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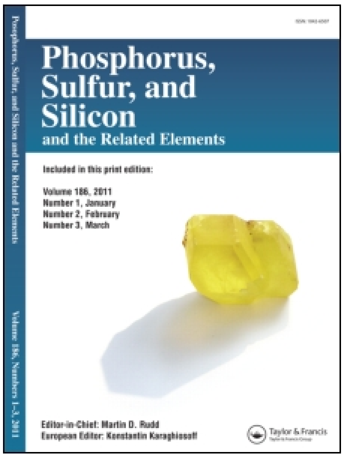

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THE SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF CARBORANE DERIVATIVES CONTAINING MAIN GROUP AND f-BLOCK ELEMENTS

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Abstract The synthesis, X-ray structural characterization, and reactivity of a number of novel metallacarborane compounds including those that exhibit η^5-dicarbollide ligands bound to aluminum, silicon, and 4f-block elements are discussed. These compounds include the first sandwich compounds to contain main group elements in their highest formal oxidation states, [*commo*-3,3'-M(3,1,2-$MC_2B_9H_{11}$)$_2$]$^{n-}$ (M = Al, n = -1; M = Si, n = 0), and the first examples of lanthanacarboranes, *closo*-$C_2B_9H_{11}$Ln(THF)$_4$ (Ln = Sm, Yb) and [3,3-(THF)$_2$-*commo*-3,3'-Sm(3,1,2-$SmC_2B_9H_{11}$)$_2$]$^-$.

INTRODUCTION

Interest in the chemistry of main group and f-block elements has been increasing in recent years. Investigations in our laboratory of main group and lanthanide element containing metallacarborane derivatives have recently resulted in the synthesis and characterization of a number of novel metallacarborane compounds which exhibit unusual structural features. These compounds include the first [Ne]-core main group element sandwich species as well as the first lanthanacarborane complexes.

CARBORANE DERIVATIVES CONTAINING ALUMINUM AND SILICON

The chemistry of aluminacarboranes continues to develop and several different structural types have now been observed for this class. A notable feature of the structural chemistry of aluminacarboranes is the variety of bonding modes exhibited by aluminum in interactions with carborane cage moieties. Compounds formally exhibiting the η^3, η^5, and bis-η^5 aluminum-carborane cage π-bonding modes, as well as the η^2 aluminum-carborane σ-bonding mode, have now been structurally characterized. In addition, the occurrence of dynamic solution behavior appears to be a general characteristic of these species.[1-8]

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Since aluminacarboranes are both highly reactive and soluble in organic solvents, they are of interest as transmetallation reagents for the synthesis of new or otherwise difficult to prepare metallacarborane derivatives. A similar use of main group element carborane derivatives for this purpose has been demonstrated by Hosmane with the high yield synthesis of a new transition metal metallacarborane complex using a stannacarborane reagent.[9] Recently, this approach has been employed by Jutzi, et al. using an aluminacarborane reagent in the preparation of other main group element metallacarborane derivatives.[10] Further synthetic applications of this kind remain to be developed.

The synthesis of the twelve-vertex aluminacarboranes *closo*-3-R-3,1,2-$AlC_2B_9H_{11}$ (R = Et, **1a**; R = Me, **1b**) and the gallium-containing analogue of **1b** has been reported previously.[1-3] Compounds **1a** and **1b** were prepared by reaction of *nido*-$C_2B_9H_{13}$ with the appropriate trialkylaluminum reagent. These reactions initially produce aluminacarboranes of the type *exo-nido*-9,10-$(\mu\text{-}H)_2AlR_2$-$C_2B_9H_{10}$ (R = Et, **2a**; R = Me, **2b**) in which a cationic dialkylaluminum moiety is bound to the anionic carborane cage by B-H-Al bridges. These species are fluxional with enantiomeric forms rapidly interconverting in solution at room temperature Upon heating **2a** or **2b** in aromatic solvent, a second equivalent of alkane is eliminated to yield **1a** or **1b**. Compounds **1a** and **2b** have been structurally characterized by single crystal X-ray diffraction studies and their structures are illustrated schematically in Figure 1. Compounds **1a** and **1b** act as Lewis bases, forming adducts with a variety of Lewis acids.

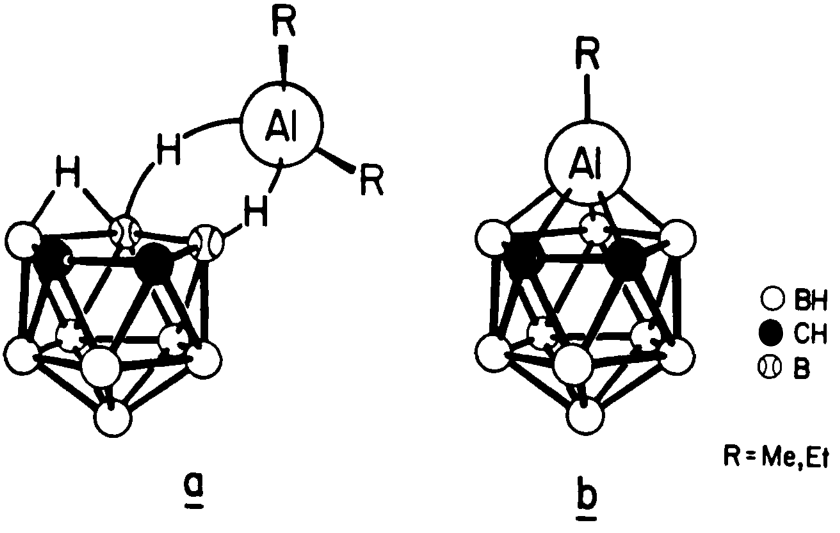

FIGURE 1 The structures of (a) *exo-nido*-9,10-(μ-H)$_2$-AlMe$_2$-C$_2$B$_9$H$_{10}$, **2b**, and (b) *closo*-3-Et-3,1,2-AlC$_2$B$_9$H$_{11}$ (**1b**) shown schematically.

Variable temperature NMR studies of **1a** coupled with molecular weight measurements indicate that this species exists in equilibrium with a dimer in solution in aromatic solvents. The concentration of this dimer is increased at elevated temperature. The dimeric species, which is of the type *commo*-3,3'-Al[{*exo*-8,9-(μ-H)$_2$-AlEt$_2$-3,1,2-AlC$_2$B$_9$H$_9$}(3',1',2'-AlC$_2$B$_9$H$_{11}$)] (**3**), has been isolated and characterized by a combination of spectroscopic techniques and a single crystal X-ray diffraction study.[4] The structure of **3** is shown in Figure 2a.

In **3**, the planar C$_2$B$_3$ bonding faces of the two dicarbollide cages are within 2.6° of a parallel relationship to one another and each cage face is coordinated to the central aluminum atom

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in η^5-fashion. In addition, a cationic diethylaluminum moiety is bound to one of the dicarbollide cages via two Al-H-B bridging interactions. This compound may be regarded formally as a zwitterion composed of the [*commo*-3,3'-Al(3,1,2-$AlC_2B_9H_{11})_2]^-$ anion complexed with the $[AlEt_2]^+$ cation. Both ^{11}B and ^1H NMR data for **3** indicate that the aluminum-bound ethyl groups and both of the dicarbollide cages are equivalent in solution on the NMR time scale at room temperature, suggesting the occurrence of a facile diethylaluminum "cage walking" process in solution.

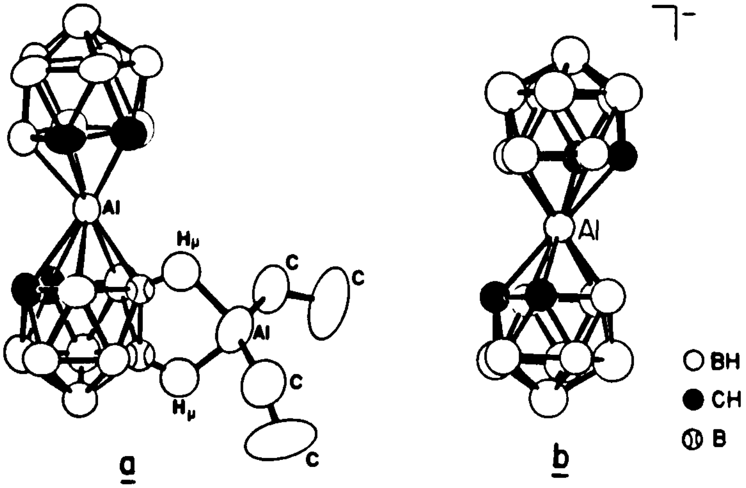

FIGURE 2 The structures of: (a) *commo*-3,3'-Al[{*exo*-8,9-$(\mu\text{-}H)_2$-$AlEt_2$ -3,1,2-$AlC_2B_9H_9$}(3',1',2'-$AlC_2B_9H_{11}$)], **3**; and (b) [*commo*-3,3'-Al(3,1,2-$AlC_2B_9H_{11})_2]^-$, $[\mathbf{4}]^-$, with all hydrogen atoms except those participating in bridging interactions omitted.

Recently it has been found that the reaction $AlEt_3$ with Tl[*closo*-3,1,2-$TlC_2B_9H_{11}$] in toluene solution results in the formation of the free aluminum sandwich anion [*commo*-3,3'-Al-(3,1,2-$AlC_2B_9H_{11})_2]^-$ ($[\mathbf{4}]^-$) in high yield.[5] This anion has been isolated as the $[Tl(toluene)]^+$ salt and structurally characterized by a single crystal X-ray diffraction study. The structure of $[\mathbf{4}]^-$ is shown in Figure 2b. In $[\mathbf{4}]^-$, the aluminum atom is formally in the +III oxidation state and the planar bonding faces of the

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two dicarbollide cages are parallel to one another and bound to the aluminum atom in η^5-fashion. This complex thus represents an unusual example of a sandwich compound that contains a main group element in its highest formal oxidation state ([Ne]-core) bound between the parallel faces of two planar π-donor ligands.

The discovery of aluminacarborane sandwich complexes prompted us to pursue the synthesis of the formally isoelectronic silicon analogue. As a result, it was found that the reaction of silicon tetrachloride with two molar equivalents of Li_2[*nido*-7,8-$C_2B_9H_{11}$] in refluxing benzene affords the desired silicon sandwich compound, *commo*-3,3'-Si(3,1,2-$SiC_2B_9H_{11}$)$_2$ (**5**) in good yield as shown in Equation 1.[12]

$$2\ Li_2[7,8\text{-}C_2B_9H_{11}]\ +\ SiCl_4\ \xrightarrow{\text{benzene}}$$

$$commo\text{-}3,3'\text{-}Si(3,1,2\text{-}SiC_2B_9H_{11})_2\ +\ 4\ LiCl \qquad (1)$$

The structure of **5**, as determined by a single crystal X-ray diffraction study, is shown in Figure 3. Compound **5** is crystallographically centrosymmetric about the silicon center with the two dicarbollide C_2B_3 bonding faces parallel to one another and bound to the silicon atom in η^5-fashion. This compound is moderately air stable, sublimable, and soluble in organic solvents including aliphatic hydrocarbons. Compound **5** acts as a Lewis acid, reacting with a variety of electron donors to form a variety of products of unusual structural types.[13] While similar main group element sandwich compounds are well known [e.g. $M(C_5Me_5)_2$, M = Si, Ge, Sn, Pb],[11] these species are 14 interstitial electron systems that contain central atoms which are formally in the +II oxidation state.

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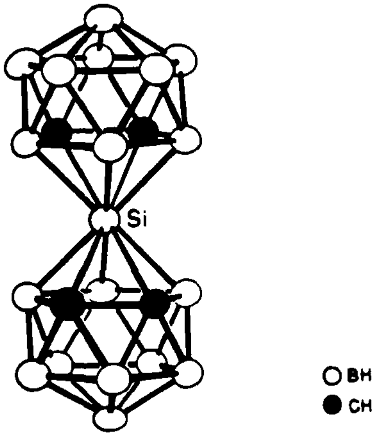

FIGURE 3 The structure of *commo*-3,3'-Si(3,1,2-$SiC_2B_9H_{11}$)$_2$, **5**, with hydrogen atoms omitted for clarity. Interatomic distances (Å): Si-C(1,2) = 2.22, Si-B(4,7) = 2.14, Si-B(8) = 2.05.

As part of a recent effort in our laboratory to explore the chemistry of non-icosahedral aluminacarborane compounds, the reaction of diethylaluminum chloride-diethyl etherate with the carborane salt Na[5,6-$C_2B_8H_{11}$]^{14} was carried out.^{6} This reaction proceeds in refluxing toluene solution to produce the neutral species, *nido*-μ-6,9-AlEt(OEt_2)-6,9-$C_2B_8H_{10}$ (**6**) in good yield, as shown in Equation 2.

$$\mathrm{Na[5,6\text{-}C_2B_8H_{11}]} \;+\; \mathrm{AlEt_2Cl{\cdot}OEt_2} \xrightarrow{\text{toluene}}$$

$$\textit{nido}\text{-}\mu\text{-}6,9\text{-}\mathrm{AlEt(OEt_2)\text{-}6,9\text{-}C_2B_8H_{10}} \;+\; \mathrm{NaCl} \;+\; \mathrm{C_2H_6} \qquad (2)$$

Compound **6** is a colorless, air-sensitive liquid. The structure of **6** shown in Figure 4a was determined by a single crystal X-ray diffraction study of its crystalline benzene solvate **6**(C_6H_6)$_{0.5}$.

The geometry of the polyhedral portion of **6** is that of a regular octadecahedron with no single open face. The aluminum atom occupies the unique vertex on the pseudo-two-fold rotation axis of the cluster. The four aluminum-boron interatomic distances are nearly equal and average 2.51 Å. The two aluminum -carbon distances are also nearly equal and average 2.03 Å. These distances suggest that bonding interactions in **6** occur only between aluminum and carbon. Regarding the 6,9-$C_2B_8H_{10}$ cage as an η^2 ligand, the geometry about aluminum is approximately tetrahedral.

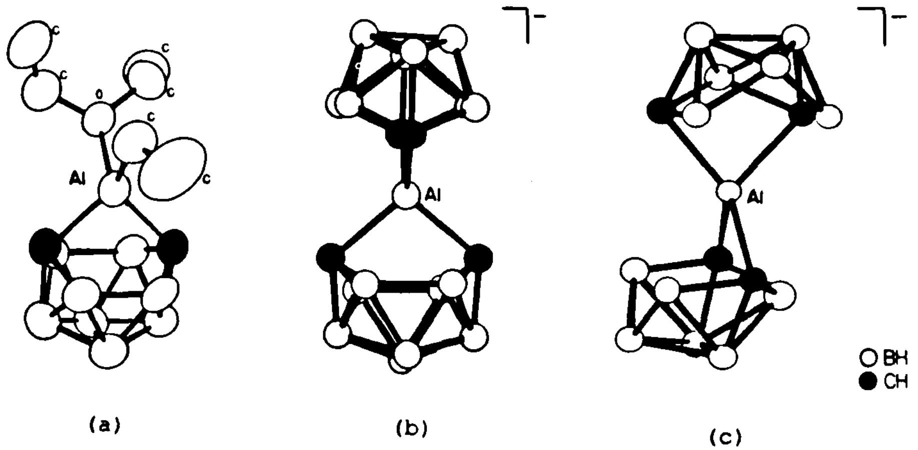

FIGURE 4 The structures of (a) *nido*-μ-6,9-AlEt(OEt$_2$)-6,9-$C_2B_8H_{10}$, **6**; (b) $[Al(\eta^2\text{-}6,9\text{-}C_2B_8H_{10})_2]^-$, $[\mathbf{7}]^-$, and (c) one enantiomer of $[Al(\eta^2\text{-}6,9\text{-}C_2B_6H_8)_2]^-$, $[\mathbf{8}]^-$, all with hydrogen atoms omitted for clarity.

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Compound **6** gives ^{11}B and ^{1}H NMR spectral data consistent with a species having C_{2v} point group symmetry. This suggests the occurrence of a dynamic process in solution involving the intermolecular exchange of the adducted diethyl ether. Furthermore, the ^{1}H NMR spectrum of of **6** in an aromatic hydrocarbon containing excess diethyl ether shows only a single set of diethyl ether resonances. The lability of the aluminum-bound ether in **6** is further indicated by the facile exchange which occurs upon addition of THF to a toluene solution of **6**, resulting in the immediate formation of adduct *nido*-μ-6,9-AlEt(THF)-6,9-$C_2B_8H_{10}$.

The structure of **6** contrasts with that of other known eleven -vertex, 26-electron main group element-containing clusters, such as $[Me_2M(\eta^4\text{-}B_{10}H_{12})]$ (M = Si, Ge, Sn), which adopt nido structures having a unique open face and a pair of bridging B-H-B moieties.[15] However, structurally similar complexes of the type *nido*-μ-6,9-ML_2-6,9-$C_2B_8H_{10}$ (M = Pt, Ni; L = Lewis base) have been reported which contain square planar rather than tetrahedral metal centers.[16]

The reaction of Na[5,6-$C_2B_8H_{11}$] with diethylaluminum chloride in refluxing toluene in the absence of ether results in the formation of the aluminacarborane salt Na[Al(η^2-6,9-$C_2B_8H_{10}$)$_2$] (Na[7]) in good yield, as shown in Equation 3.[7] The anion [7]$^-$ has been

$$2\ Na[5,6\text{-}C_2B_8H_{11}] + AlEt_2Cl \xrightarrow{\text{toluene}} Na[Al(\eta^2\text{-}6,9\text{-}C_2B_8H_{10})_2] + NaCl + 2\ C_2H_6 \qquad (3)$$

characterized as the air-stable $[N(PPh_3)_2]^+$ salt, formed by metathesis of Na[7]$^-$ with $[N(PPh_3)_2]Cl$. The structure of [7]$^-$ determined by a single crystal X-ray diffraction study is shown in Figure 4b. In [7]$^-$, the two 6,9-$C_2B_8H_{10}$ cages are bound in η^2-fashion to the approximately tetrahedral aluminum center, apparently via aluminum-carbon interactions only. The four similar aluminum-carbon interatomic distances in [7]$^-$ average 2.06 Å, while the eight similar aluminum-boron distances average 2.53 Å. The anion [7]$^-$ possesses non-crystallographic S_4 point group symmetry and may be regarded as a spiro-aluminate compound. The ^{11}B NMR spectral data for [7]$^-$ indicate that its symmetry in solution is the same, at least on the NMR time scale, as that observed in the solid state.

The reaction of the diethyl ether solvate of the carborane salt Na[1,3-$C_2B_7H_{12}$][17] with diethylaluminum chloride in refluxing toluene results in formation of the aluminacarborane salt Na[Al(η^2-2,7-$C_2B_6H_8$] Na[**8**] in moderate yield.[8] This salt, an air-sensitive, white solid, was characterized by a single crystal X-ray diffraction study. The [**8**]$^-$ anion occurs as a pair of enantiomeric stereoisomers. The structure of one enantiomer of

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$[\mathbf{8}]^-$ is shown in Figure 4c. The structure of $[\mathbf{8}]^-$ is similar to that of $[7]^-$ in that two 2,7-$C_2B_6H_8$ cages are bound to an approximately tetrahedral aluminum center apparently via aluminum-carbon interactions only. The four similar aluminum-carbon distances in $[\mathbf{8}]^-$ average 2.02 Å. Two relatively short aluminum-boron interatomic distances are present which average 2.28 Å, while another four similar aluminum-boron distances average 2.51 Å.

The high symmetry indicated by NMR spectral data for $[\mathbf{8}]^-$ indicates that the two enantiomers of this anion rapidly interconvert in solution. Variable temperature NMR studies have shown that this dynamic process can be frozen out by cooling toluene solutions containing the $[\mathbf{8}]^-$ anion to -80 °C.

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CARBORANE DERIVATIVES CONTAINING f-BLOCK ELEMENTS

The synthesis of new complexes containing lanthanide metals has been a subject of considerable interest in recent years.[18] Organolanthanide complexes with pentamethylcyclopentadienide (Cp*) ligands have been shown to possess high reactivity as well as unique structural features.[19] Prior to our recent work, the only structurally characterized dicarbollide complex with an f-block metal was $[U(C_2B_9H_{11})_2Cl_2]^{2-}$,[20] which had the two dicarbollide ligands arranged in a bent configuration around the U^{4+} ion. We have recently synthesized and characterized the first dicarbollide complexes with the 4f-block metals, the lanthanacarboranes.[21]

These new metallacarboranes can be synthesized with the divalent lanthanides samarium and ytterbium as shown in Equation 4. The neutral complexes formed from these metathetical reactions are highly air and moisture sensitive but are easily isolated due to their low solubility in THF. Complexometric analysis as well as spectroscopic and magnetic data support the formulation of both **9** and **10** as having one carborane cage per

$$\mathrm{LnI_2(THF)_x} \ + \ \mathrm{Na_2[C_2B_9H_{11}]} \xrightarrow[\mathrm{RT}]{\mathrm{THF}} \mathit{closo}\text{-}\mathrm{C_2B_9H_{11}Ln(THF)_4} + 2\ \mathrm{NaI} \qquad (4)$$

Ln = Sm (**9**), Yb (**10**)

metal. Both complexes are only marginally soluble in THF, but **10** can be solublized by other coordinating ligands such as CH_3CN and DMF (N,N-dimethylformamide) since the THF ligands are displaced by these donor solvents. The DMF adduct of **10** could be isolated as single crystals; an X-ray structure determination was carried out on this complex, *closo*-$C_2B_9H_{11}Yb(DMF)_4$ (**11**), and the results are presented in Figure 5. Due to a crystallographic disorder, it was not possible to distinguish carbon from boron in the upper belt of the carborane cage, and we were thus unable to identify this complex in accord with the accepted nomenclature. The distances from the metal to the atoms of the upper belt of the carborane cage compare rather well with Yb-C(C_5Me_5) values reported for crystallographically characterized ytterbium (II) η^5-pentamethylcyclopentadienyl complexes,[22] thereby supporting the idea that the ytterbium

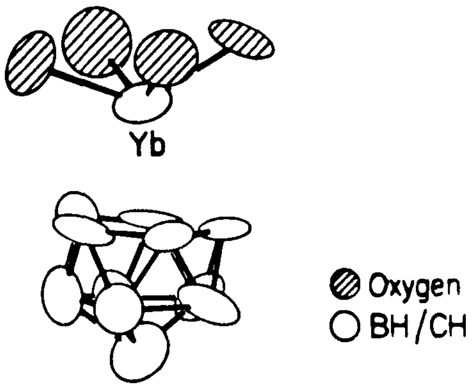

FIGURE 5 The structure of *closo*-$C_2B_9H_{11}Yb(THF)_4$, **11**, with hydrogen atoms omitted and only the oxygen atoms of the DMF ligands shown.

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ion "caps" the dicarbollide ligand to generate an icosahedron with overall closo-geometry. Mono-cage complexes of samarium and ytterbium can also be synthesized with C-substituted derivatives of the dicarbollide ligand; analogous compounds have also been prepared with the $[C_2B_{10}H_{12}]^{2-}$ ligand[23] which are the corresponding thirteen-vertex lanthanacarboranes.

To date, all of the organolanthanide complexes which possess two η^5-bound rings in their coordination sphere have these rings configured in a "bent" fashion around the lanthanide ion.[18] The synthesis of $[U(C_2B_9H_{11})_2Cl_2]^{2-}$ for the first time showed that use of an f-block metal permitted the dicarbollide ligands to adopt a bent geometry around the metal since this structure is not seen with dicarbollide complexes of d-block or main group metals. The ionic radius of the trivalent lanthanides is close to that of U^{4+},[24] so bis-dicarbollide complexes of the lanthanides might be expected to have the ligands configured with this "bent" geometry. A rational approach to the synthesis of 4f metallacarborane sandwich complexes of this type is the addition of a second dicarbollide ligand to **9** or **10**. Anaerobic addition of *closo*-$C_2B_9H_{11}Sm(THF)_4$ (**9**) to a THF solution of [PPN][*closo*-3,1,2-$TlC_2B_9H_{11}$] affords the desired bis-dicarbollide complex **12**, as shown in Equation 5. In this reaction the thallous ion is reduced

$$\textit{closo}\text{-}C_2B_9H_{11}Sm(THF)_4 + [PPN][\textit{closo}\text{-}3,1,2\text{-}TlC_2B_9H_{11}] \xrightarrow{THF} [PPN][3,3\text{-}(THF)_2\text{-}\textit{commo}\text{-}3,3'\text{-}Sm(3,1,2\text{-}SmC_2B_9H_{11})_2] + Tl + 2\,THF \quad (5)$$

to thallium metal while the divalent samarium ion is oxidized to samarium(III), thus providing for a better accommodation of the high formal negative charge provided by the two dicarbollide ligands. The analogous ytterbium complex can also be synthesized using this reaction scheme by substituting **10** for **9**. Magnetic and

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spectral data obtained for these bis-dicarbollide complexes support a formulation having the metal in the trivalent oxidation state.

A single crystal X-ray diffraction study was carried out with the $[N(PPh_3)_2]^+$ salt of **12** and the results of this study are shown in Figure 6. The coordination geometry about samarium is tetrahedral, with an average THF(O)-Sm-ring centroid angle of 108.2°. The two η^5-dicarbollide ligands and the two coordinated THF molecules occupy the coordination sphere about Sm^{3+}. The ring centroid-Sm-ring centroid angle is 131.9(5)°; this value compares well with those found for other trivalent bis-Cp* lanthanide complexes which possess other ligands in the metal's coordination sphere.[25]

An effective ionic radius[26] could be calculated for the dicarbollide ligand using X-ray data from **11** and **12** and this value

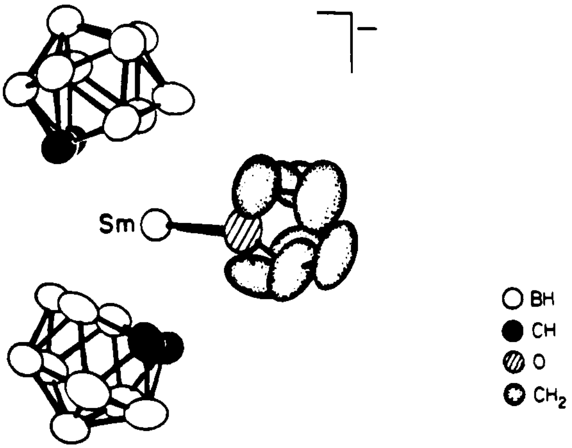

FIGURE 6 The structure of $[3,3\text{-}(THF)_2\text{-}$*commo*$\text{-}3,3'\text{-}Sm(3,1,2\text{-}SmC_2B_9H_{11})_2]^-$, **[10]**$^-$ with hydrogen atoms omitted. One of the THF ligands is eclipsed by the other in this view.

(1.66 Å) is very similar to the average value determined for the cyclopentadienyl ligand (1.64 Å) thus suggesting that the bonding in these lanthanacarboranes is the same as that found in lanthanide-Cp complexes, that is predominantly ionic.

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REFERENCES

1. A. T. Young, G. R. Willey, M. F. Hawthorne, A. H. Reis, and M. R. Churchill, *J. Am. Chem. Soc.*, **92**, 6663 (1970).
2. A. T. Young, R. J. Wiersema, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **93**, 5687 (1971).
3. M. R. Churchill, A. H. Reis, Jr., D. A. T. Young, G. R. Willey, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 298 (1971).
4. W. S. Rees, Jr., D. M. Schubert, C. B. Knobler, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **108**, 5367 (1986).
5. M. A. Bandman, C. B. Knobler, and M. F. Hawthorne, *Inorg. Chem.*, **27**, 2399 (1988).
6. D. M. Schubert, W. S. Rees, Jr., C. B. Knobler, and M. F. Hawthorne, *Organometal.*, **6**, 201 (1987).
7. D. M. Schubert, W. S. Rees, Jr., C. B. Knobler, and M. F. Hawthorne, *Organometal.*, **6**, 203 (1987).
8. D. M. Schubert, C. B. Knobler, and M. F. Hawthorne, *Organometal.*, **6**, 1353 (1987).
9. N. S. Hosmane and N. N. Sirmokadam, *Organometal.*, **3**, 1119 (1984).
10. P. Jutzi, P. and P. Galow, *Organometal. Chem.*, **319**, 139 (1987).
11. (a) J. L. Atwood, W. E. Hunter, A. H. Cowley, R. A. Jones, C. A. Stewart, *J. Chem. Soc.*, **1981**, 925, and references therein; (b) M. J. Heeg, C. Janiak, and J. J. Zuckerman, *J. Am. Chem. Soc.*, **106**, 4259 (1984).
12. W. S. Rees, Jr., D. M. Schubert, C. B. Knobler, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **108**, 5369 (1986).
13. M. F. Hawthorne, et al., to be submitted for publication.
14. (a) J. Plesek and S. Hermanek, *Chem. & Ind. (London)*, 1267 (1971); (b) J. Plesek and S. Hermanek, *Collect. Czech. Chem. Commun.*, 38, 338 (1973); (c) J. Plesek and S. Hermanek, *Collect. Czech. Chem.Commun.*, **38**, 338 (1973).
15. (a) R. E. Loffredo and A. D. Norman, *J. Am. Chem. Soc.*, **93**, 5587 (1971).; (b) R. E. Loffredo and A. D. Norman, *Inorg. Nucl. Chem. Lett.*, **13**, 599 (1977).
16. (a) B. Stibr, Z. Janousek, K. Base, S. Hermanek, J. Plesek, and I. Zakharova, *Collect. Czech. Chem.Commun.*, **49**, 1891 (1984); G. A. Kukina, M. A. Porai-Koshits, V. C. Sergienko, O. Strouf, K. Base, I. A. Zakarhova, and B. Stibr, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1686 (1980).

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17. (a) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, J. Am. Chem. Soc., 88, 607 (1966); (b) P. M. George, T. A. George, and M. F. Hawthorne, Inorg. Chem., 8, 2008 (1969).

18. W. J. Evans, Adv. Organomet. Chem., 24, 131 (1985) and references therein.

19. See for example: (a) P. L. Watson and G. W. Parshall, Accts. Chem. Res. 18, 51 (1985); (b) W. J. Evans, L. A. Hughes, T. P. Hanusa, Organometal., 5, 1285 (1986).

20. F. R. Fronczek, G. W. Halstead, and K. N. Raymond, J. Am. Chem.Soc., 99, 1769 (1977).

21. M. J. Manning, C. B. Knobler and M. F. Hawthorne, J. Am. Chem. Soc., 110, 4458 (1988).

22. W. J. Evans, Polyhedron, 6, 803 (1987), and references therein.

23. C. G. Salentine and M. F. Hawthorne, Inorg. Chem. 15, 2872 (1976).

24. R. D. Shanon, Acta Crystallogr., Sect. A, A32, 751 (1976).

25. T. D. Tilley, R. A. Andersen, B. Spencer, and A. Zalkin, Inorg.Chem., 21, 2647 (1982).

26. K. N. Raymond and C. W. Eigenbrot, Accts.Chem. Res., 13, 276 (1980).

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