Interaction of dicyclopentadienyl chloride complexes of yttrium and lutetium with sodium naphthalenide

A. V. Protchenko,[a] *E. A. Fedorova,*[a] *M. N. Bochkarev,*[a]* *H. Schumann,*[b] *J. Loebel,*[b] *and G. Kociok-Köhn*[b]

[a]*Institute of Organometallic Chemistry, Russian Academy of Sciences,*
49 ul. Tropinina, 603600 Nizhnii Novgorod, Russian Federation.
Fax: +7 (831) 235 6480
[b]*Technische Universität Berlin, Institute für anorganische und analitische Chemie,*
Str. 17 Juni 135, Secr.C2 D-10623 Berlin.
Fax: (004930) 314 221 68

The reaction of Cp_2LuCl with sodium naphthalenide gives an anionic hydride complex $[(Cp_2LuH)_3H][Na(THF)_6]$ (**1**) and complex $Cp_2Lu(2\text{-}C_{10}H_7)(THF)$ (**2**) containing a σ-bonded naphthyl ligand. The structure of **1** was confirmed by X-ray analysis. When Cp_2YCl is used as the starting material, Cp_3Y and an anionic hydride complex also containing a σ-naphthyl ligand are formed. A reaction mechanism involving the formation of an unstable complex $[(Cp_2Ln^+)_2(C_{10}H^2{}_8{}^-)]$ (**4**) and its fragmentation into hydride and σ-naphthyl species is proposed.

Key words: dicyclopentadienyl complexes of yttrium and lutetium, hydride, σ-naphthyl ligand.

In our previous study of complexes of rare-earth elements with aromatic ligands, we established that the interaction of a monocyclopentadienyl lutetium complex $CpLuCl_2$ with sodium naphthalenide in DME results in the formation of a compound containing the $2\eta^1{:}\eta^2$-bonded to lutetium naphthalene ligand, $CpLuC_{10}H_8(DME)$ (**3**).[1,2] This complex differs from the complex $[CpV(C_{10}H_8)YbCp(THF)]_n$ in which naphthalene is η^2-bonded.[3] To elucidate the influence of coordinational surroundings of the Ln atom on the nature of its bond with naphthalene, we studied similar reactions of sodium naphthalenide with dicyclopentadienyl complexes of lutetium and yttrium, Cp_2LnCl.

Results and Discussion

The addition of an equimolar amount of $C_{10}H_8Na$ to a Cp_2LuCl solution in THF results in the disappearance of the green color of the naphthalene radical anion, and the reaction mixture becomes deep red. This color changes to light brown in 30 min at room temperature. After removal of the precipitated NaCl and the addition of hexane, a lutetium hydride complex $[(Cp_2LuH)_3H][Na(THF)_6]$ (**1**) precipitates from the solution in the form of fine lemon-yellow crystals in a yield of ~30 %. Similar three-nuclear hydrides of lanthanides were obtained for the first time by Evans[4] and Schumann.[5] The further addition of hexane to the mother liquor results in the isolation of naphthyl complex $Cp_2Lu(2\text{-}C_{10}H_7)(THF)$ (**2**) in a 21 % yield in the form of slowly crystallized oil.

Complex **2** differs considerably in its properties from the previously obtained complex **3**: complex **2** is not colored, and there are no intense bands at 1100—1600 cm^{-1}, which are characteristic of the naphthalene complexes of Lu[2] and Yb.[6] The hydrolysis of **2** results in naphthalene formation (complex **3** gives dihydronaphthalene under the same conditions) and, finally, treatment of a solution of **2** in THF with CO_2 results in the formation of 2-naphthoic acid after acidification. The data obtained show that the naphthalene ligand exists as a σ-bonded 2-naphthyl anion.

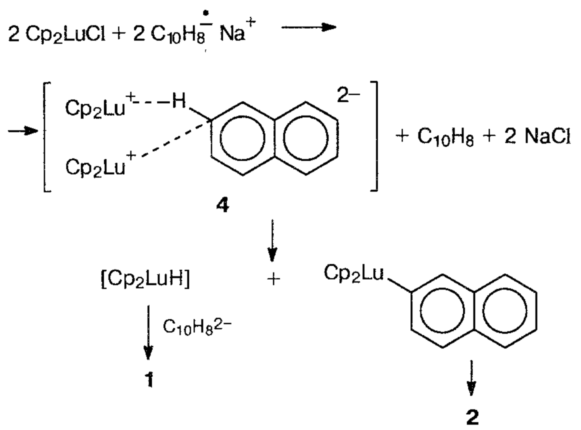
The formation of naphthyl complex **2** instead of the expected naphthalene complex similar to **3** can be the result of the greater volume of the Cp_2Lu particle than that of CpLu. Due to this fact, the initially formed complex of the naphthalene dianion **4** (evidenced by the red color of the solution after mixing of the reagents, which is typical of $C_{10}H_8{}^{2-}$) is sterically strained. In this intermediate, the C—H bond is cleaved to form hydride and naphthyl fragments (Scheme 1). The detachment of the hydride ion from the β-position agrees well with a great negative charge at the β-atom of hydrogen of the naphthalene dianion.[7]

The bulky anion $C_{10}H^2{}_8{}^-$ (which is formed in the disproportionation of two radical anions of naphthalene) prevents the formation of stable dimeric hydride $[Cp_2LuH(THF)]_2$ (**5**), converting the dimer to the three-nuclear complex **1**, similarly to the *tert*-butyl anion.[4] Complex **1** was previously obtained by the reaction of Cp_2LuCl with Na in THF.[5] However, its structure was not determined because of the fast desolvation of the

---

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 20—20, November, 1994.

Scheme 1



crystals at room temperature. Therefore, in this case all procedures of selecting crystals from the mother liquor and placing them in a diffractometer were performed at a lowered temperature in a stream of cooled nitrogen.

According to the data of X-ray analysis, compound **1** consists of separate Na(THF)$^{+}_{6}$ cations and $(Cp_2LuH)_3H^-$ anions. In the three-nuclear anion, each Lu atom is linked with two Cp-rings, two μ_2-H-, and one μ_3-H-atoms (Fig. 1). Hydride atoms of hydrogen are slightly shifted from the plane of Lu atoms (the deviation does not exceed 0.2 Å). The lengths of the Lu(2)—H(2) and Lu(2)—H(3) bonds (2.043 Å and 2.131 Å) are very close to the lengths of the Lu—H bonds in binuclear hydride **5** (1.98 Å and 2.13 Å);[5] the H(2)—Lu(2)—H(3) angle (60.3°) also slightly differs (62° in **5**). The enlarged distances of Lu(1)—H(2) (2.212 Å), Lu(1)—H(1) (2.641 Å), and Lu(2)—H(1) (2.758 Å) make it possible to consider compound **1** the dimer $[Cp_2LuH]_2$ to which the $[Cp_2LuH_2]^-$ anion is attached by three H-bridges. The values of main interatomic distances and valence angles in **1** are listed in Table 1.

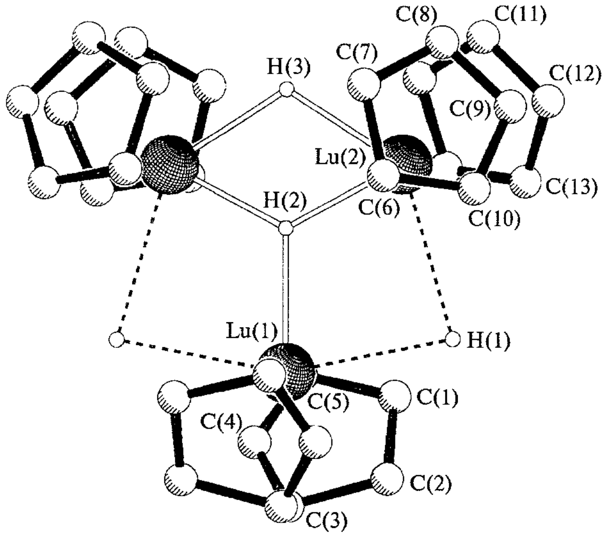


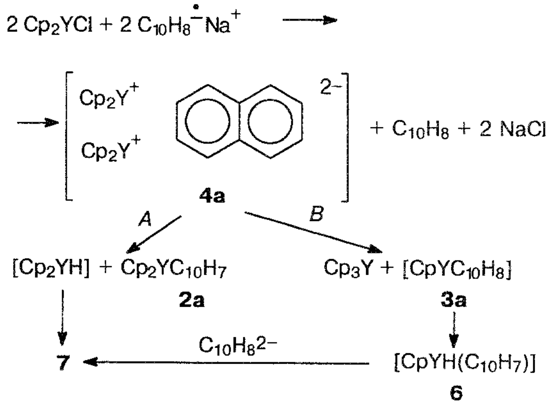
Fig. 1. Structure of the anionic fragment in compound **1**.

Table 1. Major bond lengths (*d*) and valence angles (ω) in the anion of complex **1**

Bond	*d*/Å	Angle	ω/deg
Lu(1)—H(1)	2.641	Lu(2)—H(2)—Lu(2')	123.9
Lu(1)—H(2)	2.212	Lu(2)—H(3)—Lu(2')	115.5
Lu(2)—H(1)	2.758	H(3)—Lu(2)—H(2)	60.3
Lu(2)—H(2)	2.043	H(3)—Lu(2)—H(1)	138.9
Lu(2)—H(3)	2.131		
Lu(1)· · ·Lu(2)	3.621		
Lu(2)· · ·Lu(2')	3.606		

For analogous reaction with Cp_2YCl, the green color of the naphthalene radical anion also disappears and continuously transforms from violet (caused by the complex of naphthalene dianion **4a**) to reddish-brown; however, $Cp_3Y(THF)$ was isolated in a ~30 % yield after the addition of hexane instead of the expected hydride complex, analogous to **1**. The yield of the complex with the σ-naphthyl ligand is negligible, and the major portion of the yttrium-containing product is a resin-like mixture of naphthyl and hydride complexes, which cannot be separated. The use of another solvent (DME) results in a decrease in the yield of Cp_3Y and an increase in the yield of colorless crystals of product **7** to 36 %. According to the results of complexometry, alkalimetry, and fragment analysis, the composition of these crystals corresponds to the formula $Cp_5Y_3H_4(C_{10}H_7)Na(DME)_4$. This compound can be considered the yttrium analog of complex **1** in which one Cp-ligand is displaced by the naphthyl ligand and six monodentate THF molecules are displaced by three bidentate DME ligands, *i.e.*, formula **7** can be presented as $\{(Cp_2YH)_2[CpYH(C_{10}H_7)(DME)]H\}^-[Na(DME)_3]^+$. Unlike Cp_2LuCl, two routes of decomposition are probable for the initially formed complex **4a** in the reaction of Cp_2YCl and sodium naphthalenide (Scheme 2): route

Scheme 2



A is similar to that considered in the case of Lu, and route *B* is the migration of the Cp-ligand from one Y atom to another to form Cp_3Y and unstable $CpYC_{10}H_8$ (**3a**) in which, unlike more stable Lu-analog **3**, the insertion of Y at the C—H bond of naphthalene easily occurs to form hydride naphthyl complex **6**. The interaction of the latter with [Cp_2YH] in the presence of $C_{10}H^2{}_8{}^-$ produces compound **7**. The extent to which the reaction proceeds *via* route *A* or *B* and, hence, the ratio of the products, depends on the reaction conditions.

The relevance of route *B* is confirmed by the formation of Cp_3Y and by lability of complex **3a**. The directed synthesis of this compound by the reaction of $CpYCl_2$ with sodium naphthalenide has shown that it can be isolated in the fast treatment of the reaction mixture at 0 °C but completely decomposes at room temperature within two hours.

$$CpYCl_2 + 2\ C_{10}H_8^{\cdot -} \xrightarrow{DME}$$

$$\longrightarrow CpYC_{10}H_8(DME) + 2\ NaCl + C_{10}H_8$$

3a

In this reaction the color of the solution changes from violet to light brown. The hydrolysis of the solution formed results in liberation of hydrogen and naphthalene (the hydrolysis of **3a** gives the mixture of 1,2- and 1,4-dihydronaphthalenes), which suggests the transformation of **3a** to hydride naphthyl complex **6**.

This distinction in the behavior of complexes of Lu and Y can be explained by the greater ionic radius of the latter (0.900 Å for Y^{3+} and 0.861 Å for Lu^{3+}), which results in a greater lability of the Cp_2Ln group. It should be mentioned that it is the distinction in ionic radii of Ln^{3+} that explains why compounds of the $CpLnCl_2$ and Cp_2LnCl types (where Ln are lanthanides of the beginning of the series) are not easily accessible.[8]

Thus, it is established that dicyclopentadienyl complexes of Lu and Y do not form stable compounds with the naphthalene dianion, as it was observed in the case of monocyclopentadienyl derivatives, which is explained by the increase in the steric strain of the Ln atom when the second Cp-ligand is introduced.

Stable reaction products are formed after cleavage of the C—H bond of the $C_{10}H^2{}_8{}^-$ dianion to form hydride and naphthyl complexes. In the case of Y, the reaction is complicated by the disproportionation of Cp-ligands, which results in the formation of the complex containing both hydride and naphthyl ligands.

Experimental

All reactions were performed *in vacuo* using the standard Schlenk technology. Solvents were distilled from benzophenone ketyl prior to use. Lu and Y were determined by complexometry. Volatile organic products were analyzed by GLC on a Tsvet-104 chromatograph (a column 3 m in length, 10 % of PEG-20M on Chromaton N-AW). IR spectra were recorded on a Perkin-Elmer-577 instrument.

Reaction of Cp_2LuCl with $C_{10}H_8Na$. A solution obtained from 0.172 g (7.50 mmol) of Na and 1.00 g (7.80 mmol) of naphthalene in 10 mL of THF was added to a solution of 2.067 g (7.50 mmol) of Cp_2LuCl in 15 mL of THF. The solution was centrifuged after 30 min (the residue contained 0.305 g (60 %) of NaCl) and concentrated *in vacuo* to half of the volume. Hexane (5 mL) was injected by condensation into the solution cooled to −15 °C. A lemon-yellow fine-crystalline residue was washed with small portions of the THF—hexane mixture by decantation and dried *in vacuo*. Complex **1** (1.475 g, 26 %) was isolated, whose IR spectrum coincides with that described previously.[5] The crystals suitable for X-ray analysis were prepared by slow cooling of the solution of **1** in the THF—hexane mixture (2 : 1) saturated at ~20 °C. After separation of **1**, another 5 mL of hexane were added to the mother liquor to yield oily light brown droplets, which slowly crystallized to form colorless crystals of **2**. After washing with hexane and drying *in vacuo*, the yield was 0.760 g (21 %). M. p. 130—134 °C (decomp.). The hydrolysis of **2** in toluene gives (%): C_5H_6, 23.0; C_4H_8O, 12.0; $C_{10}H_8$, 24.9; Lu, 35.1. $(C_5H_5)_2Lu(C_{10}H_7)(C_4H_8O)$. Calculated (%): C_5H_6, 25.7; C_4H_8O, 14.3; $C_{10}H_8$, 25.3; Lu, 34.7. IR spectrum (Vaseline oil), ν/cm^{-1}: 1020, 1008, 855, 812, 780, 740, 720, 545, 475.

Carboxylation of 2. Complex **2** (0.251 g, 0.498 mmol) dissolved in 5 mL of THF was treated with an excess of CO_2 and then with H_2O. After removal of THF and volatiles *in vacuo*, the residue was decomposed by dilute HCl and twice extracted with ether. Evaporation of ether and recrystallization from an aqueous EtOH gave 0.079 r (90 %) of 2-naphthoic acid with m. p. 186—187 °C.

The reaction of Cp_2YCl with $C_{10}H_8Na$. The solution obtained from 0.105 g (4.56 mmol) of Na and 0.640 g (5.00 mmol) of naphthalene in 10 mL of DME was added to the suspension of 1.143 g (4.50 mmol) of Cp_2YCl in 10 mL of DME. After two hours the solutions was centrifuged to remove the precipitated NaCl, concentrated *in vacuo* to 1/3 of the volume, and cooled to −15 °C. Colorless crystals (0.118 g, 8 %) of $Cp_3Y(DME)_{0.5}$ were isolated, whose m. p. after sublimation *in vacuo* was 288—292 °C, which corresponds to the data for Cp_3Y. The addition of hexane to the mother liquor resulted in the precipitation of colorless needle-shaped crystals (the first portion was contaminated with crystals of $Cp_3Y(DME)_{0.5}$). After washing with hexane and drying *in vacuo*, 0.545 g (34 %) of complex **7** were obtained. The substance begins to decompose with liberation of DME and partial melting at 102—105 °C and then melts with decomposition at 186—190 °C (Cp_3Y and $C_{10}H_8$ sublimate from the melt). The hydrolysis of **7** in toluene gives (the content of Na was determined by the amount of the liberated alkali) (%): C_5H_6, 26.5; $C_4H_{10}O_2$, 19.8; $C_{10}H_8$, 11.9; Y, 24.9; Na, 1.8. $(C_5H_5)_5Y_3H_4(C_{10}H_7)(C_4H_{10}O_2)_4Na$. Calculated (%): C_5H_6, 29.4; $C_4H_{10}O_2$, 32.6; $C_{10}H_8$, 11.5; Y, 24.1; Na, 2.1. The hydrolysis of 0.151 g (0.42 mmol) of **7** resulted in the liberation of 11.4 mL (0.51 mmol) of H_2, which corresponds to the ratio of Y : H = 1 : 1.2. IR spectrum (Vaseline oil), ν/cm^{-1}: 1230, 1215 (broad), 1120, 1075, 1005, 905, 855, 830, 775, 730, 665. The carboxylation of 0.186 g (0.168 mmol) of **7** performed in a manner described for complex **2** resulted in 0.012 g (55 %) of $C_{10}H_8$ and 0.008 g (28 %) of 2-$C_{10}H_7COOH$.

The reaction of $CpYCl_2$ with $C_{10}H_8Na$. The solution obtained from 0.052 g (2.27 mmol) of Na and 0.360 g (2.81 mmol) of $C_{10}H_8$ in 5 mL of DME was added at 0 °C to the suspension of 0.500 g (1.13 mmol) of $CpYCl_2(THF)_3$ in 5 mL of DME. The reaction mixture was stirred until the initial compound of Y was completely dissolved, then it was centrifuged and decanted from the precipitate of NaCl. Half the solution was concentrated *in vacuo* to the minimum volume and cooled to −15 °C. The precipitated crystals (black tetragonal pyramids) were washed with hexane and dried *in vacuo*. Complex **3a** (0.056 g, 27 %) was obtained, m.p. 117—119 °C (decomp.). The hydrolysis of **3a** gives (%): C_5H_6, 16.3; $C_4H_{10}O_2$, 7.9; $C_{10}H_{10}$, 32.5; Y, 24.2. $(C_5H_5)Y(C_{10}H_8)(C_4H_{10}O_2)$. Calculated (%): C_5H_6, 17.5; $C_4H_{10}O_2$, 34.4; $C_{10}H_{10}$, 34.4; Y, 23.9. IR spectrum (Vaseline oil), ν/cm^{-1}: 1305, 1245, 1225, 1175, 1120, 1088, 1050, 1005, 860, 775, 753, 710, 695, 475. The second portion of the solution was stored for 2 h at 20 °C and evaporated *in vacuo*; the resin-like product was washed with hexane until free $C_{10}H_8$ was completely removed, dissolved in toluene, and hydrolyzed. Hydrogen liberated, and CpH, DME, and $C_{10}H_8$ and $C_{10}H_{10}$ in the ratio of 5 : 1 were found in the organic phase.

X-ray studies. Crystal **1** (0.58×0.15×0.29 mm^3) was selected from the solution in a flow of cooled nitrogen using a modified instrument similar to that described in literature.[9] Parameters of the cell and intensities of 4094 independent reflexes were measured on a Enraf-Nonius CAD 4 four-circular diffractometer at −137 °C (irradiation Mo$K\alpha$ ($1/\lambda$ = 0.71069 Å), ω — 2θ-scanning in the range of $2° < 2\theta < 50°$). Crystals of **1** are monoclinic, a = 10.923(5) Å, b = 9.851(4) Å, c = 25.138(9) Å, β = 90.173°, V = 2705(2) Å^3; d_{cal} = 1.688 g cm^{-3}; Z = 2; spatial group $P2/c$. The absorption in the crystal (μ_{cal} = 55.6 cm^{-1}) was taken into account by the DIFABS program. The structure was solved using a combination of direct methods and a differential synthesis (SHELX-86 and SHELX-76 programs) and refined by a full-matrix least-square method with anisotropic parameters of thermal vibrations for nonhydrogen atoms. Hydride H-atoms were elucidated from the differential synthesis, while H-atoms of THF ligands were placed at the calculated positions with d(C—H) = 1.08 Å and U_{iso} = 0.06 Å^2. Due to disordering of all the Cp-rings in a molecule, coordinates of H-atoms of these ligands were not calculated. The final refinement using 4030 independent reflexes with $F_o > 4\sigma(F_o)$ and with the weighting scheme $w = 2.71/(\sigma^2(F_o) + 0.000805\ F_o^2)$ resulted in the values of the divergence factor of R = 0.046 (R_w = 0.063).

References

1. M. N. Bochkarev, A. V. Protchenko, L. N. Zakharov, and Yu. T. Struchkov, *Metalloorg. Chem.,*, 1992, **5**, 716, [*Organometall. Chem. USSR*, 1992, **5** (Engl. Transl.)].
2. . V. Protchenko, L. N. Zakharov, M. N. Bochkarev, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1993, **447**, 209.
3. . N. Bochkarev, I. L. Fedushkin, V. K. Cherkasov, C. I. Nevodchikov, H. Schumann, and F. H. Gorlitz, *Inorg. Chim. Acta,* 1992, **201**, 69.
4. W. J. Evans, J. H. Meadows, and T. P. Hanusa, *J. Am. Chem. Soc.*, 1984, **104**, 4454.
5. H. Schumann, W. Genthe, E. Hahn, M. B. Hossain, and D. van der Helm, *J. Organomet. Chem.*, 1986, **299**, 67.
6. M. N. Bochkarev, A. A. Trifonov, E. A. Fedorova, N. S. Emelyanova, T. A. Basalgina, G. S. Kalinina, and G. A. Razuvaev, *J. Organomet. Chem.*, 1989, **372**, 217.
7. J. J. Brooks, W. Rhine, and G. D. Stucky, *J. Am. Chem. Soc.*, 1972, **94**, 7346.
8. M. N. Bochkarev, G. S. Kalinina, L. N. Zakharov, and S. Ya. Khorshev, *Organicheskie proizvodnye redkozemel'nykh elementov* [*Organic Derivatives of Rare-Earth Elements*], Nauka, Moscow, 1989, 89 (in Russian).
9. M. Veith and H. Bärninghausen, *Acta Crystallogr.*, 1974, **B30**, 1806.

Received June 28, 1994