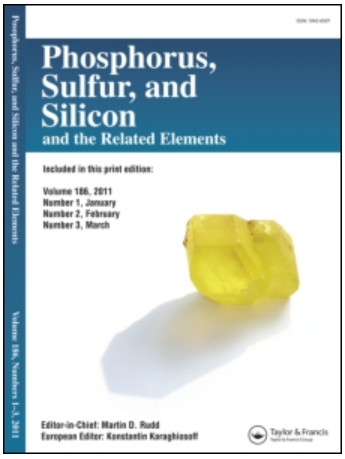

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SANDWICHED METALLACARBORANES OF *f*-BLOCK ELEMENTS

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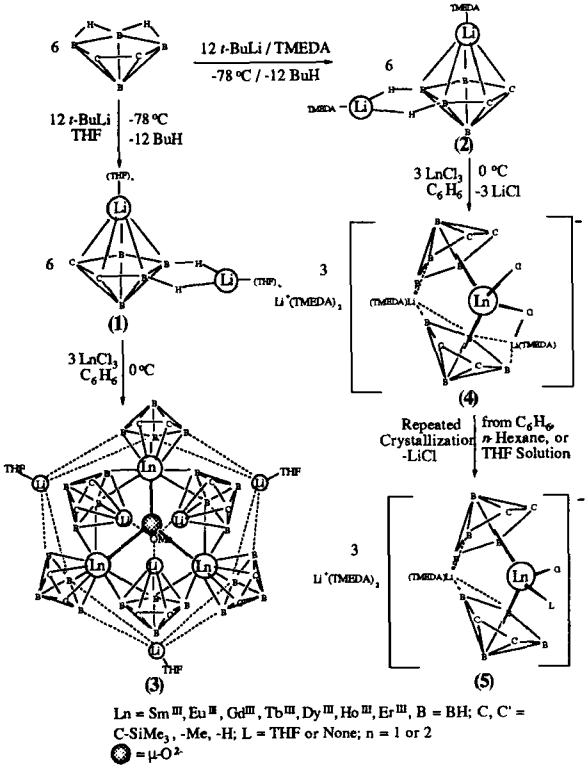
The dilithium complexed *"carbons adjacent" nido*-carborane anions of the type $[2\text{-}(SiMe_3)\text{-}3\text{-}(R)\text{-}2,3\text{-}C_2B_4H_4]^{2-}$ [R = $SiMe_3$, Me, H], as well as the disodium and dilithium complexed *"carbons apart" nido*-carborane anions $[2\text{-}(SiMe_3)\text{-}4\text{-}(R)\text{-}2,4\text{-}C_2B_4H_4]^{2-}$ [R = $SiMe_3$, Me] have exhibited different reactivity patterns toward various lanthanide halides, depending upon the solvents used in the reactions and the nature of the group 1 metal. Both the tetrahydofuran (THF) and *N, N, N, N*-tetramethylethylenediamine (TMEDA)-solvated *closo*-dilithiacarboranes have been found to be important synthons in the production of novel metallacarboranes of *f*-block elements. Several unprecedented examples of lanthanide-carborane complexes have been synthesized, their structures determined and reactivity studied.

Key Words: metallacarboranes, lanthanacarboranes, *f*-block elements, sandwich complexes

INTRODUCTION, RESULTS AND DISCUSSION

The chemistry of lanthanide-Cp and Cp* (Cp = $(C_5H_5)^-$, Cp* = $(C_5Me_5)^-$) systems has been known for some time.[1,2] However, the analogous carborane chemistry has just begun to be explored. Hawthorne and coworkers have recently reported the syntheses of a number of samara-, europa- and ytterbacarboranes involving the $[C_2B_9]^{2-}$ or $[C_2B_{10}]^{2-}$ dianionic ligands.[3] Despite these initial successes, there have been no further reports on the chemistry of such species. Our recent results on the syntheses and crystal structures of the trinuclear clusters, $\{[\eta^5\text{-}1\text{-}Ln(III)\text{-}2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_3[(\mu_2\text{-}1\text{-}Li\text{-}2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4)_3(\mu_3\text{-}OMe)][\mu_2\text{-}Li\text{-}(C_4H_8O)]_3(\mu_3\text{-}O)\}$ (Ln(III) = Sm, Gd, Tb, Dy, Ho and Er), demonstrate that the heavier lanthanide metals can also be incorporated into carborane cages.[4] The general synthesis involved the THF-solvated *closo*-dilithiacarborane and $LnCl_3$, in a molar ratio of 2:1 in dry benzene, and is shown in **Scheme I**. The structures of the lanthanacarborane clusters (see **Figure 1**, Ln = Tb, for example) show that they are composed of six C_2B_4-cages, three solvated-THF's, three Ln and six Li atoms that form a tricapped trigonal prism, with the lanthanide atoms in the capping positions of

Scheme I. Syntheses of Lanthanacarboranes



Ln = Sm^{III}, Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III}, Ho^{III}, Er^{III}, B = BH; C, C' = C-$SiMe_3$, -Me, -H; L = THF or None; n = 1 or 2

⊗ = μ-O^{2-}

the cluster.[4] The metal in each *closo*-lanthanacarborane unit is centered over the carborane face. The *closo*-lanthanacarboranes are bridged by both Li^+(THF) and *closo*-lithiacarborane moieties. The center of the cluster is an O atom, that triply bridges the Ln atoms (the ave. Ln-$O_{(central)}$-Ln angle = 119.1°), and is slightly displaced out of the Ln_3 trigonal plane by about 0.18 - 0.22 Å. Since each of the six carborane ligands and the central oxygen atom bear a 2- charge and three Ln(III) and six Li(I) metals are also present, charge compensation requires the additional $(MeO)^-$ moiety that was found bound to the apical lithium atoms of the lower triangle of *closo*-lithiacarboranes in a tetrahedral fashion (see **Figure 1**). The fact, that all of the isostructural lanthanacarborane clusters are synthesized in good, reproducible yields of about 61-70%, indicates the existence of a definite reactivity pattern in this system.[4] Therefore, the generation of an O^{2-} and OMe^- anions, *in situ*, as well as their subsequent incorporation into the trinuclear cluster (**3**) are not accidental occurrences; in fact, they are the products of a consistent solvent degradation reaction that is taking place, when $LnCl_3$ is being reacted with the THF-solvated dilthiacarborane (**1**).[4,5]

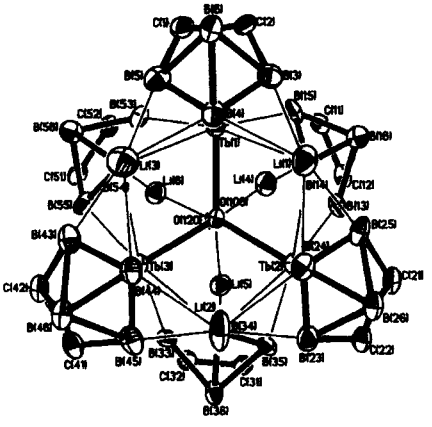


FIGURE 1 Perspective view of the trinuclear *closo*-terbacarborane cluster.

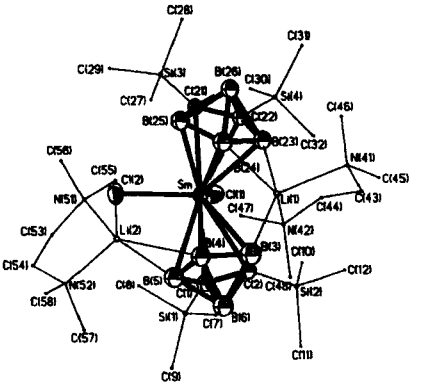


FIGURE 2 Perspective view of the mononuclear samarium(III)-carborane bent-sandwich complex.

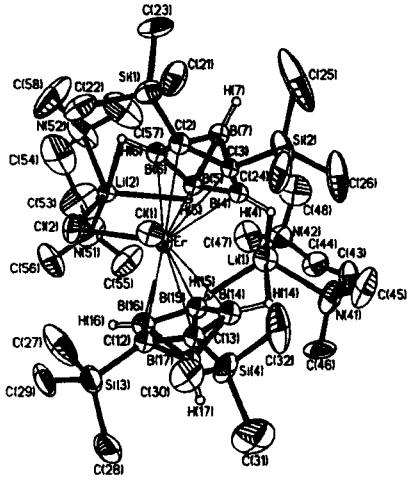


FIGURE 3 Perspective view of the *"carbons adjacent"* erbium(III)-carborane bent-sandwich complex.

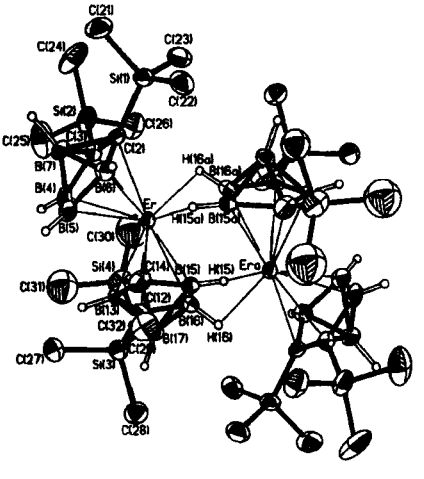


FIGURE 4 Perspective view of the mixed *"C-adjacent"* and *"C-apart"* erbacarborane bent-sandwich dimer.

Although the exact mechanism of these reactions is still unknown, it is now believed that the oxygen containing solvent, such as THF, is the source of O^{2-} and OMe^- ions.[5] This was further substantiated in an experiment in which $LnCl_3$ was reacted with the TMEDA-solvated **2**, rather than the THF-solvated **1**; in this reaction, a mononuclear, bent-sandwiched Ln(III)-carborane complex (**4**) (see **Scheme I**) was the only mtalla-carborane product. Neither **3** nor any oxygen-containing compound could be identified among the products. This seems to rule out the possibility that **3** could be a decomposition product of the reaction between **1** and $LnCl_3$ during an accidental exposure to air and/or moisture or some OMe containing impurity.[5] The crystal structures [**Figures 2** (Ln = Sm) and **3** (Ln = Er)] show the presence of two Cl atoms on the central lanthanide atom and two B-bound Li(TMEDA) units, whose net negative charge is balanced by an additional $Li(TMEDA)_2$ unit outside the coordination sphere.[5]

The presence of two Cl atoms on the lanthanide metal suggests that it could be converted to either a mixed *"carbons adjacent"* and *"carbons apart"* lanthanacarborane species, such as the dimeric erbacarborane sandwich (**Figure 4**), or a metal-alkyl complex in a manner similar to that found for Y, Zr, Hf and Ti bent-sandwich complexes.

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