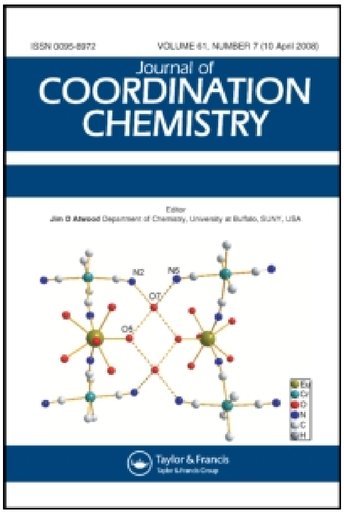

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Metathesis reactions of neodymium and dysprosium diiodide-hydrides with organopotassium compounds: structure of $[K(THF)_2][(\eta^5\text{-}C_5H_5)_3Nd(\mu\text{-}H)Nd(\eta^5\text{-}C_5H_5)_3]$ and $[K(THF)_2][Nd_3(PhO)_{10}(THF)_4]$

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Reaction of neodymium iodide-hydride NdI_2H with CpK in THF affords organoneodymium hydride $[K(THF)_2][(\eta^5\text{-}C_5H_5)_3Nd(\mu\text{-}H)Nd(\eta^5\text{-}C_5H_5)_3]$ (**1**). Dysprosium analog DyI_2H under the same conditions yields the known complex $Cp_3Dy(THF)$. The reaction of NdI_2H with potassium phenoxide in THF affords the ionic cluster $[K(THF)_2][Nd_3(PhO)_{10}(THF)_4]$ (**2**). In each case, interaction is accompanied by dihydrogen evolution. The molecular structures of **1** and **2** have been defined by X-ray diffraction analysis. The interaction of NdI_2H with CpNa or CpLi gives an intractable mixture of products. The compounds $PhC\equiv CK$, $NaN(SiMe_3)_2$, $KN(SiMe_3)_2$, $K(OC_6H_2Bu^t_3\text{-}2,4,6)$, and C_5Me_5K are inert toward NdI_2H.

Keywords: Neodymium; Dysprosium; Diiodides; Hydrides; Phenoxide

1. Introduction

Rare earth metal hydrides attract attention due to their synthetic utility and high catalytic activity. Reactivity of these compounds is described in a number of papers, reviews, and monographs [1–5]. Chemical properties of lanthanide hydrides of variable compositions, LnH_x ($x = 2, 3$) [6], are less studied. These hydrides react with water, acids and some are oxidized in air. No attempts to use LnH_x in organic or organometallic synthesis have been reported because of low reactivity of Ln–H. No information is in the literature about chemical behavior of halide–hydrides of the type LnX_nH_{3-n}.

By studying the reactivity of neodymium(II) and dysprosium(II) diiodides LnI_2 we have found that they react with dihydrogen at 120–200°C to give solvent-free iodide-hydrides LnI_2H [7]. The dysprosium hydride DyI_2H revealed relatively high activity of Ln–H towards cyclopentadiene and isopropanol. The interaction with CpH proceeds

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in THF at room temperatures and affords $Cp_2DyI(THF)_2$ as a result of disproportionation of initially formed $CpDyI_2$. In reaction with isopropanol the disproportionation does not occur and the formed diiodide $DyI_2(OPr^i)(Pr^iOH)_3$ was isolated in 75% yield. The neodymium analog NdI_2H was somewhat less reactive, not reacting with CpH and very slowly deprotonating isopropanol. However, NdI_2H reacts with phenol in THF to give phenoxide $PhONdI_2(THF)_4$ [7]. The present work investigates the reactivity of Ln–I bonds in NdI_2H and DyI_2H for use as starting reagents in synthesis of neodymium organo-hydride complexes.

2. Experimental

2.1. *General remarks*

All procedures were performed under vacuum using standard Schlenk-tube techniques. Tetrahydrofuran and hexane were dried by refluxing over sodium. NdI_2 was purchased from Synor company (Nizhny Novgorod) and used without purification. Potassium cyclopentadienyl [8] and potassium phenoxide [9] were prepared according to published procedures. The IR spectra of the samples prepared as Nujol mulls were recorded on a FSM 1201 FT IR spectrometer. The lanthanide content in the obtained compounds was determined by complexometry.

2.2. *Reaction of NdI_2H with CpK*

A suspension of CpK (0.33 g, 3.17 mmol) in THF (10 mL) was added to a suspension of NdI_2H (0.63 g, 1.58 mmol) in THF (5 mL) and the mixture was stirred at room temperature in a sealed ampoule for 10 h. The formed pale blue solution and colorless precipitate were separated from violet crystals of [bis(neodymium tricyclopentadienide) hydride][potassium di(tetrahydrofurane)] $[K(THF)_2][(\eta^5\text{-}C_5H_5)_3Nd(\mu\text{-}H)Nd(\eta^5\text{-}C_5H_5)_3]$ (**1**) by decantation. The product was dried in vacuum at room temperature. Yield 0.26 g (38%); m.p. >310°C (dec.). Anal. Calcd for $C_{38}H_{47}KNd_2O_2$ (%): C, 52.87; H, 5.55; Nd, 33.41. Found: C, 52.51; H, 5.30; Nd, 33.73. IR (nujol, KBr): 1123 (w), 1054 (s), 1011 (s), 896 (m), 780 (s), 749 (s), 665 (w), 623 (w) cm^{-1}.

2.3. *Reaction of DyI_2H with CpK*

To a mixture of CpK (0.18 g, 1.73 mmol) and DyI_2H (0.35 g, 0.84 mmol) 10 mL of freshly distilled THF was added. The mixture was stirred at room temperature in a sealed ampoule for 10 h. The formed pale yellow solution was separated from colorless precipitate by filtration. From the solution, pale yellow crystals of $Cp_3Dy(THF)$ (0.3 g, 83%) were isolated by slowly removing the solvent in vacuum. The compound was identified by X-ray analysis: the cell parameters coincide with those of a known complex [10].

2.4. *Reaction of NdI_2H with PhOK*

To a suspension of NdI_2H (0.80 g, 2.00 mmol) in THF (5 mL), a solution of PhOK (0.52 g, 3.93 mmol) in THF (15 mL) was added at room temperature. Gas evolution and dissolution of black NdI_2H were observed. The reaction mixture was stirred for 5 h in the sealed ampoule. The resulting blue-violet solution was decanted from the colorless powder-like precipitate and the solvent was removed by slow evaporation. Deposited blue-violet, fine-crystalline powder was washed with cold THF and dried in vacuum to give neodymium-potassium phenoxide $[K(THF)_2][Nd_3(PhO)_{10}(THF)_4]$ (**2**) (0.71 g, 58%). The product is soluble in toluene and THF. Anal. Calcd for $C_{84}H_{98}KNd_3O_{16}$ (%): C, 54.92; H, 5.34; Nd, 23.57. Found: C, 54.60; H, 5.10; Nd, 23.76. IR (nujol, KBr): 1691 (w), 1590 (s), 1567 (m), 1290 (s), 1256 (s), 1233 (s), 1173 (m), 1065 (w), 1024 (m), 993 (m), 876 (w), 860 (s), 830 (m), 692 (s) cm^{-1}. The crystals of **2** for X-ray analysis were obtained by slow concentration of its solution in THF/hexane mixture.

2.5. *X-ray crystal structure analysis*

The X-ray diffraction data were collected on a SMART APEX diffractometer (graphite-monochromated, Mo-Kα radiation, φ–ω-scan technique, $\lambda = 0.71073$ Å). Intensity data integrated by SAINT [11] and SADABS [12] were used to perform area-detector scaling and absorption corrections. The structures were solved by direct methods and refined on F^2 using all reflections with SHELXTL [13]. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms of **1** were found from Fourier synthesis and refined isotropically; H atoms of **2** were placed in calculated positions and refined as riding atoms. The details of crystallographic, collection, and refinement data for **1** and **2** are shown in table 1. Selected geometric characteristics for **1** and **2** are given in the legends to figures 1 and 2.

3. Results and discussion

Several methods of organolanthanide hydride preparation are known: hydrogenolysis of alkyl/aryl derivatives of Cp_2LnR type [14], β-hydrogen eliminations of similar alkyl complexes [15], reactions of Na [16], $LiAlH_4$ or $NaAlH_4$ [17, 18] with organolanthanide halides, Cp_2LnX, reactions of metathesis of ligands in organohydride complexes [19], and insertion reactions of Ln metals into C–H bonds of unsaturated hydrocarbons [20]. We have found that an ionic cyclopentadienyl-hydride complex of neodymium can be obtained by treatment of NdI_2H with two equivalents of KCp in THF. The reaction proceeds smoothly at room temperature and is accompanied by dihydrogen evolution and dissolution of black powder of NdI_2H. From the solution violet crystals of **1** were isolated in 38% yield.

$$NdI_2H + CpK \xrightarrow[-H_2]{THF} [K(THF)_2][Cp_3Nd](\mu_2\text{-}H)NdCp_3]$$

The reaction scheme is not clear but the formation of Cp_3Nd fragments suggests existence of at least two stages: (i) complete metathesis yielding KI, Cp_3Nd, and KH and (ii) subsequent interaction of the two latter products leading to **1**. A similar ate complex, $[Na(THF)_6][Cp_3Lu(\mu_2\text{-}H)LuCp_3]$, has been previously synthesized by Schumann and coworkers [16] by addition of NaH to $Cp_3Lu(THF)$. Interaction of CpNa or CpLi with NdI_2H under the same conditions affords an intractable mixture

Table 1. Details of crystallographic collection and refinement data for **1** and **2**.

	1	**2**
Empirical formula	$C_{38}H_{47}KNd_2O_2$	$C_{84}H_{98}KNd_3O_{16}$
Formula weight	863.34	1835.44
Temperature (K)	100(2)	100(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2(1)/c$
Unit cell dimensions (Å, °)		
a	8.5730(4)	18.6928(18)
b	9.6827(4)	19.2658(18)
c	11.2849(5)	22.806(2)
α	73.192(1)	–
β	69.976(1)	92.447(2)
γ	81.555(1)	–
Volume (Å^3)	841.34(6)	8205.6(14)
Z	1	4
Density (Calcd) (g cm^{-3})	1.704	1.486
Absorption coefficient (mm^{-1})	3.207	1.984
F(000)	430	3716
Crystal size (mm^3)	$0.22 \times 0.19 \times 0.05$	$0.31 \times 0.24 \times 0.21$
θ_{max} range for data collection (deg)	25.98	26.00
Index ranges	$-10 \leq h \leq 10$ $-11 \leq k \leq 11$ $-13 \leq l \leq 13$	$-23 \leq h \leq 23$ $-20 \leq k \leq 23$ $-21 \leq l \leq 28$
Reflections collected	7260	48,492
Independent reflections	3276 [$R_{int} = 0.0143$]	16,056 [$R_{int} = 0.0950$]
Absorption correction	Semi-empirical from equivalents	
Max/min transmission	0.8561/0.5389	0.6807/0.5783
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	3276/0/289	16,056/76/817
Goodness-of-fit on F^2	1.065	1.032
Final R indices [$I > 2\sigma$(I)]	$R_1 = 0.0170$ $wR_2 = 0.0402$	$R_1 = 0.0960$ $wR_2 = 0.2415$
R indices (all data)	$R_1 = 0.0183$ $wR_2 = 0.0408$	$R_1 = 0.1581$ $wR_2 = 0.2652$
Largest difference peak and hole (e Å^{-3})	1.007/−0.647	4.673/−1.582

of products from which we were unable to isolate any definite compounds. Unexpectedly, NdI_2H is inert towards C_5Me_5K.

The X-ray structure analysis has shown that **1** forms infinite chains in which $[Cp_3Nd(\mu_2\text{-H})NdCp_3]^-$ anions are bridged to each other by $[K(THF)_2]^+$. The Coulombic interaction of cations and anions is realized via Cp rings of adjacent $[Cp_3Nd(\mu_2\text{-H})NdCp_3]^-$ units (figure 1). The K···C(Cp) lengths, K(1A)–C(13A) 3.262(2) Å, K(1A)–C(14A) 3.0231(19) Å, and K(1A)-C(15A) 3.1204(19) Å are noticeably shorter than K(1A)-C(11A) 3.413(2) Å and K(1A)···C(12A) 3.497(3) Å, indicating η^5 K–Cp coordination. The geometry of $[Cp_3Nd(\mu\text{-H})NdCp_3]^-$ is similar to that of $[Cp_3Lu(\mu\text{-H})LuCp_3]^-$ in $[Na(THF)_6][Cp_3Lu(\mu\text{-H})LuCp_3(THF)_2]$ [16] and $[Cp_3Nd(\mu\text{-H})NdCp_3]^-$ in $[Li(DME)_3][Cp_3Nd(\mu\text{-H})NdCp_3]$ [21]. In the anion each neodymium is coordinated with three π-bonded cyclopentadienyl rings and bridging hydrides, resulting in coordination number 10 for Nd. The Nd–H–Nd bridge is linear with Nd–H bond distance in **1** somewhat shorter than analogous bonds in $[Li(DME)_3][Cp_3Nd(\mu\text{-H})NdCp_3]$ (2.1725(1) and 2.190 Å, respectively). The structure of $[Cp_3Nd]$ groups is the same as in $Cp_3Nd(THF)$ [22]. The average Nd–C(Cp) bond

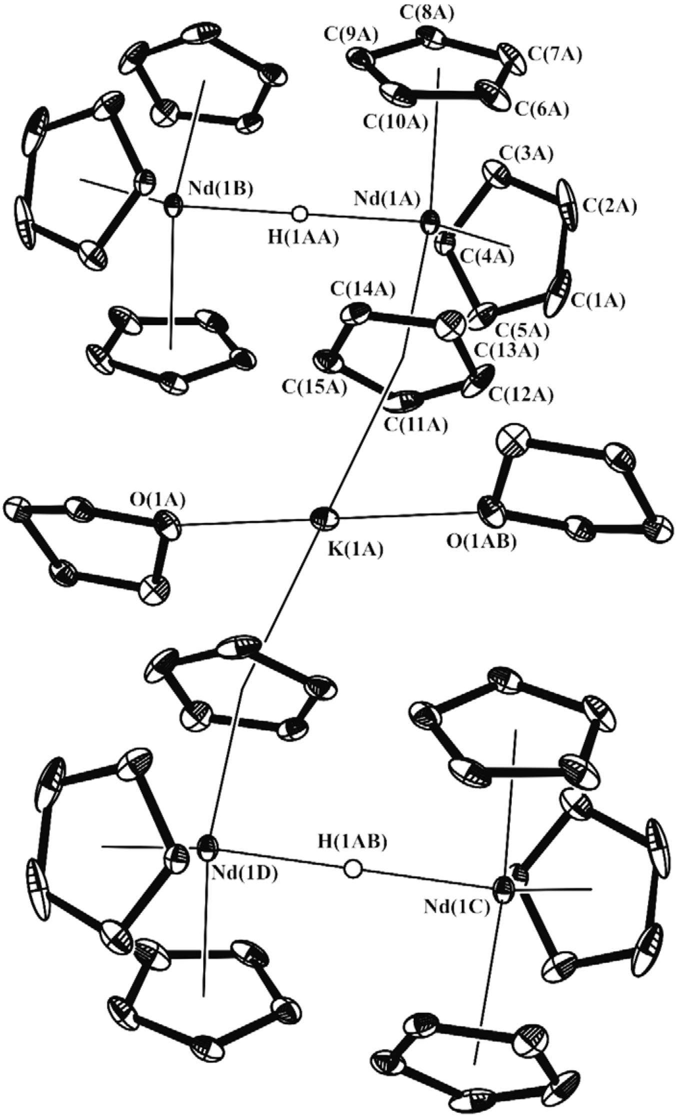

Figure 1. Molecular structure of $[K(THF)_2][Cp_3Nd(\mu\text{-}H)NdCp_3]$ (**1**). Relevant bond lengths (Å) and angles (°): Nd(1A)–H(1AA) 2.1725(1), K(1A)–C(13A) 3.262(2), K(1A)–C(14A) 3.0231(19), K(1A)–C(15A) 3.1204(19), K(1A)–O(1A) 2.8887(14), O(1A)–K(1A)–O(1AB) 180.00.

lengths and values of the centroid–Nd–centroid angles in both compounds virtually coincide.

From reaction of potassium cyclopentadienide with DyI_2H only the known $Cp_3Dy(THF)$ [10] was isolated in high yield.

To obtain neodymium hydride complexes with other than Cp ancillary ligands we treated NdI_2H with potassium 2,4,6-tri(*t*-butyl)phenoxide and PhOK in THF. The first reaction does not occur even at 60°C while the second proceeds easily at room temperature, judging by complete dissolution of NdI_2H. However, the violet crystalline

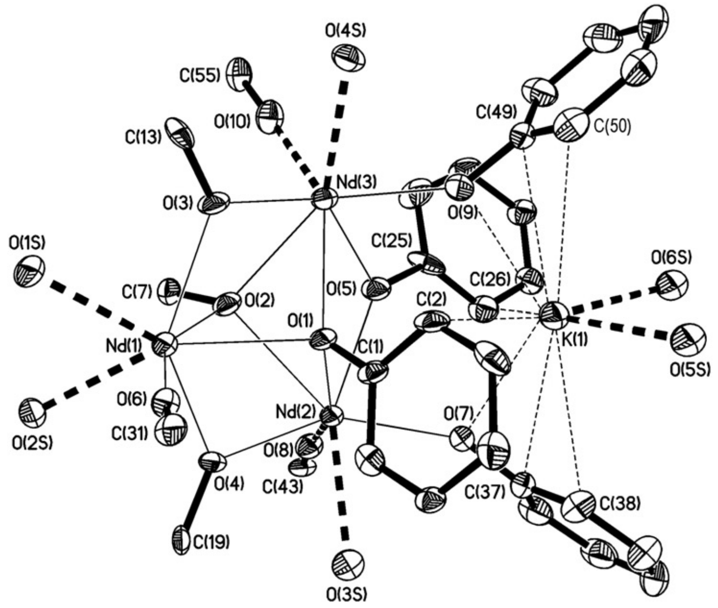

Figure 2. Molecular structure of $[K(THF)_2][Nd_3(PhO)_{10}(THF)_4]$ (**2**). All hydrogens and some Ph rings have been omitted for clarity. The O(1S–6S) are oxygens in THF molecules. The O(1–10) atoms are oxygens in OPh ligands. Relevant bond lengths (Å) and angles (°): Nd(1)–O(1) 2.550(5), Nd(1)–O(2) 2.439(6), Nd(1)–O(3) 2.400(5), Nd(1)–O(4) 2.403(5), Nd(1)–O(6) 2.173(6), Nd(2)–O(1) 2.552(6), Nd(2)–O(2) 2.632(5), Nd(2)–O(4) 2.433(5), Nd(2)–O(5) 2.404(6), Nd(2)–O(7) 2.282(5), Nd(2)–O(8) 2.216(6), K(1)–O(7) 2.703(6), K(1)–O(9) 2.655(6), K(1)–O(5S) 2.707(5), K(1)–O(6S) 2.662(5), Nd(3)–Nd(1)–Nd(2) 60.507(13), Nd(1)–Nd(2)–Nd(3) 59.06(1), Nd(1)–Nd(3)–Nd(2) 60.44(1), Nd(1)–O(1)–Nd(2) 97.08(19), Nd(1)–O(4)–Nd(2) 104.49(19), Nd(1)–O(2)–Nd(2) 97.80(19), Nd(2)–O(1)–Nd(3) 96.5(2), Nd(2)–O(5)–Nd(3) 105.2(2).

product isolated from the reaction mixture in this case did not contain Nd–H. The X-ray structure and elemental analysis reveal an ionic phenoxyneodymium cluster **2**. Liberation of dihydrogen, high yield of KI, and formation of $Cp_3Dy(THF)$ and **2** indicate that the schemes of the reactions are similar to that of reaction of NdI_2H with CpK, but the hydride-containing intermediates formed in these cases are less stable and completely expel hydrogen from Ln–H groups.

The molecule of **2** consists of cationic $[K(THF)_2]^+$ and anionic $[Nd_3(PhO)_{10}(THF)_4]^-$ moieties (figure 2). The structure of the anion is similar that of $[Nd_3(OAr)_9(THF)_4] \cdot 4THF$ [23]. The Nd atoms form a triangle linked by two μ_3-OPh ligands above and below the Nd_3 plane, as well as by six edged μ_2-OPh groups. Each Nd atom is further coordinated by one terminal OPh and THF (two THF molecules at Nd(1) and one at Nd(2) and Nd(3)). Thus, each Nd is seven-coordinate. The coordination environment of the K^+ is unusual. Along with K–O interactions (oxygens of two PhO groups and two THF's) there are six short K–C contacts (to C(49) 3.034(5) Å, to C(37) 3.091(9) Å, to C(38) 3.189(5) Å, to C(2) 3.324(6) Å, to C(26) 3.361(7) Å and to C(50) 3.425(7) Å), which indicate existence of some interaction between potassium and four neighboring Ph rings bearing partial negative charge. Lengths of the short K–C(Ph) contacts in **2** are in the same range as contacts in $K[La(OC_6H_3{}^iPr\text{-}2,6)_4]$ (3.107(5)-3.519(7) Å) [24] and are comparable with the shortest K–C(arene) distances in $K[Nd(OC_6H_3{}^iPr\text{-}2,6)_4]$ (3.097(10)-3.473(11) Å) [25] and $KBPh_4$ (3.191(5) Å) [26]. Such contacts increase saturation of coordination sphere of K and apparently stabilizes the complex as a whole.

The other alkali metal derivatives such as PhC≡CK, $NaN(SiMe_3)_2$ and $KN(SiMe_3)_2$ like C_5Me_5K do not react with NdI_2H in THF even after heating to 70°C.

4. Conclusion

The diiodide-hydride, NdI_2H, unlike lanthanide hydrides LnH_x, can be used for the direct synthesis of organoneodymium compounds, some of which retain the Nd–H. The results show the reactivity of LnI_2H and open new synthetic routes in organolanthanide chemistry.

Supplementary Material

CCDC-713838 (**1**) and 713839 (**2**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/const/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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