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Synthesis and Crystal Structure of a "Carbons Apart" Erbacarborane Sandwich: An Example of Novel, One-Pot, Two-Electron Reductive Cage Opening with Concomitant Metalation of the C_2B_4 Carborane Ligand

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*Summary: The reaction between 1,2-$(SiMe_3)_2$-closo-1,2-$C_2B_4H_4$ (**1**), $ErCl_3$, and K in a 2:1:4 molar ratio, in the absence of an outside electron-transfer agent, produced the erbacarborane sandwich 2,2′,4,4′-$(SiMe_3)_4$-3,6′-$[(\mu\text{-}H)_2K(THF)_2]$-1,1′-commo-Er($\eta^5$-2,4-$C_2B_4H_4$)$_2$ (**2**) in 82% yield. All experimental observations are consistent with a process in which the erbium metal is acting as both the capping group and an electron-transfer agent.*

The two-electron reductive cage opening of *closo*-carboranes has been well-documented in the literature.[1] In a series of papers Stone and co-workers reported the simultaneous cage reduction and metalation of *closo*-carboranes in the C_2B_n ($n = 6, 8, 9$) cage systems using a number of zerovalent nickel, platinum, and palladium complexes.[2] While the monocarbon carbaborane [*closo*-$CB_{10}H_{11}]^-$ was also found to react in a similar manner,[3] the icosahedral *closo*-$(RC)_2B_{10}H_{10}$ cage has been opened by the reaction of a group 1 metal, in the presence and absence of catalysts, to give the corresponding *nido*-carboranes.[4,5] In addition, the group 2 element Mg was also found to react with *closo*-1,2-$C_2B_{10}H_{12}$ in the presence of catalytic amounts of 1,2-dibromomethane.[6] Nevertheless, Xie and co-workers have reported the uncatalyzed reduction of Na[1-($Me_2C(C_5H_5)$-*closo*-1,2-$C_2B_{10}H_{11}$] by Na metal to form the *ansa* ligand Na_3[1-($Me_2C(C_5H_5)$-*nido*-1,2-$C_2B_{10}H_{11}$], in which a Cp^- group is tethered to a dianionic *nido*-$C_2B_{10}H_{11}$ moiety

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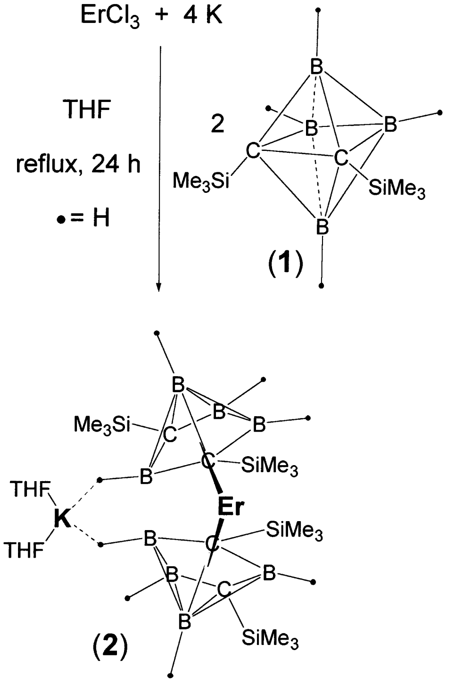
Scheme 1



via an Me_2C bridge; metal complexes of this ligand were also described.[7] In all of the reductive cage-opening processes, the resulting *nido*-carborane products have a "carbons apart" geometry where the two cage carbons are separated by at least one boron atom on the open faces of the carboranes. When the two cage carbons are bridged, by either an organic group or a metal complex, cage reduction produced the "carbons adjacent" *nido*-C_2B_{10} cage, which seem to be susceptible to further reduction to give the respective *arachno*-carboranes.[8] While a number of catalyzed and uncatalyzed approaches to reduction/opening processes have been described for the large-cage *closo*-carboranes, the methods applicable to the small C_2B_4 cage system are quite limited. Although there have been some very interesting, but isolated, reports of the reductive cage openings of *closo*-$C_2B_4H_6$ by Lewis bases, such as $(CH_3)_3N$,[9] and low-valent metal compounds,[10] the only general, high-yield method of transforming either *closo*-1,6-$(CR)_2B_4H_4$ (R = H or a cage carbon substituent) or its 1,2-isomer to the corresponding [*nido*-2,4-$(CR)_2B_4H_4]^{2-}$ species is by naphthalene-catalyzed group 1 metal reduction.[1d]

The use of naphthalene in the traditional two-electron reductive cage opening reactions has several disadvantages. It introduces an additional reagent that must be removed from the reaction mixture before the *nido*-carborane products can be reacted further. In addition, naphthalene also has a tendency to cocrystallize with any product or to substitute for a terminal B−H hydrogen, which often interferes with the reactivity of these dianionic ligands. The inability of the *closo*-C_2B_4-carboranes to undergo two-electron reduction in the absence of naphthalene led us to question whether such carborane cages could be reductively opened and simultaneously metalated by an in situ generation of activated metal atoms, similar to that reported for the larger *closo*-$(CR)_2B_{10}H_{10}$.[2,3,7,8,11]

To explore this possibility, anhydrous $ErCl_3$ was reacted with 4 equiv of freshly cut potassium metal, under refluxing conditions in THF, to produce what we believe to be an activated form of erbium metal, in addition to 1 equiv of K metal.[12] When *closo*-carborane, 1,2-$(SiMe_3)_2$-1,2-$C_2B_4H_4$ (**1**), was immediately added to this metal mixture and refluxed overnight, a light orange crystalline solid, identified as the "carbons apart" erbacarborane sandwich 2,2′,4,4′-$(SiMe_3)_4$-3,6′-[$(\mu$-H$)_2$K-$(THF)_2$]-1,1′-*commo*-Er(η^5-2,4-$C_2B_4H_4)_2$ (**2**), was formed in 82% yield, as shown in Scheme 1.[12] It is important to note that, under equivalent conditions, neither one of the metals alone reacts with **1**, nor does a 3:1 K:$ErCl_3$ molar ratio reaction mixture; in both cases the *closo*-carborane precursor **1** was recovered unchanged. The sequence is also important: if **1**, $ErCl_3$, and K are mixed in a 2:1:4 molar ratio as in eq 1, a mixture is obtained

$$\mathrm{ErCl_3 + 4K + 2}\underset{\mathbf{1}}{\textit{closo}\text{-}\mathrm{(CSiMe_3)_2B_4H_4}} \xrightarrow{\mathrm{THF}} \underset{\mathbf{2}}{\mathrm{[K(THF)_2]Er(CSiMe_3)_2B_4H_4)_2}} + \mathrm{3KCl} \quad (1)$$

in which the products are inseparable; therefore, product analysis was not possible. It is important to note that the net reaction for Scheme 1, given in eq 1, is the same as that for the naphthalene-catalyzed reduction of **1**, followed by isolation and purification of the K salt of the corresponding dianion, and then its reaction with $ErCl_3$; this is the normal synthetic route.[13] Therefore, the same driving forces are at work in both methods. Viewed from this perspective, the method outlined in Scheme 1 just substitutes Er^{3+} for naphthalene as an electron-transfer agent. The fact that the reaction of **1** with the 1:3 molar mixture of $ErCl_3$/K produced no **2** shows that even finely divided (atomic) Er metal is not a strong enough reducing agent to bring about the reaction. Therefore, the reaction shown in Scheme 1 is an unprecedented example of a new two-electron reduc-

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(12) **Synthesis of 2:** anhydrous $ErCl_3$ (0.39 g, 1.43 mmol) was added to dry THF (20 mL) under argon, and the resulting heterogeneous mixture was stirred overnight. Freshly cut K metal (0.23 g, 5.90 mmol) was added to this mixture at room temperature and refluxed for 24 h at 70 °C, during which time the mixture turned dark. Immediately after the reaction mixture was cooled to room temperature, 2.30 mmol (0.50 g) of *closo*-1,2-$(SiMe_3)_2$-1,2-$C_2B_4H_4$ (**1**) was slowly added in vacuo and the resulting mixture was refluxed again at 70 °C using an oil bath. After 24 h, the product mixture was filtered through a glass frit in vacuo to collect a clear filtrate. The solid remaining on the frit was extracted repeatedly with anhydrous benzene, and the off-white residue, identified as KCl (not measured), was discarded. The combined filtrate and the benzene extract were pooled, and the solvents were removed in vacuo to obtain a dark yellow solid. The solid was then washed repeatedly with hexane and dissolved in hot benzene (15 mL). After it was cooled to room temperature, the solution afforded light orange crystals of **2** (1.55 g, 1.89 mmol; mp >250 °C dec; soluble in polar solvents and slightly soluble in *n*-hexane) in 82% yield. IR (cm^{-1}, KBr pellet): 2563 (s), 2530 (s), 2508 (sh), 2482 (s), 2461 (sh), 2367 (s) (ν(B−H)). Anal. Calcd for $C_{16}H_{44}B_8Si_4KEr\cdot2.5THF$: C, 37.99; H, 7.85. Found: C, 37.80; H, 7.91.

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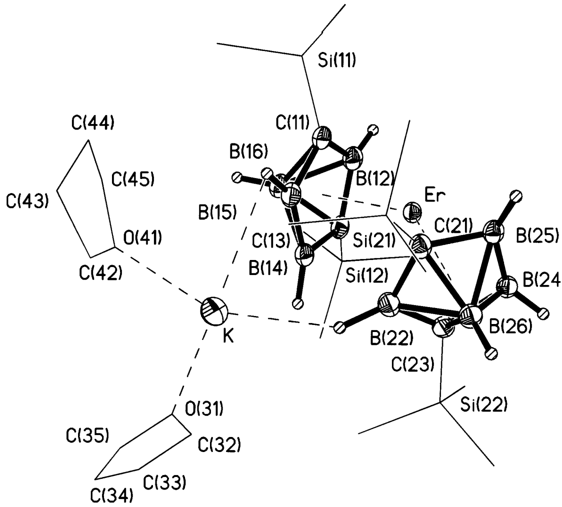

Figure 1. Molecular structure of 2,2′,4,4′-$(SiMe_3)_4$-3,6′-[(μ-H)$_2$K(THF)$_2$]-1,1′-*commo*-Er(η^5-2,4-$C_2B_4H_4$)$_2$ (**2**) with the thermal ellipsoids drawn at the 50% probability level. The exo-polyhedral $SiMe_3$ groups and the solvated THF molecules were drawn with thinner lines for clarity. Selected bond lengths (Å) and angles (deg): Er−(2,4-C_2B_3 centroid 1), 2.274; Er−(2,4-C_2B_3 centroid 2), 2.302; Er−C(11), 2.616(2); Er−B(12), 2.661(3); Er−C(13), 2.671(2); Er−B(14), 2.663(3); Er−B(15), 2.623(3); Er−C(21), 2.678(2); Er−B(22), 2.648(3); Er−C(23), 2.623(2); Er−B(24), 2.682(2); Er−B(25), 2.707(2); (2,4-C_2B_3 centroid 1)−Er−(2,4-C_2B_3 centroid 2), 137.4. See Table S-3 in the Supporting Information for a detailed list of bond lengths and angles.

tive cage-opening process in which the capping metal acts as the electron-transfer catalyst. It should also be noted that there is nothing unique about Er; the method outlined in Scheme 1 should prove to be a general route for the formation of a number of diverse metallacarboranes in the sub-icosahedral cage systems.

Compound **2** is paramagnetic with a magnetic moment (μ_{eff}) of 9.3 μ_B, which is consistent with a formal 3+ charge on the Er atom.[14] Unfortunately, the paramagnetic nature of **2** prevents its structural characterization by NMR spectroscopy. The IR spectrum[12] of **2** exhibits the expected terminal B−H stretch multiplets indicative of the unequal interactions of the boron-bound hydrogens with metal groups that are characteristic of the lanthanacarborane complexes.[15] However, because of the unprecedented nature of the cage-opening process, the structure of the title compound was unambiguously determined by X-ray diffraction analysis.[16]

The molecular structure of **2**, shown in Figure 1, is that of a bent metallacarborane in which the erbium metal is sandwiched between two "carbons apart" C_2B_4 carborane cages in an η^5 fashion, with a metal−(cage centroid) distance of 2.274 Å and a (centroid 1)−metal−(centroid 2) angle of 137.4°. This structure is quite similar to those found in the erbium complexes of "carbons adjacent" and "carbons apart" carborances and in the mixed-carborane ligand systems.[15b,17] There is no evidence for the formation of a six- or seven-membered opened face of the carborane ligand, hence eliminating the possibility of a four-electron reductive cage-opening process. Thus, the reactivity of the *closo*-C_2B_4 carborane cage distinguishes itself from the larger *closo*-C_2B_{10} cage systems. Since the erbacarborane is anionic, a $[K(THF)_2]^+$ group is also present for charge compensation. This cation is attached to the erbacarborane via two K−H−B bridges, as shown in Figure 1. The most interesting features in the structure of the erbacarborane are the absence of the coordinating solvent, THF, on the lanthanide metal and its η^5 coordination to each of the opened C_2B_3 bonding faces of the carborane ligands. This suggests that it might be possible to synthesize a number of different solvent-free lanthanacarboranes in a geometry similar to those of the metallocenes and to explore their further reaction chemistry.

To the best of our knowledge, this report constitutes the first example of a new two-electron reductive cage-opening/metalation process to form the corresponding *commo*-lanthanacarborane. An exploration of the reactions of the heavier alkaline-earth metals, as well as a number of p-, d-, and f-block metals, in the presence of excess alkali metals with different *closo*-carboranes is currently underway in our laboratories.

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Supporting Information Available: Tables of crystal data, fractional coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] The room-temperature effective magnetic moment of 9.3 μ_B for **2**, determined by using a Faraday balance (Dobson, J. C.; Helms, J. H.; Doppelt, P.; Sullivan, B. P.; Hatfield, W. E.; Meyer, Y. J. *Inorg. Chem.* **1989**, *28*, 2200−2204), is well within the reported range observed for other Er(III) π-complexes (Birmingham, J. M.; Wilkinson, G. *J. Am. Chem. Soc.* **1956**, *78*, 42−44).

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[16] X-ray structure determination: Bruker SMART CCD PLATFORM diffractometer, 173(2) K, triclinic, $P\bar{1}$, $a = 11.557(2)$ Å, $b = 12.587(2)$ Å, $c = 14.955(2)$ Å, $\alpha = 105.006(2)°$, $\beta = 92.473(3)°$, $\gamma = 106.286(3)°$, $Z = 2$, 10 336 total reflections, 6856 independent reflections, 422 parameters, $wR2(F^2) = 0.0463$, $R1 = 0.0179$ (6856 data with $I > 2\sigma(I)$), GOF = 1.044. All non-H atoms were refined anisotropically, and the B-bound H atoms were refined isotropically. All other H atoms were considered with the riding model.

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