Neodymium(III) and dysprosium(III) naphthalene hydride complexes

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Reactions of neodymium and dysprosium diiodide hydrides LnI_2H with lithium naphthalenide in THF furnished heterobimetallic naphthalene hydride clusters $(C_{10}H_8)_3Ln_5Li_5H_{14}$ (Ln = Nd, Dy). Treatment of the latter with hexamethyldisilazane in THF leads to the removal of lithium in the form of $LiN(SiMe_3)_2$ and the formation of compounds of the composition $(C_{10}H_8)_3Ln_5H_9$ (Ln = Nd, Dy). All the clusters obtained were isolated as black pyrophoric powders insoluble in THF and other organic solvents. Reactions of $(C_{10}H_8)_3Nd_5Li_5H_{14}$ and $(C_{10}H_8)_3Nd_5H_9$ with cyclopentadiene lead to $Cp_3Nd(THF)$.

Key words: dysprosium, neodymium, diiodides, hydrides, naphthalenides.

Organic compounds of rare earth metals containing a hydride group Ln—H always attracted attention of researchers due to their high synthetic and catalytic potential.[1] However, this class of compounds is not characterized by a variety of organic ligands at the Ln atom, that is to a considerable extent due to the lability of the Ln—H bond, interfering with the synthesis of such complexes. At present, only two types of ligands are virtually known for them: cyclopentadienyl (unsubstituted and with various substituents)[2] and diimine.[3] Of no less interest are lanthanide arene complexes due to the specific features of their electronic structure and high reactivity.[4] The Sm^{II}, Eu^{II}, and Yb^{II} naphthalene complexes[5] occupy a special place in this group of organolanthanides, since they are relatively available and possess exceptionally high reducing properties.[6] It was a challenge to combine both functions, the hydride (Ln—H) and the arene (Ln—naphthalene), in one molecule. We used diiodide hydrides NdI_2H and DyI_2H as the starting reagents, since they contain, from the one hand, a Ln—H group and, from the other hand, iodine anions disposed to nucleophilic substitution. Recently,[7] it was found that the indicated iodide hydrides can be easily obtained by the direct reaction of LnI_2 with hydrogen under atmospheric pressure.

Results and Discussion

The only method for the synthesis of Sm^{II}, Eu^{II}, and Yb^{II} naphthalene complexes of the composition $C_{10}H_8Ln(THF)_x$ are the reactions of diiodides LnI_2 with lithium naphthalenide in THF.[5] The products are formed as insoluble black powders, which are easy to isolate from the reaction mixtures. In contrast to this, similar reactions of iodides of trivalent lanthanides give dark brown solutions, from which no individual products can be isolated.[8]

Another result was obtained in the reactions of lithium naphthalenide with Nd^{III} and Dy^{III} iodide hydrides. When an excess of $C_{10}H_8Li$ was added to a suspension of NdI_2H in THF, the solution rapidly changed its color from dark green to brown, followed by the formation of a black jelly-like precipitate. After the precipitate was repeatedly washed with THF and dried *in vacuo* at 40 °C for 4 h, a complex of the composition $(C_{10}H_8)_3Nd_5Li_5H_{14}$ (**1**) was obtained as a black powder. A dysprosium analog $(C_{10}H_8)_3Dy_5Li_5H_{14}$ (**2**) was isolated in the corresponding reaction of lithium naphthalenide with DyI_2H. The products were identified based on the elemental analysis data, IR spectroscopy, and fragment composition. Properties of clusters **1** and **2** are similar to those of Sm, Eu, and Yb naphthalene complexes: they are insoluble in THF and other organic solvents, quite stable under inert atmosphere, rapidly hydrolyze in air, whereas their finely dispersed state is pyrophoric. Their IR spectra exhibit absorption bands at 1598, 1509, 1038, 1026, and 782 cm^{-1} characteristic of stretching vibrations of the C—C groups and bending vibrations of the C—H bonds of the naphthalene rings. Unlike the spectra of divalent lanthanide complexes, the spectra of clusters **1** and **2** exhibit broad strong bands at 1271 and 475 cm^{-1}, which can be assigned to vibrations of the Ln—H bonds, while absorption bands of the coordinatively bound THF are absent. It should be noted that in the spectra of cyclopentadienyl hydride and diimine hydride complexes of rare earth metals, the bands responsible for the hydride groups[1] are found in the region of 600—800 cm^{-1}. The difference observed can be apparently explained by the bridging nature of the hydride ligands in clusters **1** and **2**.

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Heating of compounds **1** and **2** *in vacuo* to 120 °C produces no visible changes and does not lead to the evolution of hydrogen. When the temperature was elevated to 150 °C, liberation of naphthalene was observed.

Hydrolysis of the complex **1** in THF proceeds rapidly even at –30 °C and is accompanied by the evolution of hydrogen (2.38 mol per Nd atom). GLC-MS spectrometry showed the presence of naphthalene, 1,4-dihydronaphthalene, 1,2-dihydronaphthalene, and tetralin in the ratio of 4 : 7 : 4 : 1 in the organic products of the hydrolysis. According to the molecular formula of the starting compound, the total amount of liberated naphthalene, products of its hydrogenation, and the amount of the neodymium hydroxide that formed corresponded to the molar ratio $C_{10}H_8$: Nd = 3 : 5. Similar results were obtained for the hydrolysis of dysprosium complex **2**. It should be noted that the hydrolysis of naphthalenides of divalent Sm, Eu, and Yb, as well as of complexes of trivalent lanthanides, such as $[(C_{10}H_8)Tm(DME)]_2(\mu\text{-}C_{10}H_8)$ and $(C_{10}H_8)DyI(DME)_2$, leads only to dihydronaphthalene.[9,10] Conversely, hydrolysis of the complex $[(C_5Me_5)LuH(THF)]_3(C_{10}H_7)$ containing a naphthyl anion σ-bound to the metal gives free naphthalene together with dihydronaphthalenes and tetralin.[11]

Earlier, when properties of $C_{10}H_8Yb(THF)_3$ were studied it was found[5] that this compound readily reacts with secondary amines, such as Et_2NH and $HN(SiMe_3)_2$, giving amides $Yb(NR_2)_2$ in high yields. We found that clusters **1** and **2** also react with hexamethyldisilazane, but the reaction follows a different path. In THF, the reaction takes place at ~20 °C, is accompanied by the evolution of hydrogen, and reaches completion within 5—6 h; however, no expected neodymium and dysprosium silylamide derivatives are formed. The reaction involving complex **1** gives two products: lithium amide $LiN(SiMe_3)_2(THF)$ (the yield was 90%) and new neodymium naphthalene hydride cluster $(C_{10}H_8)_3Nd_5H_9$ (**3**) as a black powder insoluble in THF. When complex **2** is treated with an excess of amine $HN(SiMe_3)_2$, analogous dysprosium cluster $(C_{10}H_8)_3Dy_5H_9$ (**4**) was obtained together with $LiN(SiMe_3)_2(THF)$.

$$[(C_{10}H_8)_3Ln_5Li_5H_{14}] + HN(SiMe_3)_2 \xrightarrow{THF}$$

1, **2**

$$\longrightarrow 5\ LiN(SiMe_3)_2(THF) + [(C_{10}H_8)_3Ln_5H_9] + 5\ H_2$$

3, **4**

Ln = Nd (**1**, **3**), Dy (**2**, **4**)

Unfortunately, properties of products **3** and **4** similar to those of complexes **1** and **2** did not allow us to use single-crystal X-ray diffraction, NMR spectroscopy, and X-ray powder diffraction for establishing their structure. The compositions of these complexes were established based on elemental and fragment analyses and IR spectra exhibiting, like the spectra of clusters **1** and **2**, absorption bands of naphthalene ligands and hydride groups Ln—H.

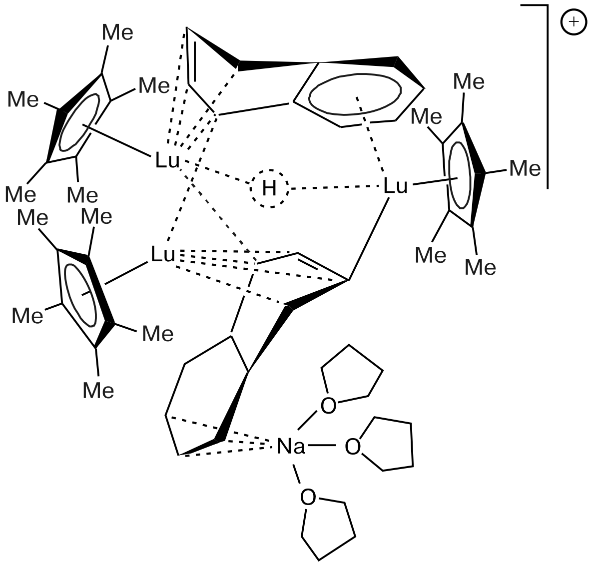
Hydrolysis of clusters **3** and **4** in THF at reduced temperature gives hydrogen (~1.5 mol per lanthanide atom), $Ln(OH)_3$ (the yield was 97—98%), naphthalene, and a mixture of reduced forms of naphthalene (1,4-dihydronaphthalene, 1,2-dihydronaphthalene, and tetralin) in the ratio of 4.4 : 3.0 : 2.3 : 1.0. The $Ln(OH)_3$ to naphthalene derivatives molar ratio is 3 : 5, that corresponds to the formulas of clusters **3** and **4**.

The reaction of alkali metal naphthalenides with halogen-containing substrates is frequently accompanied by the reduction of the latter. In order to confirm a trivalent state of neodymium in complexes **1** and **3**, we determined their effective magnetic moments (μ_{eff}). In both compounds, the μ_{eff} values are significantly higher than the μ_{eff} of divalent neodymium (2.9 μ_B),[12] and the magnetic moment of compound **3** (3.7 μ_B) is close to that calculated for the Nd^{3+} ion of $4f^3$ configuration (3.68 μ_B),[13] whereas the μ_{eff} of lithium neodymium cluster **1** (5.6 μ_B) is even higher. If for compound **3** such a magnetic moment is logically explained by the existence of the naphthalene ligands in the form of diamagnetic dianions $(C_{10}H_8)^{2-}$ (as in the complex $C_{10}H_8Yb(THF)_3$),[5] for the lithium-containing complex **1** an increased μ_{eff} value has no convincing explanation. The presence of three naphthalene ligands in the radical anion form of complex **1** could have given the μ_{eff} value close to the found one (provided that the spin exchange is absent), but in this scheme, the charge balance in the compound would have been disturbed.

While studying chemical properties of complexes **1**—**4**, we found that they, unlike compounds of divalent samarium, europium, and ytterbium $(C_{10}H_8)Ln(THF)_3$,[14,15] do not react with hydrogen at 50 °C under atmospheric pressure. However, when complexes **1** and **3** were taken as examples, it was found that they readily react with cyclopentadiene. In THF, the reaction takes place at ~20 °C and is accompanied by the evolution of hydrogen and the formation of blue solutions, from which naphthalene and $Cp_3Nd(THF)$ were isolated in both cases.

In conclusion, the reactions of iodide hydrides NdI_2H and DyI_2H with lithium naphthalenide in THF and subsequent treatment of the reaction products with hexamethyldisilazane furnished organolanthanide complexes of the new type, *viz.*, $(C_{10}H_8)_3Ln_5Li_5H_{14}$ and $(C_{10}H_8)_3Ln_5H_9$. Molecules of these compounds contain both a hydride group Ln—H and a naphthalene ligand. The structures of the complexes were not established; however, their IR spectra, hydrolysis products, and magnetic moments allow us to conclude that the hydride protons in the molecules are bridging, while the naphthalene ligands have polymodal bonds with the lanthanide cations, like in the case of the earlier[11] studied trinuclear lutetium complex $\{[Cp^*Lu)_3(C_{10}H_8)(C_{10}H_7)(H)][Na(THF)_3]\}_2(C_{10}H_8)$ (**5**;

the dianion $(C_{10}H_8)^{2-}$ distant from the lutetium atoms is not shown).



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Experimental

Syntheses were carried out under conditions excluding exposure of reagents to atmospheric oxygen and moisture using standard Schlenk technique. Tetrahydrofuran was distilled over NaOH, degassed, dried with NdI_2 (500 mL of THF, 2 g of NdI_2, 20 °C, 30 min), and condensed into the reaction tube just before use. Diiodides NdI_2 and DyI_2 were prepared according to the procedure developed earlier.[16] IR spectra were recorded on a FSM-1201 Fourier-transform infrared spectrometer in the range of 4000—400 cm^{-1}. Samples were prepared as suspensions in Nujol. The content of lanthanide in the compounds obtained was determined by complexometric titration, the content of iodine, by back titration. Magnetic measurements were carried out using the known procedure.[17] Organic hydrolysis products were analyzed on a Polaris Q GLC-MS instrument.

Reaction of NdI_2H with lithium naphthalenide. A solution of $C_{10}H_8Li$ (obtained *in situ* from Li (0.13 g, 18.6 mmol) and naphthalene (4.76 g, 37.2 mmol)) in THF (15 mL) was added to a suspension of NdI_2H (1.82 g, 4.6 mmol) in THF (5 mL). The solution turned its color from dark green to light brown. The mixture was vigorously stirred for 24 h at ~20 °C. The brown solution was decanted from the black jelly-like precipitate that formed. The precipitate was washed with fresh THF (6×10 mL) and dried *in vacuo* for 4 h at 20 °C to yield complex **1** (0.92 g, 88%) as a black pyrophoric powder. Found (%): Nd, 62.13. $C_{30}H_{38}Li_5Nd_5$. Calculated (%): Nd, 62.48. IR (Nujol, ν/cm^{-1}): 1598, 1026, 782, 475. μ_{eff} (293 K) = 5.6 μ_B.

Reaction of DyI_2H with lithium naphthalenide. The reaction was carried out similarly to the synthesis of compound **1**. Complex **2** (0.62 g, 94%) was obtained as a black powder from DyI_2H (1.10 g, 2.6 mmol), Li (0.055 g, 7.6 mmol), and naphthalene (1.35 g, 10.5 mmol). Found (%): Dy, 64.90. $C_{30}H_{38}Dy_5Li_5$. Calculated (%): Dy, 65.23. IR (Nujol, ν/cm^{-1}): 1595, 1509, 1271, 1038, 782, 475.

Hydrolysis of complex 1. A mixture of H_2O (0.2 mL, 11.11 mmol) and DME (2 mL) was added to a suspension of complex **1** (0.28 g, 0.24 mmol) in DME (1 mL) at –10 °C, which was accompanied by vigorous evolution of a gas and formation of a pale violet flocculent precipitate. The reaction was completed within 10 s, the amount of liberated hydrogen was 64 mL (s.c., 2.86 mmol, 84%), that corresponds to the ratio $H_2 : Nd = 2.38 : 1.00$. The mixture was centrifuged and the solution was separated from the precipitate of $Nd(OH)_3$ (identified as Nd_2O_3 after washing with water and calcination in air at 200 °C; the yield was 0.23 g (98%)). A mixture of $C_{10}H_8$, 1,4-$C_{10}H_{10}$, 1,2-$C_{10}H_{10}$, and $C_{10}H_{12}$ (80 mg, 86%, 4 : 7 : 4 : 1) was also found in the DME solution.

Hydrolysis of complex 2. Hydrogen (83 mL, 3.70 mmol, 82%) ($H_2 : Dy = 2.31 : 1.00$), $Dy(OH)_3$ (0.32 g, 94%), and a mixture of $C_{10}H_8$, 1,4-$C_{10}H_{10}$, 1,2-$C_{10}H_{10}$ and $C_{10}H_{12}$ (0.10 g, 81%) were obtained from complex **2** (0.40 g, 0.32 mmol) under conditions of the preceding experiment.

Reaction of complex 1 with hexamethyldisilazane. A mixture of $HN(SiMe_3)_2$ (2.28 g) and THF (3 mL) was added to a suspension of complex **1** (0.50 g, 0.43 mmol) in THF (15 mL). The reaction mixture was stirred for 48 h at 70 °C, which was accompanied by evolution of hydrogen (43 mL, s.c., 90%). A black precipitate was separated from a colorless solution by decantation, washed with THF (2×5 mL), and dried *in vacuo* for 5 h at 40 °C to yield complex **3** (0.45 g, 93%) as a black pyrophoric powder. Found (%): Nd, 65.0. $C_{30}H_{33}Nd_5$. Calculated (%): Nd, 64.42. IR (Nujol, ν/cm^{-1}): 1270, 840. The colorless solution was combined with the tetrahydrofuran extract. Recrystallization from hexane gave $LiN(SiMe_3)_2(THF)$ (0.47 g, 90%). ^7Li NMR (200 MHz, C_6D_6, 20 °C), δ: 2.954 (Li). ^1H NMR (200 MHz, C_6D_6, 20 °C), δ: 0.10 (3 H, $SiMe_3$); 0.38 (15 H, $SiMe_3$); 1.30 (4 H, β-CH_2, THF); 3.64 (4 H, α-CH_2, THF). IR (Nujol, ν/cm^{-1}): 1251, 1238, 1180, 1046, 1016, 893, 875, 828, 761, 686, 660, 604, 448.

Reaction of complex 2 with hexamethyldisilazane. The reaction of complex **2** with $HN(SiMe_3)_2$ was carried out similarly to that described above for complex **1**. The compound $LiN(SiMe_3)_2(THF)$ (0.49 g, 89%) was obtained from complex **2** (0.45 g, 0.35 mmol) and $(Me_3Si)_2NH$ (2.30 g). ^7Li NMR (200 MHz, C_6D_6, 20 °C), δ: 2.954 (Li). ^1H NMR (200 MHz, C_6D_6, 20 °C), δ: 0.10 (3 H, $SiMe_3$); 0.38 (15 H, $SiMe_3$); 1.300 (4 H, β-CH_2, THF); 3.64 (4 H, α-CH_2, THF). IR (Nujol, ν/cm^{-1}): 1251, 1238, 1180, 1046, 1016, 893, 875, 828, 761, 686, 660, 604, 448. Amount of liberated hydrogen was 33 mL (s.c., 85%). Complex **4** (0.41 g, 96%) was obtained as a black powder. Found (%): Dy, 66.70. $C_{30}H_{33}Dy_5$. Calculated (%): Dy, 67.10. IR (Nujol, ν/cm^{-1}): 1250, 870, 835.

Hydrolysis of complex 3. A mixture of H_2O (0.2 mL) and DME (2 mL) was added to a suspension of complex **3** (0.35 g, 0.31 mmol) in DME (1 mL) at –10 °C, which was accompanied by vigorous evolution of a gas and formation of a flocculent precipitate. The amount of liberated hydrogen was 54 mL (s.c., 2.41 mmol, 86%) ($H_2 : Nd = 1.55 : 1.00$). The precipitate was separated from the solution and washed with DME (2×1 mL) to yield $Nd(OH)_3$ (0.29 g, 97%).

Hydrolysis of complex 4. Hydrogen (53 mL, s.c., 2.37 mmol, 88%) ($H_2 : Dy = 1.58 : 1.00$) and $Dy(OH)_3$ (0.30 g, 94%) were obtained from complex **4** (0.36 g, 0.30 mmol) under conditions of the preceding experiment.

Reaction of complex 1 with cyclopentadiene. A solution of cyclopentadiene (0.5 g, 7.57 mmol) in THF (10 mL) was added to a suspension of complex **1** (0.26 g, 0.22 mmol) in THF (2 mL), which was accompanied by evolution of hydrogen and formation of a blue solution. The mixture was stirred for 3 h at 20 °C. The blue solution that formed was separated from the black powder residue. The solvent was removed to obtain $Cp_3Nd(THF)$ (0.26 g, 56%) as blue crystals. Found (%): C, 54.87; H, 6.05; Nd, 35.10. $C_{19}H_{23}NdO$. Calculated (%): C, 55.46; H, 5.59; Nd, 35.05.

Reaction of complex 3 with cyclopentadiene. A solution of cyclopentadiene (0.5 g, 7.57 mmol) in THF (10 mL) was added to a suspension of complex **3** (0.36 g, 0.32 mmol) in THF (2 mL), which was accompanied by evolution of hydrogen and acquiring a blue color by the solution. The reaction mixture was stirred for 8 h in a sealed tube. The blue solution that formed was separated from the black powder residue. The solvent was removed to obtain $Cp_3Nd(THF)$ (0.32 g, 48%) as blue crystals. Found (%): C, 55.00; H, 5.90; Nd, 35.23. $C_{19}H_{23}NdO$. Calculated (%): C, 55.46; H, 5.59; Nd, 35.05.

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