z + 2$.

(**3**) and $[C_5Me_5(THF)Sm(\mu\text{-}\eta^2\text{:}\eta^2\text{-}PhN{-}NPh)]_2(THF)_2$ (**4**), were obtained from biscyclopentadienyl derivatives of Ln^{II} (Cp_2Ln or C_5Me_5Ln, where Ln = Sm or Yb).[4] In this case, reduction of azobenzene to the dianion is caused by $Ln^{2+} \rightarrow Ln^{3+}$ oxidation accompanied by the reaction of redistribution of cyclopentadienyl ligands. In the case of cyclopentadienyllutetium anthracenide, the dianionic anthracenide ligand rather than lanthanide is the reducing agent. This makes it possible to carry out the redox reaction for the complex of lutetium, which belongs to lanthanides that can form stable compounds only in the oxidation state +3.

The Yb- and Sm-complexes with the azobenzene dianions, $Yb_4[\mu\text{-}\eta^2\text{:}\eta^2\text{-}(PhN{-}NPh)]_4(\mu_3\text{-}NPh)_2(THF)_4$ (**5**)[5] and $Sm_4[\mu\text{-}\eta^2\text{:}\eta^2\text{-}(PhN{-}NPh)]_4(\mu_3\text{-}NPh)_2(THF)_6$ (**6**),[6] are also known. Both compounds were synthesized by the reaction of naphthalene complexes of Ln^0 with PhN=NPh. In this case, reduction of azobenzene to its dianion, which was accompanied by reductive cleavage with the formation of the phenylimide anion, occurred due to oxidation $Ln^0 \rightarrow Ln^{3+}$.

When we carried out this work, the reaction of the naphthalenide complex of lutetium $C_5H_5Lu(C_{10}H_8)(THF)_2$ generated *in situ* with azobenzene was reported.[7] The reaction gave a product of composition $C_5H_5(THF)Lu(PhN{-}NPh)$, which was characterized only by IR spectroscopy and elemental analysis.

The results of X-ray structural analysis of single crystals of complex **2** demonstrated that compound $[C_5H_5(THF)Lu(\mu\text{-}\eta^2\text{:}\eta^2\text{-}PhN{-}NPh)]_2(THF)_2$ is isostructural to ytterbium complex **3** with the solvate toluene molecule.[4] The bond lengths and bond angles in the structure of **2** (see Table 2) are close to the analogous values for complexes **3** and **4**. The Lu atom in complex **2** is coordinated by the cyclopentadienyl ligand, two bridging azobenzene dianions, which bind two metal atoms, and the THF molecule. In the crystal of **2**, like those of compounds **3** and **4**, the Lu(1)...Lu(1′) distance is substantially shortened [3.279(2) Å] due to the attractive effect (the Sm...Sm′ and Yb...Yb′ distances in compounds **3** and **4** are 3.491(2) and 3.301(3) Å, respectively).

The Lu—C(Cp) bond lengths are in the range 2.58(1)—2.64(1) Å. The Lu—O(THF) distance is 2.351(8) Å. Both coordinated and solvate THF molecules adopt an envelope conformation. The N atoms of the azobenzene bridges are coplanar. The angle between the Lu(1)...Lu(1′) vector and the plane through the N atoms is 71.5°. The N—N bond length in compound **2** [1.49(1) Å] is close to the N—N distance in the 1,2-diphenylhydrazine molecule (1.39 Å)[8] and is substantially larger than the analogous value in azobenzene (1.24 Å).[9] It should be noted that the N—N bond length in **2** is only slightly larger compared to samarium complex **3** [1.44(1) Å] and is close to the corresponding values in complexes **4**, **5**, and **6** [1.470(6), 1.47(2), and 1.46(1) Å, respectively]. The C(6)—N(1)—N(2)—C(12) torsion angle is 63.2° (in complexes **3** and **4**, the corresponding angles are 76° and 45.7°, respectively), which also indicates that the N—N distance in the bridging ligand corresponds to a single bond.

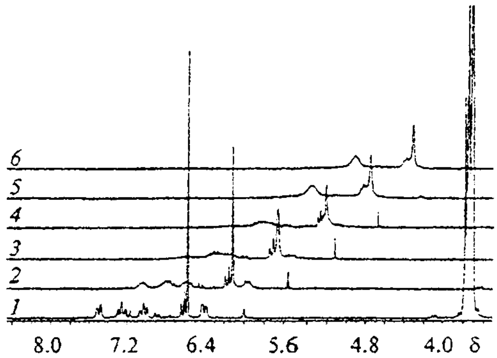


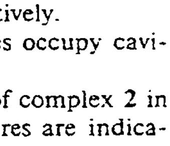
Fig. 2. Fragment of the ^1H NMR spectrum of complex **2** at 265 (*1*), 280 (*2*), 290 (*3*), 300 (*4*), 320 (*5*), and 330 K (*6*).

It should be noted that the Lu—N bond lengths in molecule **2**, like those in the ytterbium and samarium complexes, can be divided into two groups: 2.20(1) and 2.21(1); and 2.48(1) and 2.48(1) Å (see Table 2). According to the published data,[4] these values correspond to the Lu—N and Lu←:N bonds, respectively.

In the crystal, solvate THF molecules occupy cavities and do not form shortened contacts.

The ^1H NMR spectra of a solution of complex **2** in THF-d_8 recorded at different temperatures are indicative of the presence of dynamic effects (Fig. 2). The temperature dependence is most readily seen from the proton signals of the phenyl groups. It should be noted that all protons of the Ph ring are nonequivalent at low temperature. We failed to record the ^{13}C NMR spectra in the temperature range of 265—330 K with the aim of studying the dynamic effects due to the very low solubility of complex **2** in THF-d_8. For the same reason, we did not use two-dimensional ^{13}C—^1H correlation even at 330 K. We succeeded in measuring the $^{13}C\{^1H\}$ NMR spectrum only at 330 K at which a concentration of complex **2** in solution is sufficiently high.

Based on the values of the chemical shifts for the signals of the C_5H_5 groups in the ^{13}C NMR spectra of two known complexes of lutetium-containing dianionic organic ligands, $[(\eta^5\text{-}C_5H_5)_2Lu(C_{14}H_{10})^{2-}]Na$ and $(\eta^5\text{-}C_5H_5)Lu(C_{14}H_{10})^{2-}(THF)_2$ (δ 110.0 and 107.9, respectively),[2] we assigned the most intense signal at δ 112 to C atoms of the cyclopentadienyl ligand. At 265 K, the group of signals appeared instead of the signal at δ 118. Therefore, this signal corresponds to the carbon atoms C_B, C_E, C_C, and C_D.



The broadened weak signal at δ 157 corresponds to the C atom bonded to the nitrogen atom. The other signal at δ 131 corresponds to C_A (Table 3). We assigned the most intense signal in the ^1H NMR spectrum

Table 3. Parameters of the ^1H and ^{13}C NMR spectra of complex 2 (in THF-d_8)

Atom	δ ^{13}C [a]	Proton	δ ^1H [b]	$^3J_{HH}$/Hz [c]
C_A	130.7	H_A	6.59	J_{AB} = 7.7
C_B	118.2	H_B	7.24	J_{AC} = 7.3
C_C	118.2	H_C	7.00	J_{BE} = 8.5
C_D	118.2	H_D	7.57	J_{CD} = 7.9
C_E	118.2	H_E	6.39	
C(—N)	157.3			
C(Cp)	112.1	H_{Cp}	6.56	

[a] At 330 K.
[b] At 265 K.
[c] The average accuracy of measurements of J_{HH} is 0.1 Hz.

to protons of the cyclopentadienyl ligand. The average values of the vicinal spin-spin coupling constants of phenyl protons (see Table 3) were obtained based on complete analysis of the remaining spectrum (200 MHz) at 265 K using the CALM program.

Exchange processes do not cease at 265 K. This leads to broadening of the signals and results in a low accuracy of measurements of the J_{HH} constants. Even the spin-spin coupling constants $^4J_{HH}$ were not observed at this temperature. Apparently, the observed dynamic processes are caused by rotation of the Ph rings of the bridging azobenzene ligands about the C—N bond. The rotation is retarded as the temperature decreases, which is, apparently, favorable for an orientation of the phenyl rings such that all their protons are in different positions with respect to other ligands of the complex, which leads to their nonequivalence.

Previously, it has been demonstrated[4] that the reaction of bispentamethylcyclopentadienylsamarium with azobenzene can yield the complex either with the azobenzene radical anion or with the dianion depending on the ratio of the reagents. It is interesting that the reaction of compound **1** with azobenzene in THF taken in a molar ratio of 1 : 2 gave complex **2** rather than the lutetium complex with the radical anion of azobenzene, and an excess of PhN=NPh did not enter into the reaction. We obtained analogous results in the reaction of compound **1** with azobenzene in toluene. Apparently, this is attributable to the higher stability of organolanthanide complexes with dianionic ligands, which exhibit higher polarizability compared to radical-anionic ligands. Previously an analogous tendency was observed for anthracenide complexes of lutetium.[3] It should be noted that the difference in the stability of the radical-anionic and dianionic complexes should be more pronounced in the case of the $[(C_5H_5)Lu]^{2+}$ dication, which exhibits stronger polarizing effect, than in the case of the $[(C_5Me_5)_2Sm]^+$ cation.

Experimental

All operations associated with the synthesis and preparation of samples for physicochemical studies were carried out in sealed evacuated vessels of the Schlenk type. Solvents were prepared according to procedures reported previously.[2] The ^1H and ^{13}C NMR spectra of a solution of complex **2** in THF-d_8 were recorded on Bruker WM 250 (62.9 MHz for ^{13}C) and Bruker AC 200 spectrometers in a sealed evacuated tube. Signals were calibrated using the signals of the solvent: δ 1.8 and 3.7 for ^1H and δ 26.7 and 68.6 for ^{13}C.

Complex **1** was prepared by a new method, which made it possible to synthesize **1** from $LuCl_3 \cdot 3THF$ in one stage. Disodium anthracene was synthesized according to a procedure reported previously.[2]

η^5-Cyclopentadienyl-η^2-anthracenidelutetium(bistetrahydrofuranate) (1). Cyclopentadienylpotassium was prepared by dissolving metallic K (0.351 g, 9 mmol) in a solution of freshly distilled cyclopentadiene (2.380 g, 36 mmol, a fourfold excess) in anhydrous THF (30 mL). After complete dissolution, THF and an excess of cyclopentadiene were removed *in vacuo*. The residue was dried in dynamic vacuum ($2 \cdot 10^{-5}$ Torr) at -20 °C for 30 min. Then THF (30 mL) was condensed in the reaction vessel, and $LuCl_3 \cdot 3THF$ (4.533 g, 9.1 mmol) was added with intense stirring. The reaction mixture was stirred for 3 h. Then a solution of disodium anthracene (50 mL, 9 mmol), which was obtained from anthracene (1.6 g), was added. The reaction mixture immediately developed the dark-orange color. The mixture was stirred for 10 h. The solution was separated from the residue and slowly (12 h) evaporated *in vacuo*. The crystalline precipitate that formed was twice washed with a minimum amount of THF and dried *in vacuo* for 40 min. Complex **1** was obtained as red-orange crystals in a yield of 3.934 g (77%).

η^5-Cyclopentadienyl-μ-η^2:η^2-(1,2-diphenyl)hydrazidolutetium (2). A solution of azobenzene (0.305 g, 1.67 mmol) in anhydrous THF (5 mL) was added slowly with stirring to a solution of complex **1** (0.940 g, 1.67 mmol) in anhydrous THF (80 mL). The mixture was stirred for 5 min, and the color of the solution changed from red-orange to greenish-yellow. The reaction mixture was stirred for 10 h and then warmed to 55 °C, which was accompanied by dissolution of the residue. The solution was cooled slowly to -20 °C. Transparent needle-like crystals were precipitated. The solution was decanted. The crystalline precipitate was washed with THF (2×5 mL) and dried *in vacuo* at -20 °C. Colorless needle-like crystals of complex **2** were obtained in a yield of 0.263 g (30%). Found (%): Lu, 29.2. $C_{50}H_{62}N_4O_4Lu_2$. Calculated (%): Lu, 31.3.

The lutetium content was determined by direct chelatometric titration using xylenol Orange as the indicator. Single crystals of **2** suitable for X-ray structural analysis were prepared by a procedure reported previously,[3] which excluded exposure to atmospheric oxygen and moisture.

X-ray structural analysis of the $[C_5H_5(THF)Lu(\mu$-η^2:η^2-PhN—$NPh]_2(THF)_2$ complex (2) was carried out on an automated four-circle Syntex $P2_1$ diffractometer (Mo-Kα radiation, graphite monochromator, 2θ/θ scanning technique, 2θ < 45°). Crystals of compound **2** ($C_{50}H_{62}Lu_2N_4O_4$) are triclinic, at −80 °C, a = 9.150(3) Å, b = 10.043(3) Å, c = 12.448(4) Å, α = 82.02(3)°, β = 88.79(3)°, γ = 82.95(3)°, V = 1124.3(7) Å^3, Z = 1, space group $P\bar{1}$, M = 1132.98, d_{calc} = 1.673 g cm^{-3}, F(000) = 564, μ = 4.414 mm^{-1}. Of a total of 3565 measured reflections, 2457 independent reflections with $I > \sigma^2(I)$ were used in calculations. The structure was solved by direct methods and refined anisotropically by the full-matrix least-squares method based on F. Absorption correction was applied using the DIFABS program.[10]

The positions of hydrogen atoms were calculated geometrically and refined using the rigid-body model. The final values of the R factors were as follows: $R = 0.0454$, $R_w = 0.054$, GOF = 0.937. All calculations were carried out on an IBM PC/AT computer using the SHELXTL PLUS program package. The coordinates of nonhydrogen atoms are given in Table 1.

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