New frontiers in main group heterocarboranes

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Abstract - The synthetic utility of the C_2B_4-carborane dianions in the preparation of a number of main group heterocarboranes is demonstrated. The *closo*-heterocarboranes form the donor-acceptor complexes with a variety of Lewis bases. The structures of the heterocarboranes and their complexes have been determined by X-ray diffraction. The common structural features of the donor-acceptor complexes are the longer M-C (M = heteroatom) bonds due to extreme slippage of the heteroatom toward the unique boron, and the orientation of the bonded base opposite the cage carbons. The exclusive formation of the stable, 1,2-isomer of the dicarba-*closo*-hexaborane (6) from C_2B_4-carborane dianions and *closo*-stannacarboranes is described. Synthesis and structural characterizations of *closo*-gallacarboranes and their donor-acceptor complexes are also presented.

INTRODUCTION

Recently, considerable interest has been shown in the synthesis and reaction chemistry of *nido*-2,3-$C_2B_4H_8$ [dicarbahexaborane (8)] and its C,C'- substituted derivatives (ref. 1). These carborane derivatives are not only important precursors to *closo*-carboranes and tetracarbon carboranes, they also coordinate to transition, and main group, metals in an η^1, η^2, η^3 or η^5 fashion (ref. 1-4). Most recently, Grimes and coworkers were able to synthesize a number of multidecker species containing a variety of transition metals sandwiched by their C_2B_3 faces, thus showing that these small carborane derivatives are also important building blocks for the construction of the extended metallacarboranes of great significance in electrochemistry (ref. 3). Until recently, the usual method of preparation of $C_2B_4H_8$ derivatives was that described by Hosmane and Grimes (ref. 5, 6) This method is complicated by the use of Lewis bases such as $(C_2H_5)_3N$ and is limited to a maximum of 1-2 g of carboranes per synthesis. Nevertheless, in terms of yield, safety and practicality, the method is preferable to the one reported by Onak, *et al.* (ref. 7) especially for the production of small carboranes on the laboratory scale. More recently, a clean, high yield, laboratory scale preparative route to *nido*-(Me₃Si)(R)$C_2B_4H_6$ (R = SiMe₃, Me or H) derivatives was reported by us (ref. 8). Several aspects of these trimethylsilyl analogues of *nido*-2,3-$C_2B_4H_8$ make them attractive ligands for synthetic organometallic chemistry. Recent work, described in the next section, demonstrates that the C-SiMe₃ substituted carboranes are versatile reagents and that their reactivity toward main group metals and metalloids leads to a variety of heterocarborane clusters with interesting chemical, structural, and bonding features. Thus, new frontiers in main group heterocarboranes have just begun to be investigated.

MONO- AND DIANIONS: PRECURSORS TO *closo*-HETEROCARBORANES

The preparation of the monosodium salt of 2,3-dicarba-*nido*-hexaborate (1-) was first reported by Onak and Dunks nearly 25 years ago; attempts to produce the disodium salts of this carborane resulted only in failure (ref. 9).
Our recent work has shown that the *nido*-2-(SiMe₃)-3-(R)-2,3-$C_2B_4H_6$ reacts with a large excess of pure NaH in THF in a method identical to that employed by Onak and Dunks to produce exclusively the novel THF-solvated ion cluster, $(C_4H_8O \cdot Na^+)_2$ [2-(SiMe₃)-3-(R)-2,3-$C_2B_4H_5^-$]₂ (R = SiMe₃, Me, H) as shown in Scheme I (ref. 10, 11). The molecular geometry of the ion cluster was confirmed by single-crystal X-ray analysis as shown in Fig. 1 (ref. 11). The ion cluster is of an extended network of dimeric {Na⁺[(SiMe₃)₂$C_2B_4H_5$]⁻}₂ units that are layered almost
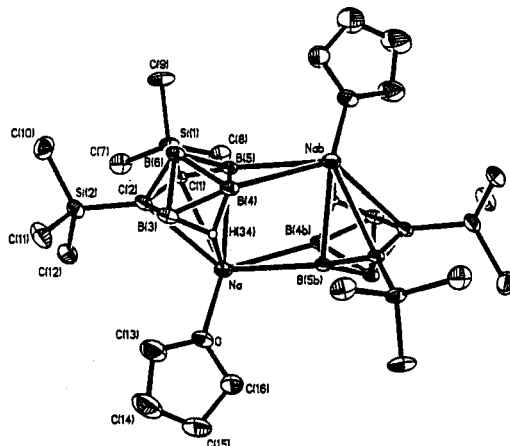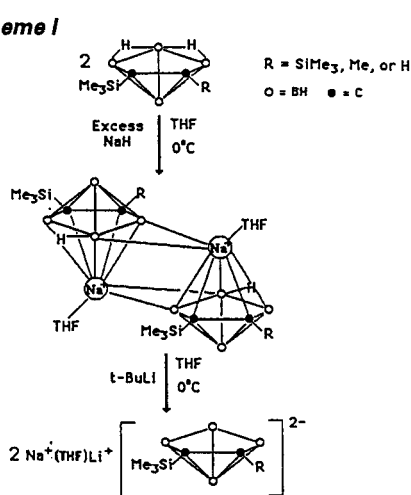
Scheme I

Figure 1. Crystal Structure of the Ion Cluster
(THF·Na⁺)₂[2,3-(SiMe₃)₂-2,3-$C_2B_4H_5^-$]₂

symmetrically on top of each other. Each unit consists of two C_2B_4-carborane cages and two THF-solvated sodium ions with a crystallographic inversion center half way between the sodium ions. All sodium-nearest neighbor distances are greater than that expected for covalent bonding and indicate that the interactions are all essentially ionic. It is apparent from Fig. 1 that the second bridge H's are very well-protected within the cluster. The protection of this hydrogen within the cluster along with the heterogeneous nature of the reaction between NaH and *nido*-carborane could be partly responsible for the inability to produce the disodium salts of the *nido*-C_2B_4 carborane dianions. Although preparation of the carborane disodium salt is not yet known, the synthesis of the first stable dianion was reported by us in 1986 (ref. 12, 13). The specific method involved the double deprotonation of *nido*-2-$(SiMe_3)$-3-(R)-2,3-$C_2B_4H_6$ (R = $SiMe_3$, Me, H) carboranes *via* reaction with NaH followed by *n* - or *t* -C_4H_9Li to give stable $Na^+Li^+[2-(SiMe_3)-3-(R)-2,3-C_2B_4H_4]^{2-}$ double salts as shown in Scheme I. Recently, Grimes *et al*, and Sneddon *et al* have found that this reaction sequence is generally applicable to C-alkyl or aryl- substituted *nido*-C_2B_4-carboranes as well (ref. 14, 15). The formation of the lithium sodium double salts of the *nido*-C_2B_4-carboranes could be primarily due to homogeneous nature of the reaction between the ion cluster, $(C_4H_8O\cdot Na^+)_2[2-(SiMe_3)-3-(R)-2,3-C_2B_4H_5^-]_2$, and BuLi in either THF or hexane as this would allow the base to reach the second bridge hydrogen through relatively small gaps of the dimeric ion cluster for abstraction since the steric crowding around the small Li^+ ion is considerably minimum. It is important to note that the dilithium salts of the C_2B_4-carboranes have been prepared in our laboratory by the treatment of the *nido*-carborane precursor with 2 equivalents of *n* - or *t* -BuLi in dry benzene, hexane, pentane, or THF at $0°$ C (ref. 10, 16). Thus, the discovery of the lithium sodium and dilithium double salts of the C_2B_4-carborane system opened up a new era in the organometallic chemistry of small carboranes.

## SYNTHESES OF HETEROCARBORANES AND THEIR DERIVATIVE CHEMISTRY

There are several monographs and a number of review articles that adequately cover the earlier literature (ref. 1, 17-19). Recent advances in the research of main group metallacarboranes containing groups 13 and 14 metals and/or metalloids covering the year 1988 have also been reviewed (ref. 4, 20). Therefore, this section describes mainly the research reported since 1988. Earlier work will be briefly mentioned only as background to current results or for purposes of comparison.

The discovery of the stable Na^+Li^+ or $Li^+_2[2-(SiMe_3)-3-(R)-2,3-C_2B_4H_4]^{2-}$ double salts (ref. 12, 13, 16) led to the production of a number of sila-, germa-, galla-, and phosphacarboranes that could not be produced from the corresponding mono-sodium salts. The general procedure for the preparation of several of these and other *closo*- and *commo*-heterocarboranes of main group elements is given in Scheme II, and the representative structures are shown in Figs. 2 and 3 (ref. 12, 13, 21-30).
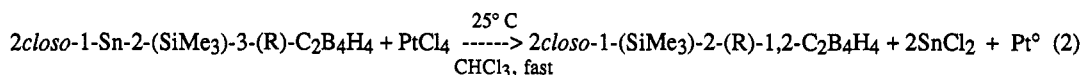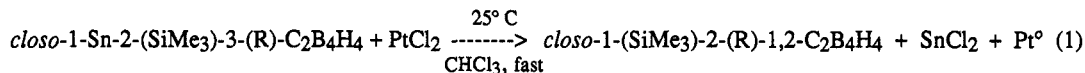

Scheme II
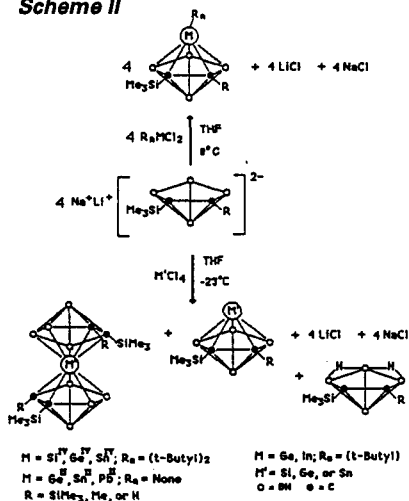
Scheme III
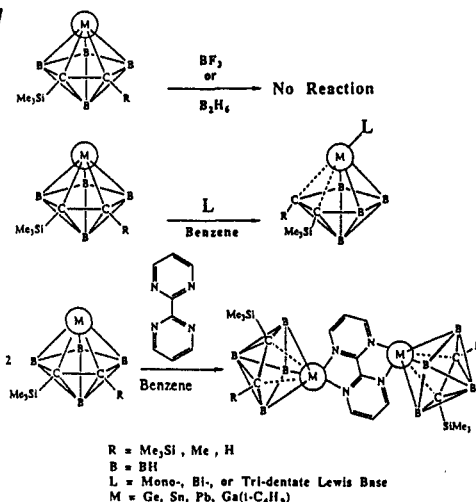
The synthetic potential of the stannacarboranes has been demonstrated in the preparation of *closo*-osmacarboranes (ref. 31), *commo*-bis(germacarborane) (ref. 32), and B-$GeCl_3$-substituted *closo*-germacarboranes (ref. 33). Quite recently, the instantaneous oxidative cage closure of the small carborane has been reported in the reaction of *closo*-1-Sn-2-$(SiMe_3)$-3-(R)-2,3-$C_2B_4H_4$ with anhydrous $PtCl_4$ or $PtCl_2$ in $CHCl_3$ at room temperature (ref. 24, 34). The *closo*-carborane 1-$(SiMe_3)$-2-(R)-1,2-$C_2B_4H_4$ (R = $SiMe_3$, Me, H) was the sole carborane product of this reaction.

$$\text{\textit{closo}-1-Sn-2-(SiMe}_3\text{)-3-(R)-C}_2\text{B}_4\text{H}_4 + \text{PtCl}_2 \xrightarrow[\text{CHCl}_3, \text{ fast}]{25°\text{ C}} \textit{closo}\text{-1-(SiMe}_3\text{)-2-(R)-1,2-C}_2\text{B}_4\text{H}_4 + \text{SnCl}_2 + \text{Pt}° \quad (1)$$

$$2\textit{closo}\text{-1-Sn-2-(SiMe}_3\text{)-3-(R)-C}_2\text{B}_4\text{H}_4 + \text{PtCl}_4 \xrightarrow[\text{CHCl}_3, \text{ fast}]{25°\text{ C}} 2\textit{closo}\text{-1-(SiMe}_3\text{)-2-(R)-1,2-C}_2\text{B}_4\text{H}_4 + 2\text{SnCl}_2 + \text{Pt}° \quad (2)$$

The tin and platinum were converted to $SnCl_2$ and elemental platinum ($Pt°$), respectively. No platinacarborane was identified among the products. These platinum halide promoted reactions are shown in eqn. (1) and (2). The *closo*-stannacarboranes, 1-Sn-2-$(SiMe_3)$-3-(R)-$C_2B_4H_4$ (R = $SiMe_3$, Me, H) also react with elemental bromine (Br_2) in benzene almost quantitatively to produce *closo*-1-$(SiMe_3)$-2-(R)-1,2-$C_2B_4H_4$. However, in the presence of 2

equivalents of bromine and at the reflux temperature of benzene, the reaction produces *closo*-2-(R)-3-(Br)-1,2-$C_2B_4H_4$ with the formation of 1 equivalent each of $SnBr_2$ and $SiMe_3Br$ as by-products (ref. 34). These reactions avoid the expensive platinum reagents that are needed to produce the *closo*-1,2-isomer of the C_2B_4-carborane derivatives, and hence make them better methods than those outlined in eqn. (1) and (2). However, the method of choice for the preparation of this particular *closo*-carborane would be the one which avoids the step that involves the synthesis of *closo*-stannacarborane precursors. In fact, our most recent work has demonstrated that the dilithium salts of the *nido*-carborane dianions produce the *closo*-C_2B_4-carboranes by reacting with Br_2 in benzene at low temperatures (ref. 34).

COORDINATION CHEMISTRY OF MAIN GROUP HETEROCARBORANES

Despite the presence of a lone pair of electrons on the "bare" heteroatom, the heterocarboranes do not react with $BH_3 \cdot THF$ or BF_3 but react almost quantitatively with a variety of Lewis bases that act as mono-, bi-, bis(bi)-, or tridentate ligands in benzene to form the donor-acceptor complexes as shown in Scheme III. The molecular geometries of these charge-transfer complexes were confirmed by single-cyrstal X-ray diffraction and the following Figures represent some of the structures of these complexes (see Figs. 4-7; ref. 22, 26, 28, 32, 35-39).
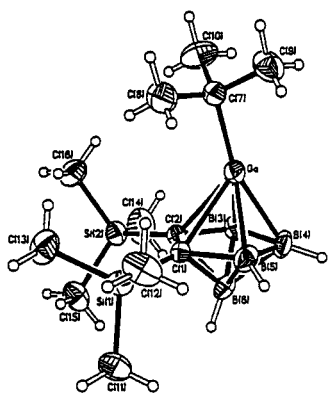

Figure 2. Crystal Structure of
closo-1-Ga(t-Butyl)-2,3-(SiMe3)2-2,3-C2B4H4
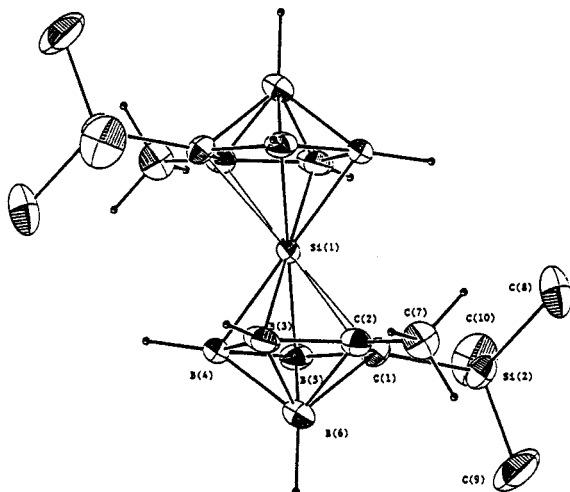

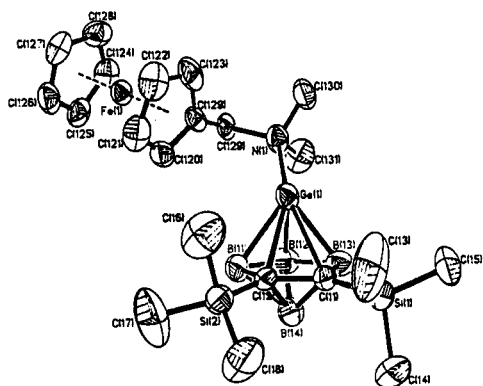Figure 3. Crystal Structure of
commo-1,1'-Si[2-(SiMe3)-3-(Me)-2,3-C2B4H4]2

Figure 4. Crystal Structure of
1-Ge(Ferrocenylmethyl-*N,N*-dimethylamine)-2,3-(SiMe3)2-2,3-C2B4H4
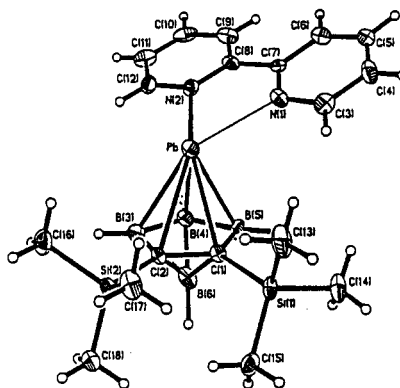

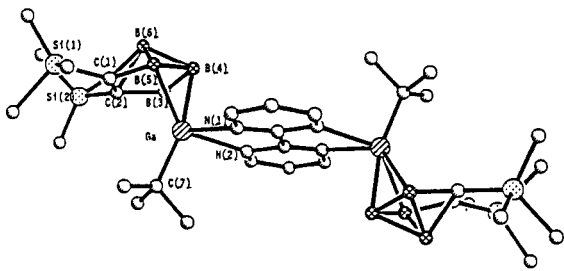Figure 5. Crystal Structure of
1-Pb(2,2'-Bipyridine)-2,3-(SiMe3)2-2,3-C2B4H4

Figure 6. Crystal Structure of
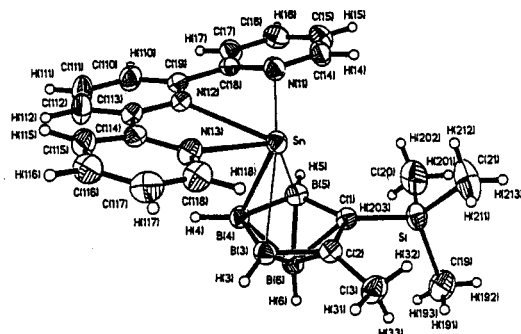1,1'-(2,2'-Bipirimidine)[1-Ge(t-Bu)-2,3-(SiMe3)2-2,3-C2B4H4]2

Figure 7. Crystal Structure of
1-Sn(2,2':6',2"-Terpyridine)-2,3-(SiMe3)2-2,3-C2B4H4

Complexation is accompanied by a slippage of the heteroatom from η^5 to η^3-bonding. The formation of these complexes shows that the apical heteroatom of the heterocarboranes is behaving as a Lewis acid. In general, the adducts with monodentate Lewis bases (ferrocenylmethyl-N, N-dimethylamine) show less slip-distortion than found in the 2,2'-bipyridine, 1,10-phenanthroline, or 2,2':6',2"-terpyridine, as does the complex with the weaker 2,2'-bipyrimidine base. However, the severe slippage of the apical gallium toward the unique boron in an η^1 fashion in Fig. 6 could be due to extreme Lewis acidity of the gallium. As in the cases of the stanna- and plumbacarborane systems, the *trans* orientation of these gallacarboranes is favored on steric grounds (ref. 28, 35a).

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