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First Chemical Transformations of Lanthanide Borohydride Compounds: Synthesis and Crystal Structures of $[(\eta\text{-}C_8H_8)Nd(BH_4)(THF)]_2$ and $[(\eta\text{-}C_8H_8)Nd(THF)_4][BPh_4]$

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*Summary: Reaction of $Nd(BH_4)_3(THF)_3$ with K_2COT ($COT = \eta\text{-}C_8H_8$) in tetrahydrofuran (THF) gave the first (cyclooctatetraene)lanthanide borohydride, $(COT)Nd(BH_4)(THF)_2$ (**1**). By treatment with $NHEt_3BPh_4$, **1** was transformed into $[(COT)Nd(THF)_4][BPh_4]$ (**3**), a unique example of a (cyclooctatetraene)lanthanide cation; both **1** and **3** gave (COT)Nd(Cp*)(THF) ($Cp^* = \eta\text{-}C_5Me_5$) upon reaction with KCp*.*

Although they have been known for a long time, the lanthanide borohydrides $Ln(BH_4)_3(THF)_x$ (Ln = lanthanide metal, THF = tetrahydrofuran) have received scant attention and their chemical reactivity has not been evaluated.[1,2] With the exception of $(THF)(BH_4)_2Nd(\mu\text{-}\eta^7{:}\eta^7\text{-}C_7H_7)Nd(BH_4)(THF)_2$, which was isolated from the reaction of $Nd(BH_4)_3(THF)_2$ with KC_7H_9,[3] the rare trivalent organolanthanide borohydrides are limited to bis(cyclopentadienyl) complexes;[4−7] these were prepared by treatment of the corresponding halides with $LiBH_4$ or $NaBH_4$. The scarcity of lanthanide borohydrides appears most peculiar in comparison to the wealth of inorganic and organometallic compounds that have been synthesized from $U(BH_4)_4$ and $U(BH_4)_3(THF)_4$.[8,9] These complexes, which in some cases were more stable than their chloride analogues and which could be conveniently converted into new derivatives by further reaction of the BH_4 groups with anionic reagents or proton acidic substrates, revealed the utility of the borohydride ligand in f-element chemistry. Taking this background into account, we decided to investigate the reactivity of the lanthanide borohydrides. With the synthesis of $(COT)Nd(BH_4)(THF)_2$ (**1**), $[(COT)Nd(THF)_4][BPh_4]$ (**3**), and (COT)Nd(Cp*)(THF) (**4**) ($COT = \eta\text{-}C_8H_8$, $Cp^* = \eta\text{-}C_5Me_5$), we present herein new chemical transformations of $Ln\text{-}BH_4$ compounds and demonstrate that the complex $Ln(BH_4)_3(THF)_x$ can be a valuable precursor of organometallic derivatives, in particular of cationic species. We also describe the crystal structures of $[(COT)Nd(BH_4)(THF)]_2$ (**2**), which, like that of $[(C_5H_3Bu^t{}_2)_2Ce(BH_4)]_2$,[6] exhibits the $(\mu_3\text{-}H)_2B(\mu_2\text{-}H)_2$ coordination mode of the BH_4 ligand, and of **3**, which is a unique example of a (cyclooctatetraene)lanthanide cation.

Reaction of $Nd(BH_4)_3(THF)_3$[2] (1507 mg, 3.72 mmol) with $K_2C_8H_8$ (678 mg, 3.72 mmol) in THF (30 mL) gave the mono(cyclooctatetraene) compound $(COT)Nd(BH_4)(THF)_2$ (**1**) (Scheme 1). After 24 h at 20 °C, the off-white precipitate of KBH_4 was filtered off and the green solution was evaporated, leaving the green powder of **1**, which was crystallized from THF−pentane (1358 mg, 3.24 mmol, 87%). The NMR spectrum of **1** (pyridine-d_5, 20 °C)[10] exhibits a singlet at −10.27 ppm and a broad resonance at 44 ppm corresponding respectively to the

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[10] ^1H NMR spectra (200 MHz, 20 °C) and elemental analyses of the complexes are as follows. For **1** in pyridine-d_5: δ 44 (br, $w_{1/2}$ = 360 Hz, 4H, BH_4), 3.49 and 1.45 (s, 8 H + 8 H, THF), −10.27 (s, 8 H, COT). Anal. Calcd for $C_{16}H_{28}BO_2Nd$: C, 47.16; H, 6.93; B, 2.65. Found: C, 46.88; H, 6.78; B, 2.74. For **3** in pyridine-d_5: δ 7.89 (br t, 8 H, *o*-Ph), 7.10 (t, *J* = 8.5 Hz, 8 H, *m*-Ph), 6.93 (t, *J* = 7.0 Hz, 4 H, *p*-Ph), 3.49 and 1.45 (s, 16 H + 16 H, THF), −10.88 (s, 8 H, COT). Anal. Calcd for $C_{48}H_{60}BO_4Nd$: C, 67.34; H, 7.06; B, 1.26. Found: C, 66.52; H, 6.59; B, 1.32. For **4** in benzene-d_6: δ 4.41 (br, $w_{1/2}$ = 90 Hz, 15 H, Cp*), 3.84 (s, $w_{1/2}$ = 25 Hz, 4 H, THF), −3.61 (br s, $w_{1/2}$ = 85 Hz, 4 H, THF), −16.2 (br s, $w_{1/2}$ = 140 Hz, 8 H, COT). Anal. Calcd for $C_{22}H_{31}ONd$: C, 57.98; H, 6.86; O, 3.51. Found: C, 57.72; H, 6.76; O, 3.33.

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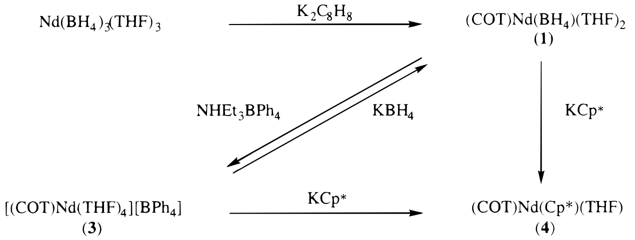
Scheme 1. Synthesis of the Compounds



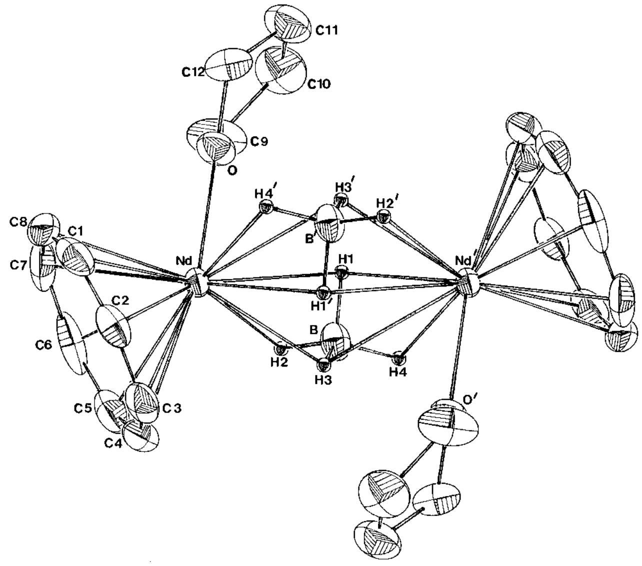


Figure 1. ORTEP drawing of $[(COT)Nd(BH_4)(THF)]_2$ with probability ellipsoids drawn at the 30% level. Atoms labeled with primes are related to unlabeled atoms by the center of symmetry.

C_8H_8 and BH_4 ligands. In the IR (Nujol) spectrum, the sharp singlet at 2424 cm^{-1} and the broad band centered at 2000 cm^{-1} are characteristic of tridentate BH_4 groups,[8] indicating that **1** would adopt a monomeric structure, like the other two organoneodymium borohydrides $(C_5H_3\{SiMe_3\}_2)_2Nd(BH_4)(THF)$[4] and $(C_5H_4CH_2CH_2OMe)_2Nd(BH_4)$,[5] and in contrast to the dimeric chloride analogue $[(COT)NdCl(THF)_2]_2$.[11] Crystallization of **1** from benzene led to the dissociation of a THF molecule, with formation of green crystals of $[(COT)Nd(BH_4)(THF)]_2$ (**2**). The IR spectrum of **2** shows, in the 2000−2500 cm^{-1} region, a single broad and strong absorption centered at 2255 cm^{-1}, which is diagnostic of bridging borohydride ligands.[6,8] The dimeric structure of **2** was determined by X-ray crystallography (Figure 1).[12] The centrosymmetric complex is built up of two monomeric units which are bridged by two BH_4 groups. Each Nd atom is in a three-legged piano-stool environment, defined by the boron and oxygen atoms and the C_8H_8 ligand; the angles B−Nd−B′, B−Nd−O, and B′-Nd−O are respectively 82.9(2), 84.3(2), and 85.0(2)° and the angles COT−Nd−B, COT−Nd−B′, and COT−Nd−O (COT is the centroid of the C_8H_8 ligand) are 129.6(1), 132.9(1), and 125.49(9)°. Coordination of the eight-membered planar ring (within ±0.02 Å) is quite similar to that found in other mono(cyclooctatetraene)neodymium compounds,[13] with Nd−C bond lengths ranging from 2.626(6) to 2.644(6) Å (average 2.63(1) Å) and the Nd−COT(centroid) distance equal to 1.906(6) Å. The Nd−O bond distance of 2.481(5) Å is also unexceptional. Most interesting is the ligation mode of the BH_4 ligand; the boron atom is linked to each metal center via a μ_2-hydrogen (H(2) and H(4)), and the other two H atoms (H(1) and H(3)) bridge the B and both Nd atoms in a μ_3 fashion. This coordination type of the borohydride ligand was encountered only once in the cerium compound $[(C_5H_3Bu^t{}_2)_2Ce(BH_4)]_2$.[6] The Nd···B distances (2.875(6) and 2.941(6) Å), which may be compared with the Ce···B distances (2.93(2) Å), are longer than that of 2.664(25) Å determined in $(C_5H_4CH_2CH_2OMe)_2Nd(BH_4)$,[5] the sole neodymium borohydride to have been previously crystallographically characterized. There is apparently no significant difference in the bond distances Nd−μ_2-H and Nd−μ_3-H, or B−μ_2-H and B−μ_3-H, which vary respectively from 2.52 to 2.93 Å and 1.12 to 1.14 Å; the average values of 2.72 and 1.13 Å for the metal−hydrogen and boron−hydrogen distances in **2** are similar to those of 2.69 and 1.19 Å in the cerium complex. The H−B−H angles in **2** range from 99.1(5) to 115.5(5)°, and the tetrahedral BH_4 group seems much less distorted than in the cerium complex, where these angles vary from 87.7(1) to 139.4(1)°. In considering the few bridging borohydride compounds of the f-elements which have been characterized by their crystal structure, it is interesting to note that the $(\mu_3\text{-H})_2B(\mu_2\text{-H})_2$ ligation was observed in the dimeric lanthanide complexes **2** and $[(C_5H_3Bu^t{}_2)_2Ce(BH_4)]_2$ while the $(\mu_2\text{-H})_2B(\mu_2\text{-H})_2$ coordination mode was

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(12) Crystal data for **2**: formula $C_{24}H_{40}B_2O_2Nd_2$, monoclinic, space group $P2_1/c$, $a = 9.801(5)$ Å, $b = 11.430(4)$ Å, $c = 12.576(4)$ Å, $\beta = 110.11(3)°$, $V = 1323(1)$ Å^3, $Z = 2$, $d_{calcd} = 1.684$ g cm^{-3}. X-ray diffraction data were collected at room temperature on an Enraf-Nonius diffractometer with graphite-monochromated Mo Kα radiation. Reflections (1736) with $2° < 2\theta < 50°$ were collected by the $\omega/2\theta$-scan technique. Three standard reflections were measured after each 1 h; a decay was observed (2% in 49 h) and linearly corrected. The data were corrected for Lorentz−polarization effects and absorption (ψ scan). The structure was solved by the heavy-atom method and refined by full-matrix least squares with anisotropic thermal parameters for non-hydrogen atoms. H atoms of the BH_4 ligand were found in the last Fourier diffraction map and introduced in the refinement at fixed positions. The COT and THF H atoms were introduced at calculated positions (C−H = 0.95 Å, $B = 6$ Å^2) and constrained to ride on their C atoms. All calculations were performed on a Vax 4000-200 computer with the Enraf-Nonius MolEN system. The final R factor was 0.020 ($R_w = 0.032$) for 1736 reflections with $|F_o| > 3\sigma(F_o)$. Crystal data for **3**: formula $C_{48}H_{60}BO_4Nd$, monoclinic, space group $P2_1/n$, $a = 11.275(7)$ Å, $b = 26.972(7)$ Å, $c = 13.936(2)$ Å, $\beta = 91.33(3)°$, $V = 4237(4)$ Å^3, $Z = 4$, $d_{calcd} = 1.342$ g cm^{-3}. X-ray diffraction data were collected at room temperature on an Enraf-Nonius diffractometer with graphite-monochromated Mo Kα radiation. Reflections (3550) with $2° < 2\theta < 44°$ were collected by the $\omega/2\theta$-scan technique. Three standard reflections were measured after each 1 h; a decay was observed (8% in 55 h) and linearly corrected. The data were corrected for Lorentz−polarization effects and absorption (ψ scan). The structure was solved by the heavy-atom method and refined by full-matrix least squares with anisotropic thermal parameters for non-hydrogen atoms. H atoms were introduced at calculated positions (C−H = 0.95 Å, $B = 6$ Å^2) and constrained to ride on their C atoms. All calculations were performed on a Vax 4000-200 computer with the Enraf-Nonius MolEN system. The final R factor was 0.035 ($R_w = 0.039$) for 3550 reflections with $|F_o| > 3\sigma(F_o)$.

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found in the polymeric uranium compounds $U(BH_4)_4$[14] and $U(BH_4)_4(OR_2)$ (R = Me, Et).[15]

Cationic complexes of the early transition metals and f-elements deserve special attention, since their participation in some catalytic processes has been recognized. With the exception of $[(Cp^*)La(CH\{SiMe_3\}_2)(THF)_3][BPh_4]$,[16] all the cationic organolanthanide complexes reported so far are bis(cyclopentadienyl) derivatives; these were most generally prepared by oxidation of the corresponding divalent compounds,[17] heterolytic cleavage of a metal-halide bond,[18] or protonolysis of a metal−carbon[16,17d,19] or metal−nitrogen[20] bond. We found that borohydride complexes could also be convenient precursors of cationic species, by protonation with acidic ammonium salts.[21] Treatment of **1** (545 mg, 1.30 mmol) with $NHEt_3BPh_4$ (548 mg, 1.30 mmol) in THF (40 mL) led, after 3 h at room temperature, to the formation of a pale green powder of $[(COT)Nd(THF)_4][BPh_4]$ (**3**), which was deposited from the light green solution; after filtering and drying under vacuum, **3** was isolated in 35% yield (390 mg, 0.46 mmol). Not surprisingly, **3** reacted with KBH_4 to give back the neutral complex **1** (quantitative yield by NMR). The NMR spectrum of **3** in pyridine-d_5 shows the COT signal at −10.88 ppm.[10] The crystals of **3** are composed of discrete cation−anion pairs.[12] The BPh_4 anion displays the expected geometry; an ORTEP drawing of the cation is represented in Figure 2. The Nd atom is in a slightly distorted square pyramidal environment; the COT−Nd−O and O−Nd−O angles average respectively 123(5) and 72.5(5)°. Coordination of the COT and THF ligands is unexceptional, with average Nd−C and Nd−O bond distances of 2.64(2) and 2.53(2) Å.

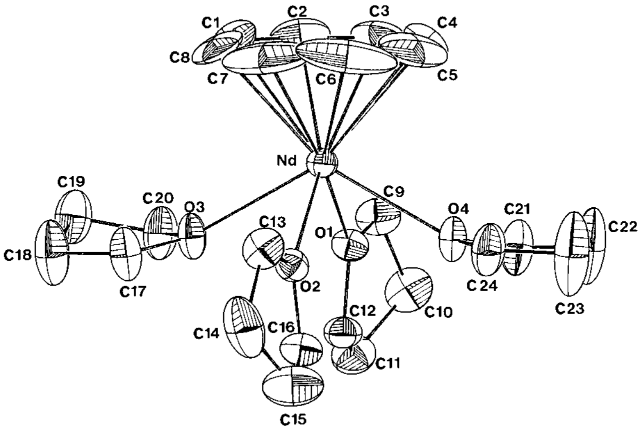

Figure 2. ORTEP drawing of $[(COT)Nd(THF)_4]^+$ with probability ellipsoids drawn at the 30% level.

Complexes **2** and **3** are valuable precursors for the synthesis of (COT)NdX derivatives, by reaction with anionic ligands (Scheme 1). For example, the mixed-ring compound (COT)Nd(Cp*)(THF) (**4**) was readily obtained in ca. 75% yield by treatment with 1 equiv of KCp* in THF and was isolated as a green powder after the usual workup. Ring opening of THF did not occur, in contrast to that observed in similar reactions of $[(Cp^*)_2Ln(THF)_x]^+$,[17b,22] suggesting that a COT ligand on a cation makes it less electrophilic than two Cp* ligands. Complex **4** is a new member of the family of compounds $(COT)Ln(Cp^*)(THF)_x$ ($x = 0, 1$); as expected from previous studies, the THF ligand in **4** is firmly attached to the metal center.[23] Further studies of the synthesis, structure, and reactivity of organolanthanide borohydride complexes are continuing.

Supporting Information Available: Tables giving positional and thermal parameters and bond distances and angles for **2** and **3** (20 pages). Ordering information is given on any current masthead page.

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