Lanthanide Borohydrides as Precursors to Organometallic Compounds. Mono(cyclooctatetraenyl) Neodymium Complexes

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Reactions of $Nd(BH_4)_3(THF)_3$ (**1**) with KCp* (Cp* = η-C_5Me_5), KC_4Me_4P, and $K_2C_8H_8$ gave the organometallic derivatives $(Cp^*)Nd(BH_4)_2(THF)_2$ (**2**), $[K(THF)][(C_4Me_4P)_2Nd(BH_4)_2]$ (**3**), and $(COT)Nd(BH_4)(THF)_2$ (**4**) (COT = η-C_8H_8), respectively. Treatment of **4** with NEt_3HBPh_4 afforded the cationic complex $[(COT)Nd(THF)_4][BPh_4]$ (**5**). The mixed ring compound (COT)-Nd(Cp*)(THF) (**6**), the alkoxide $[(COT)Nd(OEt)(THF)]_2$ (**7**), and the thiolates $Na[(COT)Nd(S^tBu)_2]$ (**8**) and $[Na(THF)_2][\{(COT)Nd\}_2(S^tBu)_3]$ (**9**) were synthesized by treating **4** or **5** with the alkali metal salt of the corresponding anionic reagent. The X-ray crystal structures of **7** and of a toluene solvate of **9** have been determined.

Introduction

Covalent borohydride complexes of d-transition metals, with the exception of those of group IV, are generally thermally unstable and readily decompose into the corresponding hydrides with elimination of diborane.[1] In contrast, f-element borohydrides can be easily isolated, thus allowing structural and chemical studies of the BH_4 ligand.[1−3] Quite a number of inorganic and organometallic complexes have been synthesized from $U(BH_4)_4$ and $U(BH_4)_3(THF)_3$. These compounds, which are in some cases more stable than their chloride analogues, can be themselves conveniently converted into new derivatives by further substitution of the borohydride groups with anionic reagents or proton acidic substrates.[3] By comparison, it seems peculiar that the potential of the rare earth borohydrides $Ln(BH_4)_3(THF)_n$ remained almost unexplored, although these have been known for a long time.[4,5] Recently, we reported in a preliminary communication the first chemical transformations of a lanthanide borohydride, $Nd(BH_4)_3(THF)_3$ (**1**) (THF = tetrahydrofuran), with the syntheses of $(COT)Nd(BH_4)(THF)_2$ (**4**) (COT = η-C_8H_8), the first cyclooctatetraenyl lanthanide borohydride, and $[(COT)Nd(THF)_4][BPh_4]$ (**5**), a unique example of a cyclooctatetraenyl lanthanide cation.[6] The borohydride **1** also served to prepare the cyclopentadienyl and phospholyl compounds $(Cp^*)Nd(BH_4)_2(THF)_2$ (**2**) (Cp* = η-C_5Me_5) and $[K(THF)][(C_4Me_4P)_2Nd(BH_4)_2]$ (**3**), which are introduced in this paper. Moreover, complexes **4** and **5** have proved to be useful precursors to mono-COT neodymium derivatives. Such compounds, which have been so far prepared from the chloride $[(COT)NdCl(THF)_2]_2$, were rather uncommon, and in particular, no alkoxide nor thiolate members of this family have been reported.[2,7] Here we present the synthesis and characterization of the mixed sandwich complex (COT)Nd(Cp*)(THF) (**6**), the alkoxide $[(COT)Nd(OEt)(THF)]_2$ (**7**), and the thiolates $Na[(COT)Nd(S^tBu)_2]$ (**8**) and $[Na(THF)_2][\{(COT)Nd\}_2(S^tBu)_3]$ (**9**); we also describe the crystal structures of **7** and of a toluene solvate of **9**.

Results and Discussion

Synthesis of $Nd(BH_4)_3(THF)_3$ (1). The neodymium borohydride **1** was first obtained by Mirsaidov et al., from the reaction of $NdCl_3$ with a 50−100% excess of $NaBH_4$ in THF.[5] We found that this compound could be more conveniently prepared using only a 10% excess of $NaBH_4$ and stirring the reaction mixture over 48 h at 60 °C, instead of 12 h at 20 °C. After evaporation of THF and drying at 20 °C under vacuum (10^{-3} Torr), the pale violet powder of **1** was isolated in 94% yield. The neodymium triflate $Nd(OSO_2CF_3)_3$ proved to be inferior to $NdCl_3$ as precursor for the synthesis of **1**, because of the solubility of $NaOSO_3CF_3$ in THF, which impeded its elimination by filtration.

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Synthesis of $(Cp^*)Nd(BH_4)_2(THF)_2$ (2), $[K(THF)][(C_4Me_4P)_2Nd(BH_4)_2]$ (3), and $(COT)Nd(BH_4)(THF)_2$ (4). The mono(pentamethylcyclopentadienyl) complex **2** was synthesized by reacting **1** with 1 equiv of KCp* in THF, according to eq 1, and was isolated as a pale blue

$$\underset{\mathbf{1}}{Nd(BH_4)_3(THF)_3} + KCp^* \xrightarrow{THF} \underset{\mathbf{2}}{(Cp^*)Nd(BH_4)_2(THF)_2} + KBH_4 \quad (1)$$

powder in 96% yield. The IR spectrum is quite complex, displaying strong bands at 2361, 2337, 2291, and 2216 cm^{-1}. This would suggest the presence of both tridentate and bidentate BH_4 ligands,[1] thus indicating that **2** might adopt a monomeric structure in the solid state. This structure would differ from that of the halides Cp^*LnX_2 (X = Cl, Br, I), which form either monomeric adducts with one more THF molecule or "ate" species,[2] such as $(Cp^*)Nd(\mu\text{-}Cl)_3Na(Et_2O)$,[8] with retention of the alkali metal halide in the complex. Upon drying under vacuum at 65 °C, **2** was desolvated into $(Cp^*)Nd(BH_4)_2$, which is most likely polymeric in the solid state, as shown by a unique strong IR absorption at 2291 cm^{-1}, characteristic of bridging borohydride ligands.[1,9]

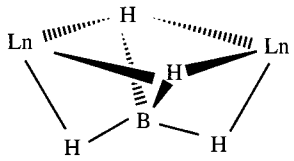
In contrast to reaction 1, which gave a neutral compound, reaction of **1** with the potassium salt of the tetramethylphospholyl anion KC_4Me_4P readily afforded the anionic complex **3** as the most stable product; the latter was obtained as a pale blue powder in almost quantitative yield, according to eq 2. Formation of **3** as

$$\underset{\mathbf{1}}{Nd(BH_4)_3(THF)_3} + 2KC_4Me_4P \xrightarrow{THF} \underset{\mathbf{3}}{[K(THF)][(C_4Me_4P)_2Nd(BH_4)_2]} + KBH_4 \quad (2)$$

an "ate" complex can be easily rationalized by the much weaker electron-donating ability of the C_4Me_4P ligand compared with the isosteric Cp* group. This distinct property of the phospholyl ligand had been clearly illustrated by the redox behavior and coordination chemistry of a variety of uranium compounds.[10,11] Complex **3** is a new example of a bis(phospholyl) lanthanide(III) derivative, which include $[(C_4Me_4P)_2LnCl_2]^-$ (Ln = Y, Nd, Sm, Lu), $(C_4Me_4P)_2Ln(CH\{SiMe_3\}_2)$ (Ln = Nd, Sm), and $(C_4Me_4P)_2NdH$.[12] Complexes **2** and **3** also represent the only organometallic bis-borohydride derivatives of a lanthanide(III).

Treatment of **1** with $K_2C_8H_8$ in THF readily afforded the mono(cyclooctatetraenyl) compound **4**, as shown in eq 3; the green powder of **4** was obtained in almost quantitative yield. In the IR spectrum, the sharp stretch at 2424 cm^{-1} and the broad band centered at 2000 cm^{-1} indicate that the BH_4 ligand is tridentate and nonbridging.[1] Complex **4** would thus adopt a monomeric structure, in contrast with the chloride analogue $[(COT)NdCl(THF)_2]_2$, which exists in the solid state as a dimer with Cl bridges.[13]

Scheme 1



$$\underset{\mathbf{1}}{Nd(BH_4)_3(THF)_3} + K_2C_8H_8 \xrightarrow{THF} \underset{\mathbf{4}}{(COT)Nd(BH_4)(THF)_2} + 2KBH_4 \quad (3)$$

The structural differences observed between **2** or **4** and their chloride analogues, which cannot be explained by steric factors since the BH_4 and Cl ligands are isosteric,[14] reflect the greater electron-donating ability of the borohydride group. It has been already pointed out, in uranium chemistry, that borohydride compounds are more electron rich than their chloride counterparts and more reluctant to form either dimers, adducts with Lewis bases, or "ate" complexes; as a consequence, borohydride ligands would favor the formation of more sterically unsaturated compounds.[15]

The THF ligands of **4** were displaced by pyridine, and $(COT)Nd(BH_4)(C_5H_5N)_2$ was found, by molecular weight determination, to be monomeric in this solvent. Dissociation of a THF ligand from **4** occurred in benzene to afford green crystals of $[(COT)Nd(BH_4)(THF)]_2$. In the IR spectrum of this dimer, the single broad and strong absorption centered at 2255 cm^{-1} is characteristic of bridging borohydride ligands.[1,9] The dimeric crystal structure of $[(COT)Nd(BH_4)(THF)]_2$ has been described in detail in the preliminary communication;[6] the most salient feature is the $(\mu_3\text{-}H)_2B(\mu_2\text{-}H)_2$ coordination mode of the BH_4 ligand, represented in Scheme 1, which was encountered only once in the cerium compound $[(C_5H_3{}^tBu_2)_2Ce(BH_4)]_2$, the only other crystallographically characterized lanthanide complex with bridging BH_4 ligands.[9] Bridging borohydride complexes of the f-elements are in fact very rare, and it is noteworthy that the more familiar $(\mu_2\text{-}H)_2B(\mu_2\text{-}H)_2$ ligation mode of the BH_4 group has been found only in the polymeric uranium compounds $U(BH_4)_4$ and $U(BH_4)_4(OR_2)$ (R = Me, Et).[16]

Synthesis of $[(COT)Nd(THF)_4][BPh_4]$ (5). The cationic complex **5** was synthesized by treating **4** with a slight excess of NEt_3HBPh_4 in THF, according to eq

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4, and isolated as a green microcrystaline powder in 75% yield. The crystal structure of **5**, which has also been previously presented,[6] shows the Nd atom in a slightly distorted square pyramidal environment.

$$\underset{\mathbf{3}}{(COT)Nd(BH_4)(THF)_2} + NEt_3HBPh_4 \xrightarrow{THF} \underset{\mathbf{5}}{[(COT)Nd(THF)_4][BPh_4]} + BH_3{\cdot}NEt_3 + 0.5H_2 \quad (4)$$

Cationic complexes of the d-transition metals and f-elements currently deserve special attention since they are potential precursors in inorganic and organometallic synthesis as well as efficient catalysts in a number of organic reactions. These complexes are most generally prepared by oxidation of the corresponding divalent compounds,[17] heterolytic cleavage of a metal−halide[18a,b] or metal−carbon[18c] bond, or protonolysis of a metal−carbon[19] or metal−nitrogen[20] bond. Except [(Cp*)La(CH{SiMe$_3$}$_2$)(THF)$_3$][BPh$_4$][19a] and the highly unstable cation [Y(MAC)(CH$_2$SiMe$_3$)][B(C$_6$F$_5$)$_3$(CH$_2$SiMe$_3$)] (MAC = deprotonated aza-18-crown-6),[18c] all the cationic organolanthanide complexes so far reported are biscyclopentadienyl derivatives. Protonolytic cleavage of the M−BH$_4$ bond with an acidic ammonium salt thus proved to be an efficient alternative route to such complexes. Besides the preparation of **5**, this method was valuable for the synthesis of the uranium(III) cation [U(BH$_4$)$_2$(THF)$_5$][BPh$_4$][21] and, more recently, of [(COT)U(BH$_4$)(THF)$_2$][BPh$_4$] and [(COT)U(HMPA)$_3$][BPh$_4$]$_2$, which are the first cationic organometallic borohydride and the first organometallic dication of an f-element, respectively.[22] This protonolysis reaction was also useful for the preparation of the zirconium borohydride complexes [(C$_5$H$_4$R)$_2$Zr(BH$_4$)(THF)][BPh$_4$].[23]

Synthesis of (COT)Nd(Cp*)(THF) (6). The mixed cyclopentadienyl−cyclooctatetraenyl complex **6** was prepared either by reaction of **2** with 1 equiv of K$_2$C$_8$H$_8$ or by treatment of **4** or **5** with KCp* in THF, according to eqs 5−7; whatever its mode of preparation, the green product was isolated with yields greater than 77%.

$$\underset{\mathbf{2}}{(Cp^*)Nd(BH_4)_2(THF)_2} + K_2C_8H_8 \xrightarrow{THF} \underset{\mathbf{6}}{[(COT)Nd(Cp^*)(THF)} + 2KBH_4 \quad (5)$$

$$\underset{\mathbf{4}}{(COT)Nd(BH_4)(THF)_2} + KCp^* \xrightarrow{THF} \underset{\mathbf{6}}{(COT)Nd(Cp^*)(THF)} + KBH_4 \quad (6)$$

$$\underset{\mathbf{5}}{[(COT)Nd(THF)_4][BPh_4]} + KCp^* \xrightarrow{THF} \underset{\mathbf{6}}{(COT)Nd(Cp^*)(THF)} + KBPh_4 \quad (7)$$

Complex **6** is a new member of the (COT)Ln(Cp*)(THF)$_x$ series (Ln = Ce, Pr, Sm, Gd, Tb, Dy, Er, Yb, Lu). These compounds, which were most generally prepared by metathesis reaction of (COT)LnCl(THF)$_n$ with NaCp*, could be obtained unsolvated for lanthanides smaller than Sm.[24] That the THF ligand in **6** remains attached to the metal center is in full agreement with this trend, which simply reflects the lanthanide contraction.

Synthesis and X-ray Crystal Structure of [(COT)Nd(OEt)(THF)]$_2$ (7). Treatment of **4** or **5** with 1 equiv of NaOEt in THF gave the alkoxide compound **7** in 77 and 71% yield, respectively, according to eqs 8 and 9; pale blue crystals of **7** were formed from a THF−pentane solution.

$$\underset{\mathbf{4}}{(COT)Nd(BH_4)(THF)_2} + NaOEt \xrightarrow{THF} 1/2\underset{\mathbf{7}}{[(COT)Nd(OEt)(THF)_2} + NaBH_4 \quad (8)$$

$$\underset{\mathbf{5}}{[(COT)Nd(THF)_4][BPh_4]} + NaOEt \xrightarrow{THF} 1/2\underset{\mathbf{7}}{[(COT)Nd(OEt)(THF)]_2} + NaBPh_4 \quad (9)$$

Reactions 8 and 9 represent alternative routes to monocyclooctatetraenyl lanthanide alkoxide complexes. Indeed, they have been so far most usually synthesized by metathetical exchange between (COT)LnCl(THF)$_n$ and the appropriate sodium alkoxide. Such compounds are limited to the monomeric derivatives (COT)Ln(OR)(THF) (Ln = Y, Lu and R = C^{t}Bu$_3$, SiPh$_3$)[25] and the dimeric species [(COT)Ln(OR)(THF)]$_2$ (Ln = Y, Lu and R = Ph or C$_6$H$_3$Me$_2$-2,6;[25] Ln = Dy and R = (CH$_2$)$_3$CH=CH$_2$);[26] only this dysprosium complex and [(COT)Y(OPh)(THF)]$_2$ have been characterized by X-ray crystallography.

A drawing of **7** is shown in Figure 1, and selected bond distances and angles are listed in Table 1. The structure is built up of two monomeric units that are linked by two alkoxide ligands. The configuration of the dinuclear molecule is edge-sharing bitetrahedral, considering the

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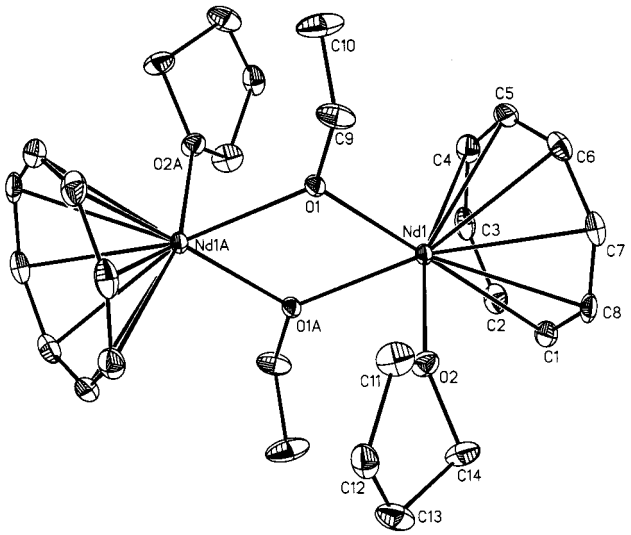

Figure 1. Molecular structure of $[(COT)Nd(OEt)(THF)]_2$ with thermal ellipsoids drawn at the 30% level.

Table 1. Selected Bond Distances (Å) and Angles (deg) for $[(COT)Nd(OEt)(THF)]_2$

Nd(1)−C(1)	2.696(4)	Nd(1)−C(2)	2.703(4)
Nd(1)−C(3)	2.694(4)	Nd(1)−C(4)	2.693(4)
Nd(1)−C(5)	2.678(4)	Nd(1)−C(6)	2.687(4)
Nd(1)−C(7)	2.690(4)	Nd(1)−C(8)	2.688(4)
Nd(1)−O(1)	2.344(3)	Nd(1)−O(1A)	2.343(2)
Nd(1)−O(2)	2.508(3)		
O(1)−Nd(1)−O(1A)	70.88(10)	O(1)−Nd(1)−O(2)	81.89(9)
O(1A)−Nd(1)−O(2)	87.03(10)	Nd(1)−O(1)−Nd(1A)	109.12(10)

COT ligand as monodentate. This geometry is similar to that of the other two crystallographically characterized $[(COT)Ln(OR)(THF)]_2$ compounds;[25,26] by symmetry, the two planar COT rings are parallel and the four-membered $(NdO)_2$ ring forms a lozenge. The Nd−C distances range from 2.678(4) to 2.703(4) Å, and the average Nd−C(COT) length is 2.69(1) Å, which is virtually identical to that encountered in $(COT)Nd(C_5H_4CH_2CH_2OMe)$ (2.697(2) Å)[27] and $(COT)Nd(2,4\text{-}C_7H_{11})$ (2.65(7) Å).[28] The Nd−O(1) bond length of 2.344(3) Å as well as the Nd−O(1)−Nd and O(1)−Nd−O(1) angles of 109.1(1)° and 70.9(1)° are quite similar to the corresponding values of 2.38(1) Å, 107(1)°, and 72(1)° found in $Nd_2(OCH^iPr)_6L_2$ (L = THF, C_5H_5N).[29] These M−O distances and these M−O−M and O−M−O angles can also be compared with those determined within the $(MO)_2$ rings of the yttrium complex $[(COT)Y(OPh)(THF)]_2$ (2.29(7) Å, 107(1)° and 72(1)°);[25] the observed bond length difference corresponds to the trend in the metallic ion radii of Nd^{3+} (1.109 Å) and Y^{3+} (1.019 Å).[30] The bridging oxygen atom O(1) is sp^2 hybridized, being bonded to the adjacent carbon atom C(9) and to the metallic centers with a planar coordination. The two Nd atoms are separated by 3.819(3) Å, precluding any bonding interaction.

Synthesis of $Na[(COT)Nd(S^tBu)_2]$ (8) and $[Na(THF)_2][\{(COT)Nd\}_2(S^tBu)_3]$ (9); X-ray Crystal Structure of a Toluene Solvate of 9. The first organometallic neodymium thiolate compound **8** was prepared by treating **4** or **5** with 2 equiv of NaS^tBu in THF and was isolated in 88% yield as a pale green powder. The monothiolate complexes $Na[(COT)Nd(BH_4)(S^tBu)]$ and $(COT)Nd(S^tBu)(THF)_x$ were found, by NMR spectroscopy, to be intermediates in reactions 10 and 11, respectively.

Complex **8**, like **6** and **7**, was more conveniently prepared from the cation **5** rather than the borohydride **4**, thus highlighting the superiority of the cation in synthesis.

$$\underset{\mathbf{4}}{(COT)Nd(BH_4)(THF)_2} + 2NaS^tBu \xrightarrow{THF} \underset{\mathbf{8}}{Na[(COT)Nd(S^tBu)_2]} + NaBH_4 \quad (10)$$

$$\underset{\mathbf{5}}{[(COT)Nd(THF)_4][BPh_4]} + 2NaS^tBu \xrightarrow{THF} \underset{\mathbf{8}}{Na[(COT)Nd(S^tBu)_2]} + NaBPh_4 \quad (11)$$

That reactions 10 and 11 readily gave the anionic product **8**, in contrast with those of **4** or **5** with NaOEt which afforded the neutral complex **7** (eqs 8 and 9), can be accounted for by the weaker electron-donating power of the thiolate group. The distinct electronic effects of the SR and OR ligands have been clearly pointed out with uranium complexes.[31] For example, reactions of UCl_4 with 4 equiv of alkali metal thiolate or alkoxide reagents led to the formation of the anion $[U(SR)_6]^{2-}$ [32] or the neutral compound $U(OR)_4$,[33] respectively. However, the other monocyclooctatetraenyl lanthanide thiolate complexes so far reported are the neutral dimeric samarium derivatives $[(COT)Sm(SAr)(THF)_n]_2$ (Ar = Ph or $C_6H_2Me_3$-2,4,6 and $n = 2$; Ar = $C_6H_2{}^iPr_3$-2,4,6 and $n = 1$)[34] and the mononuclear HMPA adduct $(COT)Sm(SC_6H_2{}^iPr\text{-}2,4,6)(HMPA)_2$.[35] The latter have been in fact synthesized by reaction of samarium metal with cyclooctatetraene and diarylsulfide, to avoid the formation of "ate" complexes.

Crystallization of **8** from THF−toluene afforded pale green crystals of $[Na(THF)_2][\{(COT)Nd\}_2(S^tBu)_3]$ (**9**), which were obviously formed by coupling of two complexes **8** with elimination of 1 equiv of NaS^tBu. The sodium salt was firmly attached in **9**, which was not further transformed into $[(COT)Nd(S^tBu)(THF)_x]_2$.

The crystal structure of a toluene solvate of **9** is shown in Figure 2; selected bond distances and angles are listed in Table 2. The two (COT)Nd fragments are bridged by three S^tBu groups, two of these being coordinated to the $Na(THF)_2$ moiety. Each Nd atom has a pseudo-tetrahedral arrangement, if the cyclooctatetraenyl group is considered as a monodentate ligand. The

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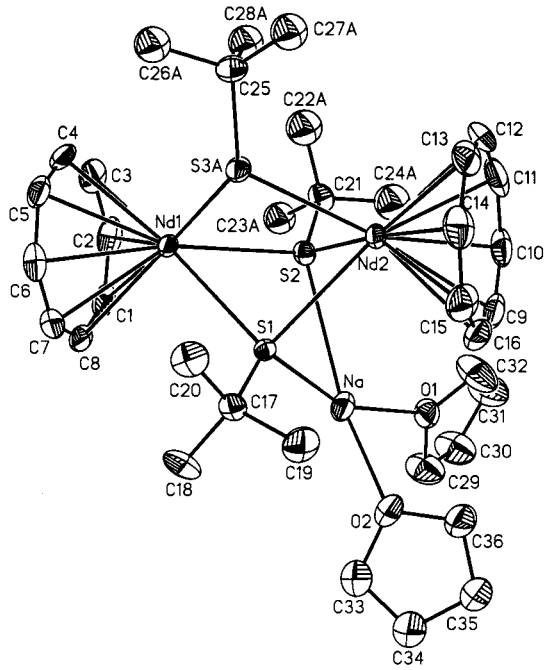

Figure 2. Molecular structure of $[Na(THF)_2][\{(COT)Nd\}_2(S^tBu)_3]$ with thermal ellipsoids drawn at the 20% level. One of the two disordered S^tBu and ^tBu groups is represented (see text).

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Na(THF)_2][\{(COT)Nd\}_2(S^tBu)_3]\cdot$toluene

Nd(1)−C(1)	2.651(8)	Nd(1)−C(2)	2.650(8)	Nd(1)−C(3)	2.669(8)
Nd(1)−C(4)	2.679(8)	Nd(1)−C(5)	2.695(8)	Nd(1)−C(6)	2.667(8)
Nd(1)−C(7)	2.663(8)	Nd(1)−C(8)	2.656(8)	Nd(2)−C(9)	2.673(8)
Nd(2)−C(10)	2.667(8)	Nd(2)−C(11)	2.647(9)	Nd(2)−C(12)	2.661(9)
Nd(2)−C(13)	2.683(9)	Nd(2)−C(14)	2.676(9)	Nd(2)−C(15)	2.671(9)
Nd(2)−C(16)	2.669(8)	Nd(1)−S(1)	2.912(2)	Nd(1)−S(2)	2.931(2)
Nd(1)−S(3A)	2.883(2)	Nd(1)−S(3B)	2.896(10)	Nd(2)−S(1)	2.949(2)
Nd(2)−S(2)	2.946(2)	Nd(2)−S(3A)	2.892(2)	Nd(2)−S(3B)	2.852(10)
Na−S(1)	2.884(3)	Na−S(2)	3.160(4)	Na−O(1)	2.294(7)
Na−O(2)	2.393(7)				

S(1)−Nd(1)−S(2)	64.36(5)	S(1)−Nd(1)−S(3A)	75.02(6)
S(1)−Nd(1)−S(3B)	86.9(2)	S(2)−Nd(1)−S(3A)	85.99(7)
S(2)−Nd(1)−S(3B)	71.3(2)	S(1)−Nd(2)−S(2)	63.72(5)
S(1)−Nd(2)-S(3A)	74.32(6)	S(1)−Nd(2)−S(3B)	87.0(2)
S(2)−Nd(2)−S(3A)	85.55(6)	S(2)−Nd(2)−(3B)	71.7(2)
Nd(1)−S(1)−Nd(2)	88.81(5)	Nd(1)−S(2)−Nd(2)	88.50(5)
Nd(1)−S(3A)−Nd(2)	90.51(7)	Nd(1)−S(3B)−Nd(2)	91.0(3)
S(1)−Na−S(2)	61.78(7)	O(1)−Na−O(2)	86.5(3)

two tetrahedra share the common trigonal basis defined by the S atoms. This basal plane is parallel to the planar COT rings and perpendicular to the COT(centroid)−Nd(1)−Nd(2)−COT(centroid) axis; Nd(1) and Nd(2) are at 2.044(2) and 2.057(2) Å from this plane, respectively. The COT ligation is quite similar to that found in **7**, with an average Nd−C bond length of 2.67(3) Å. The Nd−S−Nd angles range from 88.50(5)° to 91.0(3)° (average 90(2)°); the S(1)−Nd−S(2) angles (64(1)°) are smaller than the other S−Nd−S angles, which vary from 71.3(2)° to 87.0(2)°, due to coordination of S(1) and S(2) to the sodium atom. The Na−S(1) and Na−S(2) distances of 2.884(3) and 3.160(4) Å can be compared with those of 2.965(8) and 3.060(3) Å in $[Na(THF)_3]_2[U(SR)_6]$ (R = ^{t}Bu or Ph)[32] and 3.014(9) Å in [Na(18-crown-6)][$W(CO)_5(SH)$].[36]

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Conclusion

The results reported here demonstrate that the lanthanide borohydride $Nd(BH_4)_3(THF)_3$ is, like $U(BH_4)_4$ and $U(BH_4)_3(THF)_3$, a valuable precursor for the synthesis of various organometallic derivatives. Substitution of the BH_4 ligand with the alkali metal salts of anionic reagents enabled the preparation of pentamethylcyclopentadienyl, cyclooctatetraenyl, and tetramethylphospholyl compounds. The two complexes (COT)-$Nd(BH_4)(THF)_2$ and $[(COT)Nd(THF)_4][BPh_4]$ were useful for the development of the chemistry of mono(cyclooctatetraenyl) neodymium compounds. A variety of (COT)-NdX derivatives, with X = Cp*, C_4Me_4P, OEt, or S^tBu, were obtained; the structure of these monomeric, dimeric, or "ate" complexes was found to depend essentially on the electronic effects of the X ligand.

Experimental Section

All preparations and reactions were carried out under argon (<5 ppm oxygen or water) using standard Schlenk-vessel and vacuum-line techniques or in a glovebox. Solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately before use. Deuterated solvents were dried over Na−K alloy.

Elemental analyses and molecular weight determination were performed by Analytische Laboratorien at Lindlar (Germany). The ^{1}H NMR spectra were recorded on a Bruker DPX 200 instrument and were referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0). The ^{31}P NMR spectra were recorded on a Bruker AC 200 instrument, the external reference being 85% H_3PO_4. The IR spectra were obtained on a Perkin-Elmer 1725X spectrometer. $NdCl_3$ (Aldrich) was used without purification, KC_4Me_4P was prepared by the published method,[10a] and the salt NEt_3-$HBPh_4$ was made by mixing NEt_3HCl and $NaBPh_4$ in water.

$Nd(BH_4)_3(THF)_3$ (1). A flask was charged with $NdCl_3$ (5.590 g, 22.3 mmol) and $NaBH_4$ (2.786 g, 73.6 mmol), and THF (75 mL) was condensed in. The reaction mixture was stirred at 60 °C for 48 h. The solvent was evaporated off and the residue dried under dynamic vacuum for 18 h. The solid was thoroughly extracted with THF (50 mL), and the solution was then filtered and evaporated to dryness at 20 °C (10^{-3} Torr), leaving the product as a pale violet powder (8.50 g, 94%). ^{1}H NMR (pyridine-d_5): δ 79 ($w_{1/2}$ = 1350 Hz, 12H, BH_4), 3.48 and 1.45 (s, 12H + 12H, THF); (THF-d_8): δ 92 ($w_{1/2}$ = 470 Hz, BH_4).

(Cp*)$Nd(BH_4)_2(THF)_2$ (2). A flask was charged with **1** (465.9 mg, 1.15 mmol) and KCp* (200.5 mg, 1.15 mmol), and THF (50 mL) was condensed in. The reaction mixture was stirred at 20 °C for 20 h, and after filtration, the light blue solution was evaporated to dryness, leaving the pale blue powder of **2** (500.5 mg, 96%). ^{1}H NMR (pyridine-d_5): δ 67 ($w_{1/2}$ = 950 Hz, 8H, BH_4), 10.0 (br s, $w_{1/2}$ = 85 Hz, 15H, Cp*), 3.54 and 1.45 (s, 8H + 8H, THF); (THF-d_8): δ 69 ($w_{1/2}$ = 750 Hz, 8H, BH_4), 7.4 (br s, $w_{1/2}$ = 110 Hz, 15H, Cp*). IR (Nujol): 2361, 2337, 2291, and 2216 s cm^{-1}. Upon drying under vacuum at 65 °C, **2** was transformed into the solvent-free compound (Cp*)-$Nd(BH_4)_2$. Anal. Calcd for $C_{10}H_{23}B_2Nd$: C, 38.85; H, 7.50; B, 6.99. Found: C, 38.44; H, 7.34; B, 7.07. IR (Nujol): 2421 w, 2291 s, 2218 m cm^{-1}.

$[K(THF)][(C_4Me_4P)_2Nd(BH_4)_2]$ (3). A flask was charged with **1** (77.0 mg, 0.19 mmol) and KC_4Me_4P (69.5 mg, 0.39 mmol), and THF (25 mL) was condensed in. After 18 h at 20 °C, the off-white precipitate of KBH_4 was filtered off and the pale blue solution evaporated. The light blue powder of **3** thus obtained was washed with cold THF (5 mL) and dried under vacuum (103.8 mg, 97%). Anal. Calcd for $C_{20}H_{40}B_2OP_2KNd$: C, 42.63; H, 7.16; P, 10.99. Found: C, 42.40; H, 6.98; P, 10.74. ^{1}H NMR (pyridine-d_5): δ 52 (br, $w_{1/2}$ = 430 Hz, 8H, BH_4), 14.3

(s, $w_{1/2}$ = 80 Hz, 12H, Me), 3.65 (s, 4H, THF), 2.6 (s, $w_{1/2}$ = 70 Hz, 12H, Me), 1.61 (s, 4H, THF); (THF-d_8): δ 49 (br, $w_{1/2}$ = 360 Hz, BH_4), 14.2 (s, $w_{1/2}$ = 40 Hz, 12H, Me), 2.0 (s, $w_{1/2}$ = 35 Hz, 12H, Me). ^{31}P NMR (THF-d_8): δ 413.

(COT)Nd(BH$_4$)(THF)$_2$ (4). A flask was charged with **1** (2.220 g, 5.48 mmol) and $K_2C_8H_8$ (1.001 g, 5.49 mmol), and THF (50 mL) was condensed in. After 20 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 **4** (2.25 g, 98%). 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. Molecular weight in pyridine (osmometry measurement): 389; calcd for $C_{18}H_{22}BN_2Nd$, 421. ^{1}H NMR (pyridine-d_5): δ 44 (br, $w_{1/2}$ = 360 Hz, 4 H, BH_4), 3.49 and 1.45 (s, 8H + 8H, THF), −10.27 (s, 8H, COT). IR (Nujol): 2424 s, 2000 s cm^{-1}. Crystallization of **4** from benzene afforded green crystals of $[(COT)Nd(BH_4)(THF)]_2$, the X-ray crystal structure of which has been previously reported.[6] IR (Nujol): 2255 s cm^{-1}.

Reactions of **4** with either $K_2C_8H_8$, sodium amalgam, LiMe, or KH gave the bisCOT complex M[$(COT)_2$Nd] (M = Li, Na, K). ^{1}H NMR (THF-d_8): δ −8.95 (br s, $w_{1/2}$ = 180 Hz).[37]

[(COT)Nd(THF)$_4$][BPh$_4$] (5). A flask was charged with **4** (713 mg, 1.70 mmol) and NEt_3HBPh_4 (914.5 mg, 2.17 mmol), and THF (50 mL) was condensed in. After 4 h at 20 °C, the solution was filtered and the green powder of **5** washed several times with THF and then dried under vacuum (1.078 g, 75%). 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. ^{1}H NMR (pyridine-d_5): δ 7.89 (br t, 8H, *o*-Ph), 7.10 (t, J = 8.5 Hz, 8H, *m*-Ph), 6.93 (t, J = 7.0 Hz, 4H, *p*-Ph), 3.49 and 1.45 (s, 16H + 16H, THF), −10.88 (s, 8H, COT).

Attempted syntheses of **4** or **5** from NdX_3 (X = OSO_2CF_3, Cl) remained less selective than those using the trisborohydride precursor, because of the solubility of triflate and chloride salts. The reaction of **4** with $TlBPh_4$ or $AgBPh_4$ failed to give the cation **5**; instead unidentified species were formed.

(COT)Nd(Cp*)(THF) (6). (a) From (Cp*)Nd(BH$_4$)$_2$(THF)$_2$ (2). A flask was charged with **2** (145.1 mg, 0.32 mmol) and $K_2C_8H_8$ (58.4 mg, 0.32 mmol), and THF (35 mL) was condensed in. After 4 h at 20 °C, the green solution was filtered and evaporated to dryness, and the residue was extracted with toluene (20 mL). After filtration, evaporation, and drying under vacuum, **6** was recovered as a green powder (112.3 mg, 77%). This represents the most direct preparation of **6**. Anal. Calcd for $C_{22}H_{31}ONd$: C, 57.98; H, 6.86. Found: C, 57.72; H, 6.76. ^{1}H NMR (benzene-d_6): δ 4.95 (br, $w_{1/2}$ = 90 Hz, 15H, Cp*), 3.79 (s, $w_{1/2}$ = 25 Hz, 4H, THF), −3.27 (br s, $w_{1/2}$ = 85 Hz, 4H, THF), −15.9 (br s, $w_{1/2}$ = 135 Hz, 8H, COT).

(b) From (COT)Nd(BH$_4$)(THF)$_2$ (4). An NMR tube was charged with **4** (5.7 mg, 13.7 μmol) and KCp* (2.5 mg, 14.3 μmol) in THF-d_8 (0.5 mL). After 4 h at 20 °C, the spectrum showed the presence of **6** (ca. 85% yield) with other unidentified species.

(c) From [(COT)Nd(THF)$_4$][BPh$_4$] (5). A flask was charged with **5** (196.9 mg, 0.23 mmol) and KCp* (44.7 mg, 0.26 mmol), and THF (30 mL) was condensed in. After 4.5 h at 20 °C, the green solution was filtered and evaporated to dryness, the solid was extracted with toluene (20 mL), and the solution was filtered and evaporated to dryness, leaving the green powder of **6** (91.2 mg, 87%).

[(COT)Nd(OEt)(THF)]$_2$ (7). (a) From (COT)Nd(BH$_4$)(THF)$_2$ (4). A flask was charged with **4** (197.1 mg, 0.47 mmol) and NaOEt (32.0 mg, 0.47 mmol), and THF (25 mL) was condensed in. After 24 h at 20 °C, the off-white precipitate of KBH_4 was filtered off and the pale blue solution evaporated, leaving the blue powder of **7**, which was crystallized from THF−pentane (132.3 mg, 77%). Anal. Calcd for $C_{28}H_{42}O_4Nd_2$: C, 46.00; H, 5.79. Found: C, 46.03; H, 5.66. ^{1}H NMR (THF-d_8): δ 18.4 (br s, $w_{1/2}$ = 150 Hz, 2H, CH_2), 1.31 (br s, $w_{1/2}$ = 60 Hz, 3H CH_3), −6.97 (br s, $w_{1/2}$ = 100 Hz, 8H, COT).

(b) From [(COT)Nd(THF)$_4$][BPh$_4$] (5). A flask was charged with **5** (239.7 mg, 0.28 mmol) and NaOEt (19.1 mg, 0.28 mmol), and THF (30 mL) was condensed in. The flask was immersed in an ultrasound bath (60 W, 40 kHz) for 2.5 h. After filtration, the pale blue solution was evaporated to dryness, leaving the blue powder of **7**, which was crystallized from THF−pentane (72.7 mg, 71%).

Na[(COT)Nd(S^{t}Bu)$_2$] (8). (a) From (COT)Nd(BH$_4$)(THF)$_2$ (4). A flask was charged with **4** (503.3 mg, 1.20 mmol) and NaS^{t}Bu (269.1 mg, 2.40 mmol), and THF (50 mL) was condensed in. After 24 h at 20 °C, the off-white precipitate of KBH_4 was filtered off and the pale green solution evaporated, leaving the green powder of **8**, which was dried under vacuum (474.9 mg, 88%). Anal. Calcd for $C_{16}H_{26}NaS_2Nd$: C, 42.73; H, 5.83; S, 14.26. Found: C, 42.40; H, 5.60; S, 14.08. ^{1}H NMR (THF-d_8): δ −0.6 (br s, $w_{1/2}$ = 30 Hz, 18H, ^{t}Bu), −11.4 (br s, $w_{1/2}$ = 95 Hz, 8H, COT). The reaction monitored by NMR spectroscopy showed the intermediate formation of Na[(COT)Nd(BH$_4$)(S^{t}Bu)]. ^{1}H NMR (THF-d_8): δ 28.9 (br, $w_{1/2}$ = 350 Hz, 4H, BH_4), −0.69 (br s, $w_{1/2}$ = 50 Hz, 9H, ^{t}Bu), −11.74 (s, 8H, COT).

(b) From [(COT)Nd(THF)$_4$][BPh$_4$] (5). An NMR tube was charged with **5** (5.9 mg, 6.9 μmol) and NaS^{t}Bu (0.9 mg, 8.0 μmol) in THF-d_8 (0.5 mL). After 4 h at 20 °C, the spectrum showed the formation of **8** and (COT)Nd(S^{t}Bu)(THF)$_x$. ^{1}H NMR (THF-d_8): δ −2.5 (br s, $w_{1/2}$ = 45 Hz, 9H, ^{t}Bu), −11.8 (br s, $w_{1/2}$ = 70 Hz, 8H, COT). Further addition of NaS^{t}Bu (0.8 mg) led to the complete conversion of **5** into **8**.

[Na(THF)$_2$][{(COT)Nd}$_2$(S^{t}Bu)$_3$] (9). Pale green crystals of **9** were obtained by crystallization of **8** from toluene−THF (ca. 60% yield); these were separated from a white precipitate and dried under vacuum. Anal. Calcd for $C_{36}H_{59}NaO_2S_3Nd_2$: C, 46.42; H, 6.38; S, 10.33. Found: C, 46.36; H, 6.21; S, 10.17. ^{1}H NMR (THF-d_8): δ −0.6 (br s, $w_{1/2}$ = 35 Hz, 27H, ^{t}Bu), −11.3 (br s, $w_{1/2}$ = 95 Hz, 16H, COT).

X-ray Data Collection, Structure Determination, and Refinement for [(COT)Nd(OEt)(THF)]$_2$ (7). Diffraction

Table 3. Crystal Data and Summary of Data Collection and Refinement for [(COT)Nd(OEt)(THF)]$_2$ and [Na(THF)$_2$][{(COT)Nd}$_2$(S^{t}Bu)$_3$]·toluene

	7	**9**·toluene
formula	$C_{28}H_{42}Nd_2O_4$	$C_{43}H_{67}NaNd_2O_2S_3$
fw	731.10	1023.62
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a (Å)	10.225(2)	11.286(2)
b (Å)	12.197(2)	14.805(4)
c (Å)	11.998(2)	15.032(4)
α (deg)	90.00	90.77(2)
β (deg)	109.29(3)	104.18(2)
γ (deg)	90.00	100.26(2)
V (Å^3)	1412.3(5)	2392(3)
Z	2	2
D(calcd) (g/cm^3)	1.719	1.421
μ (cm^{-1})	3.665	2.317
cryst size (mm)	0.25 × 0.20 × 0.20	0.30 × 0.25 × 0.20
radiation type	Mo Kα	Mo Kα
temp (K)	123(2)	293(2)
θ range, deg	2.7−24.7	1.4−23.0
no. of reflns collected	8833	6473
no of reflns merged	2293	6116
no of reflns obsd	1974	5131
observn criterion	$I > 2\sigma(I)$	$I > 2\sigma(I)$
no of params refined	154	416
R^a	0.023	0.037
$R_w{}^b$	0.046	0.095
goodness of fit	0.943	1.070

^{a} $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. ^{b} $R_w = [\sum w(||F_o| - |F_c||)^2/\sum w(|F_o|)^2]^{1/2}$.

(37) Hodgson, K. O.; Mares, F.; Starks, D. F.; Streitwieser, A. *J. Am. Chem. Soc.* **1973**, *95*, 8650.

collection was carried out on a Nonius diffractometer equipped with a CCD detector. The lattice parameters were determined from 10 images recorded with 1° Φ-scans and later refined on all data. A 180° Φ-range was scanned with 2° steps with a crystal-to-detector distance fixed at 30 mm. Data were corrected for Lorentz polarization and absorption effects.[38] The structure was solved by the heavy-atom method and refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for all non H atoms. H atoms were introduced at calculated positions as riding atoms with an isotropic displacement parameter equal to 1.2(CH, CH_2) or 1.5(CH_3) times that of the parent carbon atom. All calculations were performed on an O2 Silicon Graphics Station with the SHELXTL package.[39] Crystal data and summary of data collection and refinement are given in Table 3.

X-ray Data Collection, Structure Determination, and Refinement for a Toluene Solvate of [Na(THF)$_2$][{(COT)Nd}$_2$(S^{t}Bu)$_3$] (9). Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromatized Mo Kα radiation with the ω-scan technique. Data were corrected for Lorentz polarization effects, decay (loss of 0.16% in 29 h, linearly coorected), and absorption (ψ-scans). The structure was solved by the heavy-atom method and refined by full-matrix least-squares. One of the ^{t}BuS groups was found disordered on two sites sharing a common central C atom; the two positions were refined with occupations constrained to sum to unity and isotropic displacement parameters restrained to be roughly equal for the atoms of a same group. Another ^{t}Bu group was disordered with six terminal C atoms, which were refined with occupations constrained to sum to unity and isotropic displacement parameters restrained to be roughly equal for the atoms of a same group. The toluene solvent molecule was refined as a rigid hexagon with isotropic displacement parameters. All nondisordered non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms were introduced at calculated positions as riding atoms with an isotropic displacement parameter equal to 1.2(CH, CH_2) or 1.5(CH_3) times that of the parent carbon atom. All calculations were performed on an O2 Silicon Graphics Station with the SHELXTL package.[39] Crystal data and a summary of data collection and refinement are given in Table 3.

(38) Spek, A. L. *MULABS*. *PLATON*; University of Utrecht, 1997.
(39) Sheldrick, G. M. *SHELXTL*, Program for the Refinement of Crystal Structures; University of Göttingen, 1993.

Supporting Information Available: Tables giving data collection and refinement details, atomic coordinates, thermal parameters, and bond lengths and bond angles of the crystallographically characterized complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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