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A Novel Full-Sandwich Lanthanacarborane Complex Bearing an η^7-Carboranyl Ligand, $\{\{[\eta^7\text{-}Me_2Si(C_{13}H_9)(C_2B_{10}H_{11})]_2Yb^{III}\}_2Yb^{II}\}\{Na_8(THF)_{20}\}$

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Summary: The first full-sandwich lanthanacarborane containing an η^7-carboranyl ligand was prepared and structurally characterized, which indicates that the arachno-carboranyl ligand can effectively stabilize the high oxidation state of the metal.

We have recently reported a brand new coordination mode for carboranes.[1−4] The tetraanionic [*arachno*-$R_2C_2B_{10}H_{10}]^{4-}$ ligands are capable of being η^7-bound to actinides,[2] lanthanides,[3,4] and the yttrium ion,[4] leading to a novel class of 13-vertex *closo*-metallacarboranes. In all these metallacarboranes, the metal ion is bonded to only one *arachno*-carboranyl ligand. Since the [*arachno*-$R_2C_2B_{10}H_{10}]^{4-}$ tetraanion is a 10-electron donor,[4] it is anticipated that only f-block transition metal ions could possibly form full-sandwich metallacarboranes incorporating two [*arachno*-$R_2C_2B_{10}H_{10}]^{4-}$ ligands. Treatment of UCl_4 with 2 equiv of *o*-$C_2B_{10}H_{12}$ in the presence of excess K metal gave, however, the mixed sandwich metallacarborane $[\{(\eta^7\text{-}C_2B_{10}H_{12})(\eta^6\text{-}C_2B_{10}H_{12})U\}\{K_2(THF)_5\}]_2$; no fully sandwiched uranacarborane with two $\eta^7\text{-}C_2B_{10}H_{12}{}^{4-}$ ligands was isolated.[2] On the other hand, we did not isolate the desired full-sandwich product from the reaction of $LnCl_3$ with 2 equiv of *o*-$R_2C_2B_{10}H_{10}$ (R = H, $CH_2C_6H_5$) or $Me_2A(Cy)(C_2B_{10}H_{11})$ (A = C, Si; Cy = C_5H_5, C_9H_7)[5] in the presence of excess alkali metals. We then turn our attention to the new ligand and describe herein the synthesis and structural characterization of the first full-sandwich metallacarborane bearing two tetraanionic *arachno*-carboranyl ligands.

Treatment of $Me_2Si(C_{13}H_9)Cl$[6] with 1 equiv of $(C_2B_{10}H_{10})Li_2$ in a toluene/ether solution gave a new ligand, $[Me_2Si(C_{13}H_8)(C_2B_{10}H_{11})]Li(OEt_2)_2$ (**1**), as yellow crystals in 88% yield.[7] Interaction between $YbCl_3$, 1 equiv of **1**, and excess finely cut Na metal in THF at room temperature followed by treatment with 1 equiv of dry Me_3NHCl gave, after workup, a novel full-sandwich, mixed valent metallacarborane complex $\{\{[\eta^7\text{-}Me_2Si(C_{13}H_9)(C_2B_{10}H_{11})]_2Yb^{III}\}_2Yb^{II}\}\{Na_8(THF)_{20}\}$ (**2**) as red crystals in 48% yield (Scheme 1).[8] Many attempts were made without success to grow X-ray-quality crystals of the product before treating with ammonium salt. Since the experiment is repeatable and there is no reaction between $YbCl_3$ and **1** in THF,[9] it is reasonable to assume that the added Me_3NH^+ just protonates the appended fluorenyl anion and the core structure remains intact. Complex **2** is soluble in polar organic solvents such as THF and pyridine, slightly soluble in toluene, and insoluble in hexane. Like other paramagnetic species, the spectroscopic data of **2** do not offer much structural information except the presence of carborane and approximately five THF molecules per carboranyl ligand.

An X-ray diffraction study[10] reveals that **2** is a novel centrosymmetric mixed-valent complex with the Yb^{II} sitting at an inversion center. Two full-sandwich metallacarboranes that are connected by a Yb^{2+} ion through four sets of two B−H−Yb bonds form the core structure

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(7) ^1H NMR (300 MHz, pyridine-d_5): δ 8.08 (d, J = 7.8 Hz, 2H), 7.83 (d, J = 8.4 Hz, 2H), 7.26 (dd, J = 7.8 and 7.5 Hz, 2H), 7.05 (dd, J = 7.5 and 8.4 Hz, 2H) ($C_{13}H_8$), 2.67 (br s, 1H) (cage CH), 2.52 (q, J = 6.9 Hz, 8H), 0.42 (t, J = 6.9 Hz, 12H) $[O(CH_2CH_3)_2]$, 0.83 (s, 6H) $[Si(CH_3)_2]$. ^{13}C NMR (75 MHz, pyridine-d_5): δ 141.36, 127.05, 125.72, 123.61, 120.50, 119.86, 115.89 ($C_{13}H_8$), 72.39, 62.47 (cage C), 65.05, 14.06 $[O(CH_2CH_3)_2]$, 1.89 $[Si(CH_3)_2]$. ^{11}B NMR (128 MHz, pyridine-d_5): δ −2.9 (2), −7.4 (3), −11.5 (2), −13.0 (3). IR (KBr, cm^{-1}): ν_{BH} 2585 (vs). Anal. Calcd for $C_{21}H_{35}B_{10}LiOSi$ (**1** − Et_2O): C, 56.47; H, 7.90. Found: C, 56.16; H, 8.10.

(8) To a suspension of $YbCl_3$ (0.28 g, 1.0 mmol) in THF (20 mL) was added a THF solution of **1** (0.52 g, 1.0 mmol) and finely cut Na metal (0.17 g, 7.39 mmol), and the reaction mixture was stirred at room temperature for 5 days to afford a red solution. After removal of excess Na metal, a dry solid of Me_3NHCl (0.095 g, 1.0 mmol) was added in portions under stirring. The reaction mixture was then stirred at room temperature for 1 h. Removal of the precipitates and solvent gave a red solid that was extracted with a mixed solvent of toluene and THF (7:1, 3 × 10 mL). The solutions were combined and concentrated to about 15 mL, from which red crystals were obtained after this solution stood at room temperature for a week (0.43 g, 48% based on carborane). ^1H NMR (300 MHz, pyridine-d_5): δ 8.87 (d, J = 8.1 Hz, 8H), 8.58 (d, J = 7.5 Hz, 8H), 7.28 (dd, J = 8.1 and 7.8 Hz, 8H), 7.04 (dd, J = 7.8 and 7.5 Hz, 8H), 5.98 (m, 4H) ($C_{13}H_9$), 3.60 (m, 80H), 1.56 (m, 80H) (THF), 0.79 (s, 24H) $[Si(CH_3)_2]$. ^{13}C NMR (75 MHz, pyridine-d_5): δ 136.41, 128.81, 127.52, 127.16, 126.93, 126.45, 116.81 ($C_{13}H_9$), 68.16, 26.13 (THF). ^{11}B NMR (128 MHz, pyridine-d_5): many very broad, unresolved resonances. IR (KBr, cm^{-1}): ν_{BH} 2409 (vs), 2356 (s), 2332 (s). Anal. Calcd for $C_{132}H_{232}B_{40}Na_8O_{16}Si_4Yb_3$ (**2** − 4THF): C, 47.66; H, 7.04. Found: C, 47.81; H, 6.86.

(9) This reaction led to the isolation of $YbCl_3(THF)_3$ and $[Me_2Si(C_{13}H_8)(C_2B_{10}H_{11})]Li(THF)_2$, respectively.

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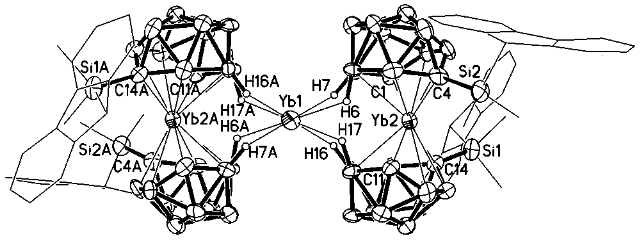
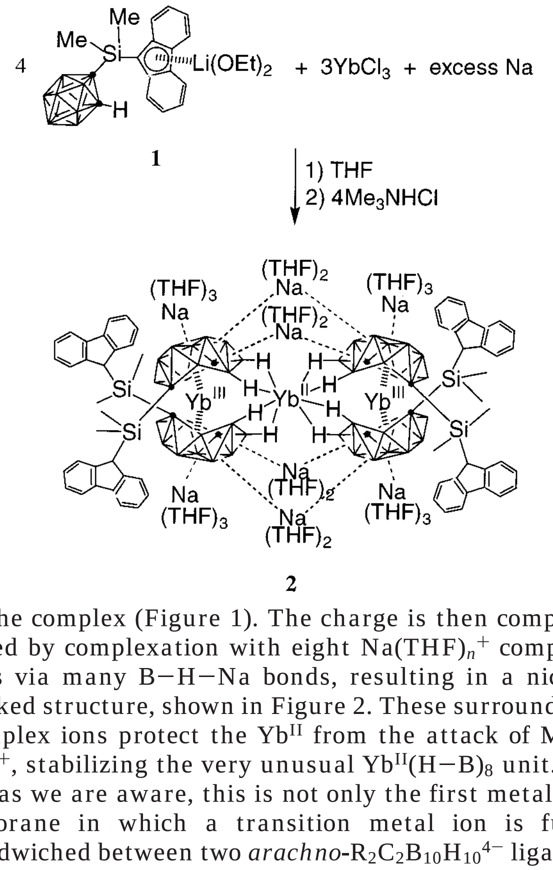


Figure 1. Core structure of **2**. Selected distances (Å): Yb2−C1 2.435(4), Yb2−C4 2.456(4), Yb2−B2 2.786(4), Yb2−B3 2.798(4), Yb2−B5 2.780(4), Yb2−B6 2.761(4), Yb2−B7 2.723(4), Yb2−C11 2.431(4), Yb2−C14 2.483(4), Yb2−B12 2.765(4), Yb2−B13 2.794(4), Yb2−B15 2.760(4), Yb2−B16 2.797(4), Yb2−B17 2.749(4), Yb1···B6 2.905(4), Yb1···B7 2.882(4), Yb1···B16 2.888(5), Yb1···B17 2.872(4).

Scheme 1



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of the complex (Figure 1). The charge is then compensated by complexation with eight $Na(THF)_n^+$ complex ions via many B−H−Na bonds, resulting in a nicely packed structure, shown in Figure 2. These surrounding complex ions protect the Yb^{II} from the attack of Me_3NH^+, stabilizing the very unusual $Yb^{II}(H-B)_8$ unit. As far as we are aware, this is not only the first metallacarborane in which a transition metal ion is fully sandwiched between two *arachno*-$R_2C_2B_{10}H_{10}^{4-}$ ligands but also a very rare structurally characterized example of a Yb^{II} compound supported only by B−H bonds.

It is well-documented that organoytterbium(III) compounds can be readily reduced by Na metal to form the Yb^{II} species.[11] Complex **2** is an exceptional example in which the capping Yb^{III} remains intact in the presence of excess Na metal, suggesting that the *arachno*-$R_2C_2B_{10}H_{10}^{4-}$ tetraanion can effectively stabilize high oxidation states of the metals.

Each Yb^{3+} ion is η^7-bound to two *arachno*-carboranyl ligands in a bent sandwich structure with a Cent−Yb−Cent angle of 160.2° (Cent is the centroid of the C_2B_5 bonding face), which results in a formal coordination number of 10 for each Yb(III) ion. The cage geometry of the [*arachno*-$Me_2Si(C_{13}H_9)(C_2B_{10}H_{11})$]$^{4-}$ tetraanion is very similar to those observed in $[\{(\eta^7\text{-}C_2B_{10}H_{12})(\eta^6\text{-}C_2B_{10}H_{12})U\}\{K_2(THF)_5\}]_2$,[2] $[\{[\eta^5{:}\eta^7\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{11})]Er\}_2\{Na_4(THF)_9\}]_n$,[3] and $\{[\eta^7\text{-}(C_6H_5CH_2)_2C_2B_{10}H_{10}]Ln(THF)\}_2\{Na(THF)_3\}_2$.[4] The average Yb−C and Yb−B distances of 2.451(4) and 2.771(4) Å are comparable to the corresponding values of 2.359(5) and 2.667(6) Å found in $[\{\eta^7\text{-}(C_6H_5CH_2)_2C_2B_{10}H_{10}\}Er(THF)]_2^{2-}$,[4] respectively, if the differences in Shannon's ionic radii are taken into account.[12]

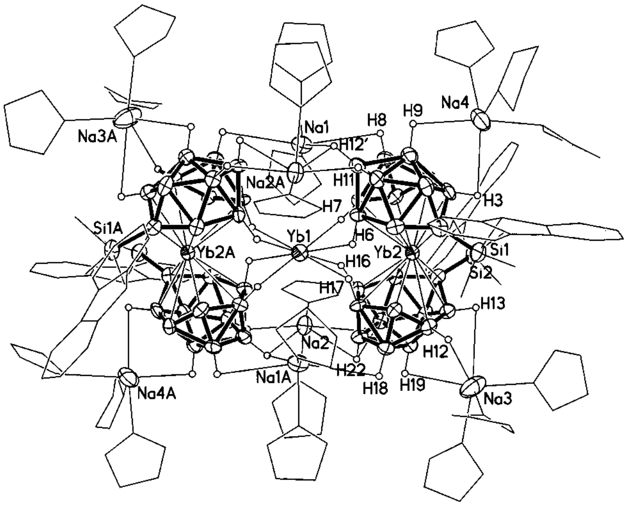

Figure 2. Molecular structure of **2**.

The Yb^{2+} ion in **2** is coordinated to eight B−H bonds with a formal coordination number of eight. Such a coordination environment is very unusual for lanthanides. Although lanthanide(II) complexes with boron hydride or hydrido ligands have recently been reported, they are always stabilized by a bulky ligand or many donor solvents.[13] The average Yb(1)−B distance of 2.887(4) Å in **2** is comparable to the 2.894(7) Å in $(DME)_3Yb[(\mu\text{-}H)_2C_2B_{10}H_8(CH_2C_6H_5)_2]$ (DME = 1,2-dimethoxyethane),[14] 2.929(8) Å in $[(THF)_3Yb\{(\mu\text{-}H)_5C_2B_9H_4(CH_2C_6H_5)_2\}]_2$,[14] and 2.94(2) Å in $(CH_3CN)_6Yb[(\mu\text{-}H)_2B_{10}H_{12}]$,[15] but is significantly longer than the 2.666(6) Å observed in $(CH_3CN)_4Yb[(\mu\text{-}H)_3BH]_2$.[13b]

In summary, the first fully sandwiched metallacarborane bearing an η^7-carboranyl ligand has been prepared and structurally characterized. It also represents a very rare structurally characterized example of a lanthanide complex supported only by B−H bonds. The results show that the *arachno*-$R_2C_2B_{10}H_{10}^{4-}$ tetraanion can effectively stabilize high oxidation states of the metals.

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(10) Crystal data for **2** ($C_{148}H_{264}B_{40}Na_8O_{20}Si_4Yb_3$; fw, 3611.4): triclinic, space group $P\bar{1}$, $a = 14.348(2)$ Å, $b = 16.091(2)$ Å, $c = 21.811(2)$ Å, $\alpha = 106.15(1)°$, $\beta = 105.36(1)°$, $\gamma = 98.69(1)°$, $V = 4524(1)$ Å^3, $T = 293$ K, $Z = 2$, $d_{calcd} = 2.651$ g cm^{-3}, $2\theta_{max} = 50°$, μ(Mo Kα) = 0.71073 Å, $R_1 = 0.074$, $wR_2(F^2) = 0.180$.

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Supporting Information Available: Tables of crystallographic data and data collection details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates and figures containing the atom-numbering schemes for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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