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Synthesis and Structural Characterization of the First Mixed Lanthanacarborane Incorporating η^5-Cyclopentadienyl and η^6-Carboranyl Ligands

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*Summary: Treatment of $SmI_2(THF)_x$ with 2 equiv of $[Me_2Si(C_2B_{10}H_{11})(C_5H_4)]Na$ in THF, followed by extraction with toluene, gave $[Me_2Si(C_2B_{10}H_{11})(C_5H_4)]Sm(THF)_2$ (**1**), which represents the first structurally characterized example of the mixed lanthanacarborane incorporating η^5-cyclopentadienyl and η^6-carboranyl ligands. Unlike the SmI_2 case, interaction of $YbI_2(THF)_x$ with 2 equiv of $[Me_2Si(C_2B_{10}H_{11})(C_5H_4)]Na$ in THF afforded $[Me_2Si(C_2B_{10}H_{11})(C_5H_4)]_2Yb(THF)_2$ (**2**).*

All of the lanthanacarboranes described in the literature are those in which a lanthanide metal is bonded to either one or two identical or similar carborane ligands.[1-3] There are no definitive reports on the mixed-ligand organolanthanide complexes having either a cyclopentadienyl or some other cyclic organic π donor as the companion ligand to a carborane, despite the fact that this mixed-ligand type of complexes is well-known in d-block transition-metal chemistry.[4] Attempts to prepare the mixed-ligand complex $[(C_5Me_5)Eu(C_2B_{10}H_{12})(THF)_2]^-$ failed, probably due to the ligand redistribution of the complex with the formation of $(C_5Me_5)_2Eu(THF)_2$ and $[(C_2B_{10}H_{12})_2Eu(THF)_2]^{2-}$.[1d] This kind of ligand redistribution reaction is also found in other lanthanacarboranes with C_2B_9[3] and C_2B_4[2e] systems. Here, we report the first structurally characterized example of a mixed lanthanacarborane incorporating η^5-cyclopentadienyl and η^6-carboranyl ligands, which was prepared via an unexpected redox reaction.

Treatment of $SmI_2(THF)_x$[5] with 2 equiv of $[Me_2Si(C_2B_{10}H_{11})(C_5H_4)]Na$[6] in dry THF at room temperature, removal of the THF, extraction of the residual with toluene, and evaporation of the solvent does not give the expected intensely colored complex $[Me_2Si(C_2B_{10}H_{11})(C_5H_4)]_2Sm(THF)_2$; instead, a yellow compound with the formulation of $[Me_2Si(C_2B_{10}H_{11})(C_5H_4)]Sm(THF)_2$ (**1**) was isolated in 32% yield.[7] This color change indicates

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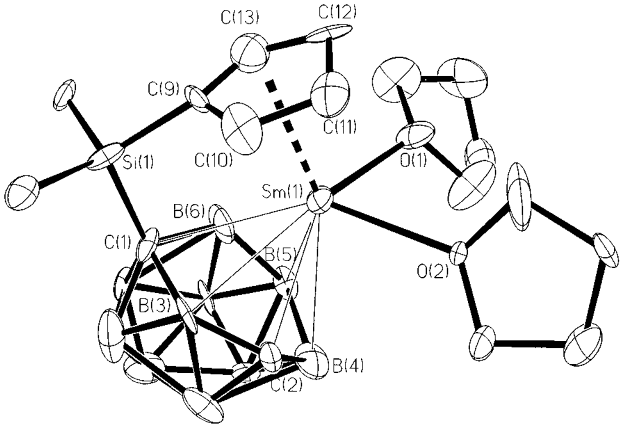

Figure 1. ORTEP diagram, with thermal ellipsoids drawn at the 35% probability level, of compound **1**. All hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): average Sm(1)−C (C_5 ring) = 2.664(2) [2.748(2)]; average Sm(1)−cage atom = 2.841(3) [2.764(3)]; Sm(1)−O(1) = 2.409(2) [2.350(2)]; Sm(1)−O(2) = 2.517(2) [2.434(2)]; O(1)−Sm(1)−O(2) = 76.76(6) [83.63(6)]; C(1)−Si(1)−C(9) = 106.4(1) [93.9(1)]; Cnt(1)−Sm(1)−Cnt(2) = 123.4(1) [126.7(1)]. Distances and angles in brackets are those of a second molecule.

that the oxidation state of Sm has been changed from +2 to +3. The ^{1}H NMR spectrum of the hydrolysis products shows the presence of free THF and $[Me_2Si(C_2B_{10}H_{12})(C_5H_5)]^{-}$ [1d] in the ratio of 2:1. The $^{11}B\{^1H\}$ NMR spectrum consists of extremely broad, unresolved resonances, implying the neutral carborane has been reduced to the dianion, which may have a strong interaction with the paramagnetic center Sm^{3+}.[1c,d] The solid-state IR spectrum exhibits a unique doublet centered at 2513 cm^{-1}, typical of the ionic interaction of a positive metal center and an anionic carborane ligand.[1−3,8] The molecular structure of this compound has been confirmed by single-crystal X-ray analysis,[9] which shows two crystallographically independent molecules in the unit cell (Figure 1). The Sm ion is η^5-bound to the cyclopentadienyl ring, η^6-bound to the hexagonal C_2B_4 face of $C_2B_{10}H_{11}$ cage, and coordinated to two THF molecules in a distorted tetrahedral geometry.

The average Sm−C (C_5 ring) distances of 2.664(2) and 2.748(2) Å compare rather well with those found in other Me_2Si-bridged cyclopentadienylsamarium(III) complexes.[10] The average Sm−cage atom (C_2B_4 face) distances of 2.764(3) and 2.841(3) Å are close to the values of 2.805−2.859 Å, which would be expected by subtracting the difference, 0.171 Å, between Shannon's ionic radii[11] of Sm^{3+} (1.079 Å) and Eu^{2+} (1.250 Å) from the average Eu-cage atom distances, 2.976 and 2.989 Å in $[(C_2B_{10}H_{12})Eu(MeCN)_3]_n$[1d] or 3.03 Å in $[(C_2B_{10}H_{12})_2Eu(THF)_2]^{2-}$.[1d] On the other hand, the Sm−Cnt(1) (centroid of C_5 ring) distances (2.390 and 2.465 Å) are significantly longer than those (2.226 and 2.298 Å) of Sm−Cnt(2) (centroid of C_2B_4 face). These differences should be due to the much larger C_2B_4 face of the carborane cage, not to the ligating properties of the anions. Otherwise, the ligand redistribution products would be expected to be isolated.[1d]

Compound **1** is believed to be formed through an unexpected redox reaction in which Sm^{2+} was oxidized to Sm^{3+} and, meanwhile, the neutral carborane was reduced to the dianion. To gain some insight into this reaction, ^{11}B NMR was used as a probe to examine some reactions. The results show that $SmI_2(THF)_x$ cannot reduce $C_2B_{10}H_{12}$,[1] $Me_2Si(C_2B_{10}H_{11})(C_5H_5)$,[6] or $C_2B_{10}H_{10}(CH_2C_6H_5)_2$[3] to the corresponding dianions, although it is well-known reducing agent.[5,12] $[(Me_3Si)_2C_5H_3]_2Sm(THF)_2$,[13] however, can slowly reduce $C_2B_{10}H_{12}$ or $C_2B_{10}H_{10}(CH_2C_6H_5)_2$ to the corresponding dianions. These observations suggest that cyclopentadienylsamarium(II) species may serve as an intermediate during the reaction of $SmI_2(THF)_x$ with $[Me_2Si(C_2B_{10}H_{11})(C_5H_4)]Na$. On the other hand, $C_2B_{10}H_{10}R_2^{2-}$ (R = H, Me) is also known to be a powerful reducing species, which can reduce M(IV) to M(II) (M = Ti, Zr, Hf)[14] and Eu(III) to Eu(II).[1d] The reducing properties of both $SmI_2(THF)_x$ and $C_2B_{10}H_{10}R_2^{2-}$ make it extremely difficult to prepare a compound containing both reducing and oxidizing sites, such as compound **1** via other methods. For example, the reaction of $[Me_2Si(C_2B_{10}H_{11})(C_5H_4)]SmCl_2(THF)_3$ with an excess amount of K metal or treatment of $SmCl_3$ with 1 equiv of $[Me_2Si(C_2B_{10}H_{11})(C_5H_4)]K_3$[6] in THF gave the same Sm(II) compound.

Unlike the SmI_2 case, interaction of $YbI_2(THF)_x$[5] with 2 equiv of $[Me_2Si(C_2B_{10}H_{11})(C_5H_4)]Na$ in THF at room temperature, removal of the solvent, extraction with toluene, and hexane vapor diffusion afforded a red compound $[Me_2Si(C_2B_{10}H_{11})(C_5H_4)]_2Yb(THF)_2$ (**2**) in 66% yield.[15] It was characterized by complexometric metal analysis, IR and NMR spectroscopy as well as X-ray

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(7) Complete synthetic procedures are given in the Supporting Information. ^{1}H NMR (pyridine-d_5): δ 3.43 (m, 8H), 1.38 (m, 8H), 0.14 (s, 6H). ^{13}C NMR (pyridine-d_5): δ 128.4, 119.2, 118.5, 113.5, 112.8, 67.3, 25.3, −3.6. IR (KBr, cm^{-1}): ν 3087 (w), 3053 (m), 2979 (m), 2892 (m), 2528 (vs), 2498 (vs), 1248 (m), 1046 (s), 1007 (s), 870 (s), 835 (s), 793 (s). $^{11}B\{^1H\}$ NMR spectrum consisted of extremely broad, unresolved resonances. Complexometric Anal. Calcd for $C_{17}H_{37}B_{10}O_2SiSm$ (**1**): Sm, 26.85. Found: Sm, 26.97. Combustion analyses of compounds of this type are normally inaccurate. See: refs 1 and 3.

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(9) Crystal data for **1** ($C_{17}H_{37}B_{10}O_2SiSm$; fw, 560.0): Monoclinic, space group $P2_1$, $a = 10.030(2)$ Å, $b = 17.933(4)$ Å, $c = 14.368(3)$ Å, $\beta = 91.43(3)°$, $V = 2583.5(9)$ Å^3, $d_{calcd} = 1.440$ g/cm^3, $Z = 2$, $R_1 = 0.067$ ($I > 2.0\sigma(I)$), w$R_2 = 0.168$, data-to-parameter ratio 9.0. Data were collected at 294 K on a MSC/Rigaku RAXIS-IIC Image Plate using Mo Kα radiation ($\lambda = 0.710\ 73$ Å) from a Rigaku rotating-anode X-ray generator operating at 50 kV and 90 mA. The structure was solved by direct methods and refined on F^2 using the Siemens SHELXTL V 5.03 program package (PC version) (SHELXTL V5.03 program set; Siemens Analytical X-ray Instruments, Inc.; Madison, WI 1995).

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(15) Complete synthetic procedures are given in the Supporting Information. ^{1}H NMR (pyridine-d_5): δ 6.08−6.20 (m, 8H), 3.43 (m, 8H), 2.64 (s, br, 2H), 1.38 (m, 8H), 0.20 (s, 12H). ^{13}C NMR (pyridine-d_5): δ 116.8, 114.7, 111.6, 110.6, 107.3, 69.7, 67.3, 62.5, 25.3, −2.94. ^{11}B NMR (pyridine-d_5): δ −3.5 (2), −7.8(2), −14.1 (4), −15.0 (2). IR (KBr, cm^{-1}): ν 3073 (w), 3038 (m), 2961 (m), 2591 (vs), 1254 (m), 1037 (s), 807(s), 760 (s). Complexometric Anal. Calcd for $C_{26}H_{58}B_{20}O_2Si_2Yb$ (**2**): Yb, 20.40. Found: Yb, 19.93. Combustion analyses of compounds of this type are normally inaccurate. See: refs 1 and 3.

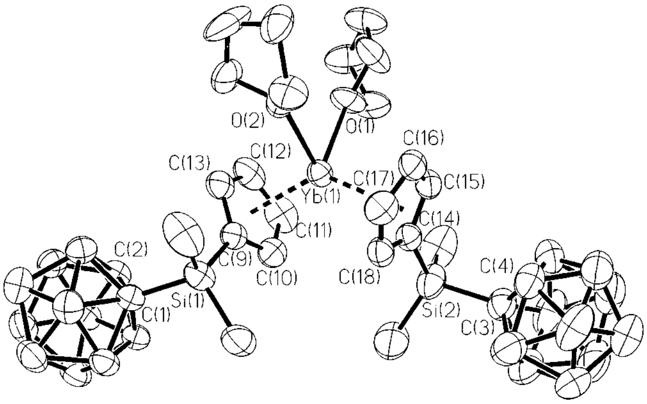

Figure 2. ORTEP diagram, with thermal ellipsoids drawn at the 35% probability level, of compound **2**. All hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): average Yb(1)−C = 2.725(2); Yb(1)−O(1) = 2.391(2); Yb(1)−O(2) = 2.460(1); Yb(1)−Cnt = 2.447(2) and 2.455(2); O(1)−Yb(1)−O(2) = 83.27(7); Cnt−Yb(1)−Cnt = 134.0(1).

crystallography.[16] As shown in Figure 2, the compound adopts the pseudotetrahedral, bent-metallocene motif commonly observed for $Cp_2Yb(II)L_2$ complexes.[17] There is no interaction between Yb^{2+} and any one of the B−H bonds from the carboranes. The two cages stay away from each other to avoid the repulsion. The average Yb−C distance of 2.725(2) Å, the average Yb−O distance of 2.426(2) Å, the Cnt−Yb−Cnt (Cnt = centroid of C_5 ring) angle of 134.0(1)° and the O(1)−Yb−O(2) angle of 83.3(1)° fall in the range normally observed for Cp_2YbL_2-type of complexes.[17]

In conclusion, an unexpected redox reaction led to the preparation and structural characterization of the first mixed lanthanacarborane incorporating η^5-cyclopentadienyl and η^6-carboranyl ligands. This reaction does *not* take place with YbI_2, which is the less powerful reducing agent. This work also shows that the cyclopentadienyl and C_2B_{10} dianion should have an identical or a very similar ligating ability.

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Supporting Information Available: Tables of crystallographic data collection information, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates and figures containing the atom-numbering schemes for complexes **1** and **2** and text giving the experimental procedures (28 pages). Ordering information is given on any current masthead page.

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(16) Crystal data for **2** ($C_{26}H_{58}B_{20}O_2Si_2Yb$; fw, 848.2): Orthorhombic, space group *Pbca*, $a = 12.938(3)$ Å, $b = 16.832$ (3) Å, $c = 40.341(8)$ Å, $V = 8785(3)$ Å^3, $d_{calcd} = 1.283$ g/cm^3, $Z = 8$, $R_1 = 0.054$ ($I > 2.0\sigma(I)$), w$R_2 = 0.153$, data-to-parameter ratio 12.5.

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