An Oxide Ion Encapsulating Tetraholmium Tetrahedron Stabilized by Complexation with the “Carbons Apart” C_2B_4-Carborane Ligands

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Received July 7, 2003

Summary: The reaction of closo-exo-5,6-Na(THF)$_2$-1-Na-(THF)$_2$-2,4-(SiMe$_3$)$_2$-2,4-$C_2B_4H_4$ with HoCl$_3$ and H_2O in a molar ratio of 5:4:1 produces the new holmacarborane cluster {[η^5-1-Ho(THF)-2,3-(SiMe$_3$)$_2$-2,3-$C_2B_4H_4$]$_4$(μ-Cl)$_2$-(μ_4-O)} *as a pale yellow crystalline solid in 86% yield. The crystal structure shows that the core of the cluster consists of four Ho atoms that tetrahedrally surround an oxygen atom.*

Interactions of organic compounds with metal oxides are of great interest because of the numerous catalytic processes involving such protocols.[1] One very interesting, and well-studied, series of such compounds are the alkoxo- and aryloxolanthanides of the form Ln(OR)$_3$.[2] In many cases these compounds, as well as their monocyclopentadienyl complexes, have complex oligomeric structures, which are often stabilized by interstitial anions such as oxides.[3−5] Oxygen coordination numbers from 3 to 6 have been reported.[2−6] Our interest in oxolanthanide compounds stems from our previous observation that, unlike their larger cage (C_2B_9 and C_2B_{10}) analogues, the small-cage carboranes could form unusual oxolanthanacarboranes of the type {[η^5-1-Ln-2,3-(SiMe$_3$)$_2$-2,3-$C_2B_4H_4$]$_3$[(μ-1-Li-2,3-(SiMe$_3$)$_2$-2,3-$C_2B_4H_4$)$_3$(μ_3-OMe)][μ-Li(THF)]$_3$(μ_3-O)} (Ln = Nd, Sm, Gd, Tb, Dy, Ho).[7] These compounds were the unexpected products of the 2:1 molar ratio reactions of the THF-solvated dilithium compound of [2,3-(SiMe$_3$)$_2$-2,3-$C_2B_4H_4$]$^{2-}$ with anhydrous LnCl$_3$ in a solvent mixture of dry benzene and THF. Although the mechanism of these reactions is not known, it may involve the initial formation of the respective half-sandwich lanthanacarborane, which then reacts with the remaining lithiacarborane precursors in the presence of degraded fragments of the THF solvent to yield the corresponding trinuclear oxo−Ln(III)−carborane clusters. Support for this sequence was found in the report of the formation of a monomeric, half-sandwich samaracarborane, {1,1-(t-C_4H_9OH)$_2$-1-(t-C_4H_9O)-2,3-(SiMe$_3$)$_2$-4,5-[Li(THF)Cl]-*closo*-η^5-1-Sm-2,3-$C_2B_4H_4$}·THF.[8] On the other hand, when THF was substituted by TMEDA, the course of the reactions was quite different in that the expected full-sandwich lanthanacarboranes [Li(TMEDA)$_2$][1-Cl-1-(μ-Cl)-2,2′,3,3′-(SiMe$_3$)$_4$-5,6-[(μ-H)$_2$Li(TMEDA)]-4,4′,5′-[(μ-H)$_3$Li(TMEDA)]-1,1′-Ln(2,3-$C_2B_4H_4$)$_2$] were the only discernible products.[9] It should be noted that only the “carbons adjacent” (2,3-C_2B_4) carboranes seem to show

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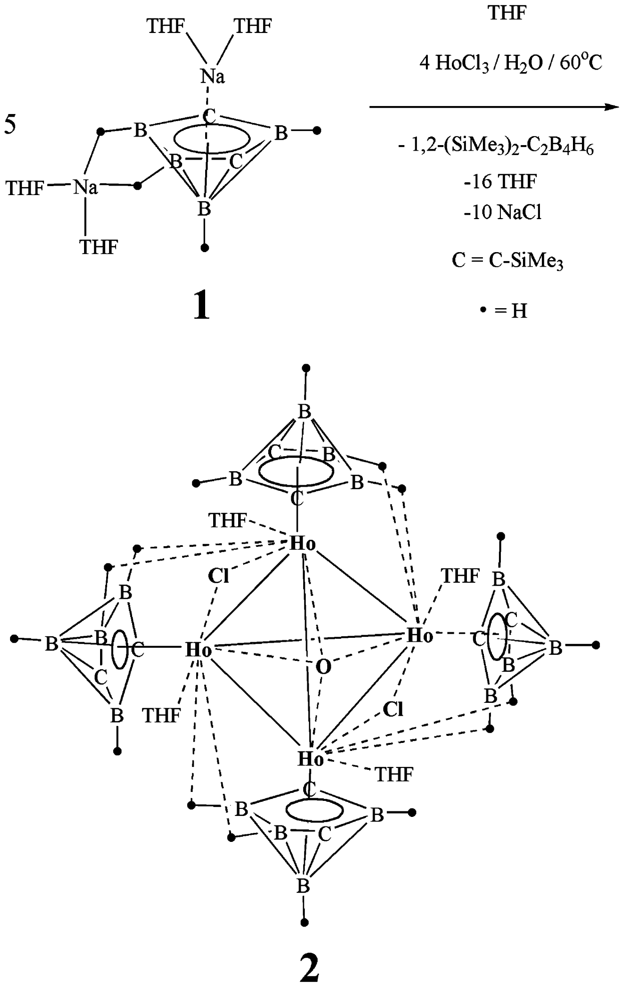
10.1021/om034019x CCC: $25.00
Publication on Web 09/26/2003

this sensitivity to solvent; the analogous "carbons apart" (2,4-C_2B_4) isomers,[10] as well as the larger cage (C_2B_9) carboranes,[11] gave only the simpler full- and half-sandwich lanthanacarboranes. The use of THF as an oxygen source in the syntheses of trinuclear oxolanthanacarborane has several disadvantages. It greatly complicates the development of any general synthetic scheme, it is difficult to control the stoichiometry of the synthesis, and it introduces a number of other degradation products such as MeO^- which can influence the reaction. These complexities led us to question whether there could be alternative methods to synthesize oxolanthanacarborane routinely. Herein we report the directed synthetic approach and the crystal structure of the first oxide ion encapsulating tetraholmium tetrahedron that is stabilized by complexation with the small-cage "carbons apart" C_2B_4-carborane ligands.

In this synthesis,[12] anhydrous $HoCl_3$ was first treated with freshly distilled water under reflux conditions in THF. The THF solution of *closo-exo*-5,6-Na(THF)$_2$-1-Na-(THF)$_2$-2,4-(SiMe$_3$)$_2$-2,4-$C_2B_4H_4$ (**1**) was then poured in vacuo onto the holmium chloride solution at −78 °C to give an overall **1**:$HoCl_3$:H_2O mole ratio of 5:4:1. After the mixture was refluxed overnight with constant stirring, the new oxoholmacarborane $\{[\eta^5\text{-1-Ho(THF)-2,3-(SiMe}_3)_2\text{-2,3-C}_2\text{B}_4\text{H}_4]_4(\mu\text{-Cl})_2(\mu_4\text{-O})\}$ (**2**) was obtained as a pale yellow crystalline solid in 86% yield (see Scheme 1 and Figure 1). It is important to note that the $HoCl_3/H_2O$ mixture must be refluxed until a homogeneous THF solution is obtained. If $HoCl_3$ and water were added to a solution of **1** without prior refluxing, the water decomposed the carborane; such decomposition occurred rapidly at room temperature. However, prior refluxing and a −78 °C reaction temperature produced the oxo product in good yield.

Scheme 1. Synthesis of the Lanthanacarborane Oxide Cluster of Holmium 2



Compound **2** is paramagnetic with a magnetic moment (μ_{eff}) of 10.3 μ_B, which is close to the value of 10.4 μ_B found for $Ho_2(SO_4)_3{\cdot}8H_2O$[13] and the theoretical magnetic moment of 10.6 μ_B[14] and is consistent with an oxidation state of +3 for the holmium atoms ($^5I_8$ ground state).

The IR spectrum of **2** exhibits the expected terminal B−H stretch multiplets indicative of unequal interactions of the boron-bound hydrogen atoms with metal groups that are characteristic of lanthanacarborane complexes.[7,8,15] Because of the unprecedented nature of the synthetic route shown in Scheme 1, the structure of the title compound was unambiguously determined by X-ray diffraction analysis.[16]

The molecular structure of **2**, depicted in Figures 1 and 2, shows that an oxide ion is tetrahedrally encap-

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(12) All manipulations were carried out either under a dry argon atmosphere or on a high-vacuum line. The solvents were thoroughly dried over sodium/benzophenone and distilled under argon. Deionized water was freshly distilled in vacuo before use. Synthesis of **2**: a 0.35 g (1.27 mmol) sample of anhydrous $HoCl_3$ was added to dry THF (20 mL) under argon, and the resulting heterogeneous mixture was stirred overnight. This mixture was cooled to −78 °C, and then 0.0058 g (0.32 mmol) H_2O in 5 mL of THF was added dropwise with constant stirring over a period of 10 min. The resulting mixture was slowly warmed to room temperature and stirred for 4 h at this temperature. At this point, the temperature of the reaction mixture was increased to 60 °C with constant stirring over another 12 h period until a clear solution was obtained. The solution was cooled to −78 °C, and to this was added 0.90 g (1.59 mmol) of *closo-exo*-5,6-Na(THF)$_2$-1-Na(THF)$_2$-2,4-(SiMe$_3$)$_2$-2,4-$C_2B_4H_4$ (**1**) (Hosmane, N. S.; Jia, L.; Zhang, H.; Bausch, J. W.; Prakash, G. K. S.; Williams, R. E.; Onak, T. P. *Inorg, Chem.* **1991**, *30*, 3793−3795) in 20 mL of THF slowly in vacuo, and the resulting reaction mixture containing a 5:4:1 molar ratio of **1** to $HoCl_3$ to H_2O was warmed to room temperature slowly with constant stirring. After 4 h of stirring at room temperature, the reaction mixture was refluxed for 24 h at 70 °C, during which time the color of the heterogeneous mixture turned pale yellow. This product mixture was then filtered through a glass frit in vacuo to collect a clear yellow filtrate. The solid remaining on the frit was extracted repeatedly with anhydrous benzene, and the resulting off-white residue, identified as NaCl, was discarded. The combined filtrate and the benzene extracts were pooled and the solvents removed in vacuo to obtain a yellow solid. This solid was then washed repeatedly with hexane and dissolved in hot benzene (15 mL). After it was cooled to room temperature, the solution afforded pale yellow crystals of **2** (0.46 g, 0.27 mmol; mp 147−8 °C dec; soluble in polar solvents and slightly soluble in *n*-hexane) in 86% yield. IR (cm^{-1}, KBr pellet): 2554 (s), 2535 (w), 2526 (s), 2499 (s), 2483 (w) 2435 (sh), 2375 (s) [ν(B−H)]. Anal. Calcd for $C_{32}H_{88}B_{16}Cl_2Ho_4OSi_4{\cdot}THF$: C, 25.59; H, 5.73. Found: C, 25.40; H, 5.61.

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(16) The X-ray structure of **2** was determined on a Bruker SMART CCD PLATFORM diffractometer at 173(2) K. The unit cell and cell parameters were as follows: monoclinic, $C2/c$, a = 28.403(5) Å, b = 12.835(2) Å, c = 27.879(5) Å, β = 117.820(3)°, Z = 4. Of 17 492 total reflections, 7732 were independent. wR2(F^2) = 0.0794, R1(7732 data with $I > 2\sigma(I)$) = 0.0367, and GOF = 1.446. All non-H atoms were refined anisotropically. All H atoms were treated isotropically with the riding model.

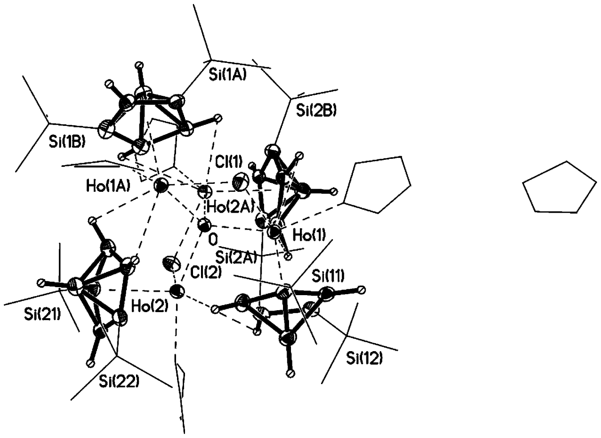

Figure 1. Molecular structure of $\{[\eta^5\text{-1-Ho(THF)-2,3-(SiMe}_3)_2\text{-2,3-C}_2\text{B}_4\text{H}_4]_4[(\mu\text{-Cl})_2(\mu_4\text{-O})\}$ (**2**), with the thermal ellipsoids drawn at the 50% probability level. The *exo*-polyhedral SiMe_3 groups and the solvated THF molecules were drawn with thinner lines for clarity. Selected bond lengths (Å) and angles (deg): Ho(1)−(2,4-C_2B_3 centroid 1), 2.325; Ho(2)−(2,4-C_2B_3 centroid 2), 2.331; Ho(1A)−(2,4-C_2B_3 centroid 1A), 2.325; Ho(2A)−(2,4-C_2B_3 centroid 2A), 2.330; Ho−O(THF), 2.392−2.397; Ho(1)−Ho(2), 3.651; Ho(1A)−Ho(2A), 3.651; Ho(1A)−Ho(2), 3.654; Ho(1A)−Ho(1), 3.875; Ho(2A)−Ho(2) 3.873; Ho(1)−O−Ho(2), 106.2; Ho(1)−O−Ho(1A), 116.2; Ho(1)−O−Ho(2A) 106.2; (2,4-C_2B_3 centroid 1)−Ho(1)−Cl(1), 110.7; (2,4-C_2B_3 centroid 2)−Ho(2)−Cl(2), 110.5. See Table S-3 in the Supporting Information for a detailed list of bond lengths and angles.

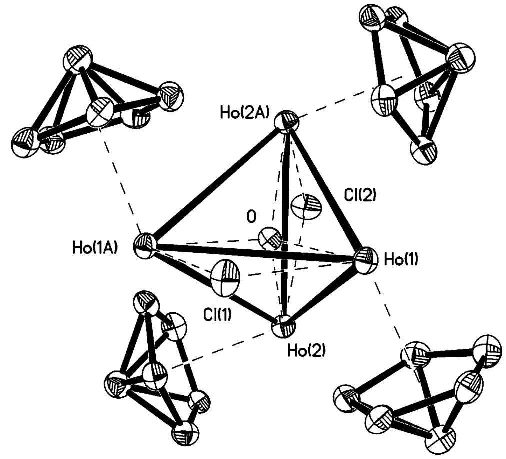

Figure 2. Perspective view of the $[(\text{C}_2\text{B}_4\text{Ho})_4\text{Cl}_2\text{O}]$ cluster core of **2**.

sulated by four holmium ions, each of which is stabilized by η^5 bonding to "carbons apart" C_2B_4-carborane cages; Figure 2 details the core cluster of **2**. Each holmium ion is also coordinated, via two Ho−H−B bridges, to a neighboring C_2B_4 cage. The average O−metal distance is 2.283 ± 0.001 Å.[17] The metal−oxygen−metal bond angles (Ho(1)−O−Ho(2) = 106.2°, Ho(1)−O−Ho(1A) = 116.2°, and Ho(1)−O−Ho(2A) =106.2°) suggest a slightly distorted tetrahedral arrangement of the metals about the oxygen. The average Ho−cage centroid distance of 2.328 ± 0.003 Å[17] is comparable to those found in the lanthanide complexes of both the "carbons adjacent" and "carbons apart" C_2B_4-carborane ligand systems.[7,9] Figure 2 shows that for charge balance each diagonal pair of Ho^{III} ions is linked by a bridging chloride ion to give a $[(\text{C}_2\text{B}_4\text{Ho})_4\text{Cl}_2\text{O}]$ core. Figure 1 shows that each holmium ion is also coordinated to a THF molecule.

Four-coordinate oxygen centers have been reported in main-group,[18] d-block,[19] and f-block[3,5b,20−22] metal complexes. However, there does not seem to be any consistency in their structures. The clusters of $[\text{Ln}_4(\mu_4\text{-O})(\text{NHPh})_3(\text{OSiMe}_2\text{NPh})_6\cdot\text{Na}_5(\text{THF})_7]$ (Ln = Gd, Yb) were obtained in low yields (8.9%) from the reaction of LnBr_3, NaNHPh, and $(\text{Me}_2\text{SiO})_3$ in THF, whose solid-state structures showed a tetrahedral Ln_4O core.[20] This is similar to compound **2**, except that these have more complex geometries with polydentate oxadimethylsilyl-*N*-phenylamido ligands over all edges and anilido ligands on three of the four vertexes. On the other hand, both $[\text{Tb}_4\text{L}_2(\text{NO}_3)_4(\text{MeOH})_2(\mu_4\text{-O})]$ (H_3L = 1,3-bis(2-hydroxy-3-methoxybenzylamino)propan-2-ol) and $\text{Na}_6\{[(\text{C}_6\text{H}_5\text{SiO}_2)_8]_2\text{Nd}_4(\mu_4\text{-O})$ show planar Ln_4O cores,[21,22] while $\text{Ce}_4(\mu_4\text{-O})(\mu_3\text{-O}^i\text{Pr})_2(\mu_3\text{-O}^i\text{Pr})_4(\text{O}^i\text{Pr})_7(^i\text{PrOH})$ has a butterfly core, as does $[\text{Y}_4(\mu_3\text{-OCMe}_3)_2(\mu\text{-OCMe}_3)_4(\text{OCMe}_3)_4(\mu_4\text{-O})(\mu\text{-Cl})_2\text{Li}_4(\mu\text{-OCMe}_3)_2]_2$.[3] All of these structures are complex, and it is difficult to assess the forces that dictate the geometry of the Ln_4O core. However, the reaction procedure as shown in Scheme 1 could well prove to be a general one that could provide a systematic synthetic route to a number of oxo organometallics of the f-block metals involving a variety of π-complexing species, including large- and small-cage carborane ligands. Such studies are currently underway in our laboratories.

Acknowledgment. This work was supported by grants from the National Science Foundation (Grant No. CHE-0241319), the Deutsche Forschungsgemeinschaft, the donors of the Petroleum Research Fund, administered by the American Chemical Society, The Robert A. Welch Foundation (Grant No. N-1322 to J.A.M.), and Northern Illinois University through a Presidential Research Profesorship. The Forschungspreis der Alexander von Humboldt-Stiftung (to C.C.C. and N.S.H.) is also hereby gratefully acknowledged. We also thank one of the reviewers for some helpful comments about the manuscript.

Supporting Information Available: Tables of crystallographic data, including fractional coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates, of **2**; these data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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[17] The uncertainty shown is the average deviation in the four distances.

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