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Dicarbollide Complexes of Samarium and Ytterbium. Synthesis and Structural Characterization of the First *closo*-Lanthanacarboranes

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Recognition of the isolobal analogy between the cyclopentadienyl anion, $C_5H_5^-$, and the dicarbollide dianion, [*nido*-7,8-$C_2B_9H_{11}]^{2-}$, **1**, formed the basis for the discovery of the field of metallacarborane chemistry.[1] It was this realization that also led to the synthesis of the first actinide metallacarborane, $[U(C_2B_9H_{11})_2Cl_2]^{2-}$.[2] However, no further work has been reported concerning complexes of the dicarbollide ligand with the f-block metals,[3] despite the recent growth of organo-f-element chemistry involving complexes of the lanthanides with the pentamethylcyclopentadienyl ligand.[4] We now report the synthesis and structural characterization of the first η^5-bound metallacarboranes incorporating the lanthanide metals, the *closo*-lanthanacarboranes.

Slow anaerobic addition of a THF[5] solution of the sodium salt of **1** to a stirred equimolar solution of LnI_2 (Ln = Sm; Yb)[6] in THF at room temperature resulted in the precipitation of an amorphous solid whose formulation has been established as $Ln(C_2B_9H_{11})(THF)_4$ (Ln = Sm (**2**); Yb (**3**)).[7] The neutral complexes formed in these metathetical reactions are highly air and moisture sensitive, do not melt or sublime up to 200 °C, and can be obtained in reasonable yields (>55%). Compound **2**, a brick-red solid, is only sparingly soluble in THF and reacts with other coordinating solvents.[8] Bright yellow **3** is soluble in a variety of coordinating solvents, allowing the THF to be replaced by the solvent ligand, $Yb(C_2B_9H_{11})L_4$ (L = CH_3CN (**3a**); DMF (**3b**)).[5]

In order to elucidate the bonding interaction between the metal and the dicarbollide ligand, a single-crystal X-ray analysis was carried out with the Yb-DMF adduct (**3b**). The dicarbollide ligand is η^5-bound to the Yb ion and four DMF molecules are coordinated to Yb through oxygen as shown in Figure 1. The metal to cage distances range from 2.73 to 2.77 Å, comparing rather well with Yb-C(C_5Me_5) values for crystallographically characterized Yb(II) η^5-pentamethylcyclopentadienyl complexes.[9] Due to a disorder, especially pronounced for the DMF methyl carbons, the structure would not satisfactorily refine,[10] and it was not possible to distinguish carbon from boron on the top belt of the cage. Although the carbon atoms could not be unambiguously located, the possibility of polyhedral carbon atom rearrangement[11] could essentially be ruled out by the high degree of symmetry

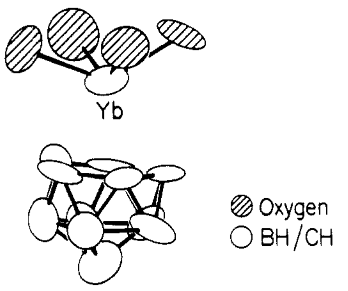

Figure 1. Structure of $Yb(C_2B_9H_{11})(DMF)_4$, (**3b**). Only the oxygen atoms of the coordinated DMF ligands are shown.

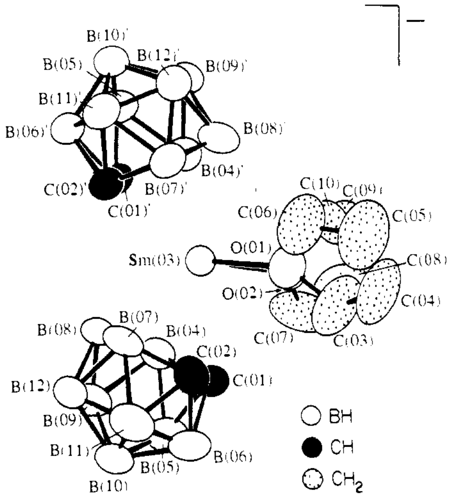

Figure 2. Structure of $[3,3\text{-}(THF)_2\text{-}commo\text{-}3,3'\text{-}Sm(3,1,2\text{-}SmC_2B_9H_{11})_2]^-$ showing the atom labeling scheme. Selected values of interatomic distances from Sm(03) to: C(01') 2.732 (8), C(02') 2.731 (8), B(04') 2.712 (9), B(07') 2.695 (10), B(08') 2.734 (10), C(01) 2.722 (8), C(02) 2.785 (9), B(04) 2.693 (10), B(07) 2.776 (12), B(08) 2.776 (10), centroid' 2.318 (16), and centroid 2.356 (16) Å. Selected angles (degrees): centroid-Sm(03)-O(01) 105.6 (4), centroid-Sm(03)-O(02) 104.2 (4), centroid'-Sm(03)-O(01) 111.5 (4), centroid'-Sm(03)-O(02) 111.7 (4), centroid-Sm(03)-centroid' 131.9 (5).

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[1] Hawthorne, M. F.; Young, D. C.; Andrews, T. D.; Howe, D. V.; Pilling, R. L.; Pitts, A. D.; Reintjer, M.; Warren, L. F., Jr.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 879.

[2] Fronczek, F. R.; Halstead, G. W.; Raymond, K. N. *J. Am. Chem. Soc.* **1977**, *99*, 1769.

[3] The synthesis of σ-bound *C*-carboranyllanthanoids with La, Tm, and Yb has been communicated: Suleimanov, G. Z.; Bregadze, V. I.; Koval'chuk, N. A.; Beletskaya, I. P. *J. Organomet. Chem.* **1982**, *235*, C17. A carboranyl complex with a Tm-B bond has also been reported: Bregadze, V. I.; Koval'chuk, N. A.; Godovikov, N. N.; Suleimanov, G. Z.; Beletskaya, I. P. *J. Organomet. Chem.* **1983**, *241*, C13. A communication on the reactions of *C*-lithiocarboranes with LnI_2 (Ln = Sm, Eu, and Yb) has also appeared: Suleimanov, G. Z.; Bregadze, V. I.; Koval'chuk, N. A.; Khalilov, Kh. S.; Beletskaya, I. P. *J. Organomet. Chem.* **1983**, *255*, C5. No structural data appeared with any of these reports.

[4] For examples, see: (a) Evans, W. J. *Adv. Organomet. Chem.* **1985**, *24*, 131. (b) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51 and the references contained therein.

[5] THF = tetrahydrofuran; DMF = *N,N*-dimethylformamide; PPN^+ = bis(triphenylphosphoranylidene)ammonium cation.

[6] Namy, J. L.; Girard, P.; Kagan, H. B.; Caro, P. E. *Nouv. J. Chim.* **1981**, *5*, 479.

[7] (a) Data for **2**: IR (Nujol mull, NaCl) ν_{BH} 2537 (s), 2439 (s), ν_{THF} 1025 (s), 876 (s) cm^{-1}; $^{11}B\{^1H\}$ NMR (in THF; chemical shifts referenced to external $BF_3 \cdot OEt_2$ in C_6D_6, peaks upfield of the reference are designated as negative, areas given in parentheses) -16.1 (1), -19.6 (2), -25.0 (2), -42.6 (1), -45.1 (2) (width at half-height, 258 Hz), -51.5 (1) (width at half-height, 241 Hz) ppm; ^1H NMR (THF-d_8, referenced to residual β-methylene THF protons at 1.72 ppm) B-H resonances are weak and very broad, they range from 2.6 to 2.0, 0.4 to -0.6, -4.2 to -6.0 ppm, carboranyl C-H 3.04 ppm (s, broad). (b) Data for **3**: IR (Nujol mull, NaCl) ν_{BH} 2540 (s), 2453 (s), ν_{THF} 1024 (s), 877 (s) cm^{-1}; $^{11}B\{^1H\}$ NMR for **3b** (in DMF) -12.3 (1), -15.1 (2), -16.3 (3), -22.8 (2), -39.2 (1) ppm; ^1H NMR for **3b** (in DMF-d_7, referenced to residual solvent methyl protons at 2.74 ppm) B-H resonances 1.9-0.6 ppm (weak and broad), carboranyl C-H 1.23 ppm (s, broad). (c) Integration of the ^1H NMR spectra for the hydrolysis products of both **2** and **3** (in CD_3CN) support the ratio of four THF's to one dicarbollide cage (16 THF α-methylene protons relative to two carboranyl C-H protons).

[8] Compound **2** decomposes in coordinating solvents to give [*nido*-7,8-$C_2B_9H_{12}]^-$ and an as yet uncharacterized Sm^{3+} species that contains no boron.

[9] A M-C(C_5Me_5) of 2.74 (4) Å has been determined for $(C_5Me_5)_2Yb(pyridine)_2$: Tilley, T. D.; Andersen, R. A.; Spencer, B.; Zalkin, A. *Inorg. Chem.* **1982**, *21*, 2647. Other reported values range from 2.66 to 2.77 Å. See: Evans, W. J. *Polyhedron* **1987**, *6*, 803 and the references contained therein.

[10] A room temperature data set was collected on a dark red crystal of **3b** mounted in a sealed glass capillary. The compound crystallized in the orthorhombic space group Pbca with the following unit cell parameters: a = 10.208 (1) Å, b = 17.005 (3) Å, c = 31.627 (5) Å, V = 5479 Å^3, Z = 8. The Yb-B (top belt) distances ranged from 2.73 (4) to 2.77 (4) Å with an average value of 2.74 Å. Attempts at collection of a low-temperature data set were unsuccessful. We are currently trying to obtain diffraction quality crystals of **3** with other, more rigid, coordinating ligands, in hopes of alleviating the disorder problem.

[11] Since we could not unambiguously identify the positions of the carborane carbon atoms, it was not possible to number this complex in accordance with the accepted nomenclature; it is clearly evident, however, that the Yb ion "caps" the dicarbollide ligand giving an icosahedron with overall closo geometry. There is ample precedent for polyhedral carbon atom rearrangement in metallacarboranes; for an example, see: Doi, J. A.; Mizusawa, E. A.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1984**, *23*, 1482 and the references contained therein.

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present in the ^{11}B NMR spectra.[7]

Although transition metal dicarbollide complexes which are structurally similar to the "bent" metallacenes[12] are unknown, synthesis of the uranium complex[2] demonstrated that use of a larger metal permitted two $C_2B_9H_{11}^{2-}$ ligands to be configured in a bent fashion. A lanthanide metal in the +3 oxidation state should allow a more favorable accommodation of the high negative charge brought to a complex by two dicarbollide ligands. One rational approach to the synthesis of a 4f metallacarborane sandwich complex of this type is the addition of a second dicarbollide ligand to **2** or **3** with concomitant oxidation of the metal to the +3 state. Reaction of **2** with $[PPN]^+[\textit{closo}\text{-}3,1,2\text{-}TlC_2B_9H_{11}]^-$ [13] affords the desired bis(dicarbollide) complex in accord with this strategy.

An equimolar amount of **2** (0.88 mmol) was added anaerobically as a solid to a THF solution of $[PPN]^+[\textit{closo}\text{-}3,1,2\text{-}TlC_2B_9H_{11}]^-$, the resultant slurry was stirred for 12 h at room temperature and then filtered to remove the Tl metal that had formed. Reduction of the volume of the filtrate afforded greenish-yellow crystals; an X-ray diffraction study[14] established the composition and structure as $[PPN]^+[3,3\text{-}(THF)_2\text{-}\textit{commo}\text{-}3,3'\text{-}Sm(3,1,2\text{-}SmC_2B_9H_{11})_2]^-$, **4**.[15] Compound **4** could be isolated in 47% yield in accord with eq 1.

$$Sm(C_2B_9H_{11})(THF)_4 + [PPN]^+[\textit{closo}\text{-}3,1,2\text{-}TlC_2B_9H_{11}]^- \xrightarrow[\text{rt}]{\text{THF}} [PPN]^+[3,3\text{-}(THF)_2\text{-}\textit{commo}\text{-}3,3'\text{-}Sm(3,1,2\text{-}SmC_2B_9H_{11})_2]^- + Tl^0 + 2THF \quad (1)$$

As shown in Figure 2, the coordination geometry of **4** can be described as a distorted tetrahedron (average ring centroid–Sm–O(THF) angle is 108.2°). The two η^5-dicarbollide ligands and the two THF solvate molecules comprise the coordination sphere about Sm. The centroid–Sm–centroid angle of 131.9 (5)° is similar to the values found for trivalent bis (C_5Me_5) lanthanide complexes that contain other ligands in the metal's coordination sphere.[16]

Raymond has advanced a structural model[17] that has been very successful in predicting metal to ligand bond lengths in organo-f-element complexes, lending support to the idea that the bonding in these compounds is predominantly ionic. By use of this criterion, an effective ionic radius for the dicarbollide ligand can be determined: 1.66 Å in both 7-coordinate **3b** and 8-coordinate **4**. The fact that the effective radius is the same in both complexes and is also similar to the value for the cyclopentadienyl ligand (1.64 ± 0.04 Å)[17] suggests that the bonding in these lanthanide dicarbollide compounds is largely ionic and does not differ greatly from the bonding observed in the analogous cyclopentadienyl compounds.

Complexes of Sm and Yb have also been synthesized with the $C_2B_{10}H_{12}^{2-}$ ligand,[19] and characterization data[20] supports their formulation as neutral monocage compounds analogous to **2** and **3**. Reactivity studies with these new classes of organo-f-element complexes[21] incorporating the $C_2B_9H_{11}^{2-}$ and $C_2B_{10}H_{12}^{2-}$ ligands are currently under way, and these results will be reported in a full paper.[20]

Acknowledgment. We gratefully acknowledge the support of this work by the Office of Naval Research. We also thank Dr. A. Varadarajan for helpful discussions and Andrea Owyeung for the illustrations.

Supplementary Material Available: Tables of positional and thermal parameters, interatomic distances and angles, and details of crystallographic data collection for **4** (10 pages). Ordering information is given on any current masthead page.

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(12) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729 and the references contained therein.

(13) The $[PPN]^+[\textit{closo}\text{-}3,1,2\text{-}TlC_2B_9H_{11}]^-$ is prepared via anhydrous metathesis of PPN^+Cl^- with $(Tl)[\textit{closo}\text{-}3,1,2\text{-}TlC_2B_9H_{11}]$ in CH_3CN. The $(Tl)[\textit{closo}\text{-}3,1,2\text{-}TlC_2B_9H_{11}]$ was prepared according to Spencer, J. L.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1972**, 1178.

(14) (a) A greenish-yellow crystal of **4** was mounted in a 0.5-mm glass capillary in a glovebox. Diffraction data were collected at 25 °C on a diffractometer equipped with a small Huber circle built by Prof. C. E. Strouse of this department, with Mo Kα radiation, to a maximum 2θ of 45°. Data were corrected for Lorentz, polarization, and absorption effects. The structure was solved by a combination of conventional Patterson, Fourier, and full-matrix least-squares techniques. (b) Crystallographic data for **4**: triclinic space group $P\bar{1}$; a = 8.9374 (3) Å, b = 17.8703 (6) Å, c = 18.4989 (7) Å, α = 107.5402 (9)°, β = 91.085 (1)°, γ = 90.705 (1)°, V = 2816 Å^3, Z = 2; unique data ($I > 3\sigma(I)$), 5324; $R(R_w)$, 5.3% (6.5%). All calculations were performed on the DEC VAX 750 of the J. D. McCullough Crystallography Laboratory with the UCLA crystallographic package.

(15) Data for **4**: IR (Nujol mull, NaCl) ν_{BH} 2523 (s), ν_{THF} 1011 (s), 859 (s) cm^{-1}; $^{11}B\{^1H\}$ NMR (in CH_2Cl_2) –6.0 (2), –11.1 (1), –16.8 (2), –19.5 (1), –25.2 (3); ^1H NMR (in CD_2Cl_2, referenced to residual solvent protons at 5.32 ppm) B–H resonances 10.5 to 9.7, 4.0 to 2.6, –2.0 to –3.1 ppm, (weak and broad), carboranyl C–H 4.89 (s, broad), coordinated THF 2.74 (s, broad), 1.34 (s, broad).

(16) Evans, W. J.; Grate, J. W.; Choi, H. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 941 and the references contained therein.

(17) Raymond, K. N.; Eigenbrot, C. W. *Acc. Chem. Res.* **1980**, *13*, 276. Subtracting the ionic radius[18] of the metal from the metal–ligand distance gives the effective ionic radius of the ligand. **3b**: 2.74 – 1.08 Å (7-coordinate Yb^{2+}) = 1.66 Å. **4**: 2.735 – 1.079 Å (8-coordinate Sm^{3+}) = 1.656 Å.

(18) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751.

(19) Salentine, C. G.; Hawthorne, M. F. *Inorg. Chem.* **1976**, *15*, 2872.

(20) Manning, M. J.; Knobler, C. B.; Hawthorne, M. F., manuscript in preparation.

(21) Magnetic measurements on the paramagnetic complexes **2** and **4** are in progress and these results will be reported in a full paper.[20]

An EXAFS Study on the Morphology Change of Ru Catalyst by CO Adsorption

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Great attention has recently been paid to the reconstruction of clean metal surface upon adsorption.[1] Then a question naturally arises what happens to the small metal clusters in supported catalyst upon adsorption, which is the first step of catalytic reaction. Surface spectroscopic techniques like LEED are not available for small particles on the surface of supports, and mainly infrared absorption spectroscopy has provided information, rather indirectly, through the number of observed vibrations and the frequency shifts of adsorbed species such as CO. Recently Van't Blik et al. reported in a series of papers[2-4] direct evidence of a structural change of Rh clusters supported on Al_2O_3 upon CO adsorption. They observed a drastic change in EXAFS (extended X-ray absorption fine structure) by the admission of CO. It was concluded that this change was caused by the disruption of the metal–metal bond, resulting in formation of $Rh(CO)_2$ species. As far as we know, this is the only example of straightforward evidence of morphology changes caused by adsorption, and it is not certain whether or not this phenomenon is general. In this communication we present another example of the morphology change upon adsorption for Ru supported on γ-Al_2O_3 and show this phenomenon is not limited to Rh.

Highly dispersed Ru/γ-Al_2O_3 catalyst was prepared according to Okuhara et al.[5] In short, $Ru_3(CO)_{12}$ was adsorbed from hexane

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(1) Estrup, P. J. *Chemistry and Physics of Solid Surface*; Vaniselow, R., Howe, R., Eds.; Springer Verlag: Berlin, 1984; p 205.

(2) Van't Blik, H. F. J.; Van Zon, J. B. A. D.; Huizinga, T.; Vis, J. C.; Koningsberger, D. C.; Prins, R. *J. Phys. Chem.* **1983**, *87*, 2264-2267.

(3) Van't Blik, H. F. J.; Van Zon, J. B. A. D.; Koningsberger, D. C.; Prins, R. *J. Mol. Catal.* **1984**, *25*, 379-396.

(4) Van't Blik, H. F. J.; Van Zon, J. B. A. D.; Huizinga, T.; Vis, J. C.; Koningsberger, D. C.; Prins, R. *J. Am. Chem. Soc.* **1985**, *107*, 3139-3147.

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