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STRUCTURAL DISTORTIONS IN MAIN GROUP METALLACARBORANES

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The group 13 and 14 metallacboranes in the pentagonal bipyramidal system show a consistent pattern of structural distortions. The metal is not symmetrically bonded to the C_2B_3 face of the carborane but is slipped, along its pseudo-mirror plane. In metallacboranes where the cage carbons are adjacent, slippage is always towards the unique boron atom in the mirror plane of the bonding face, while in complexes where the cage carbons are separated by a boron atom, slippage is in the opposite direction. Such slippage is accompanied by a folding of the C_2B_3 bonding face. The structural determination of $1-(C_8H_6N_4)(t-CMe_3)Ga-2,4-(SiMe_3)_2-2,4-C_2B_4H_4$, described herein, along with the previously reported structures of the "carbons adjacent" metallacboranes, show that the direction of ring folding depends on the magnitude and direction of metal slippage. This relationship is investigated theoretically using semiempirical molecular orbital calculations on the model complexes, $1-Sn-2,3-C_2B_4H_6$ and $1-Sn-2,4-C_2B_4H_6$.

Key Words: metallacboranes, gallacboranes, stannacboranes, slip distortion, ring folding

INTRODUCTION

The organometallic complexes formed from the *nido*-carborane dianions, $[R_2C_2B_4H_4]^{2-}$ and $[R_2C_2B_9H_9]^{2-}$ ($R = \textit{exo}$ -polyhedral substituent on the cage carbons, or H) and metal ions have been the subject of numerous studies.¹⁻⁴ In these complexes the metal is incorporated into the cage structure and occupies the apical position above the C_2B_3 bonding face of the carborane, giving rise to half-sandwich compounds, such as, $1-Sn-2-(SiMe_3)-3-R-2,3-C_2B_4H_4$ ($R = SiMe_3, Me, H$).⁵ The metals are coordinatively unsaturated and can bond to either another carborane dianion, to give full-sandwich, *commo*-complexes, or to other bases to give adducts. The structures show that the metals do not occupy centroidal positions above the bonding face of the carborane, but are dislocated, or slipped, along the pseudo-mirror plane of the C_2B_3 bonding face. The extent and direction of slippage is a function of the nature of the capping metal group and the relative positions of the carbon atoms in the bonding face of the carborane. Most of the structural reports have been on the base-metallacborane complexes in which the cage carbons in the C_2B_3 bonding face of the carborane are directly bonded to one another in the so-called "carbons adjacent" metallacboranes.² In these complexes slippage is always towards the unique

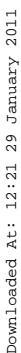
boron atom that lies in the pseudo-mirror plane of the carborane.^{2,6-9} Slip distortion of the metal is also accompanied by a folding of the C₂B₃ bonding face such that the unique boron is moved slightly below the plane of the other four atoms, away from the metal group. The amount of this ring folding seems to be related to the extent of metal slippage.⁸ We have recently reported the structures of several "carbons apart" stannacarborane complexes, in which the cage carbons are separated by a boron atom.¹⁰ These structures show that the tin is slightly slipped away from the unique boron atom, and the bonding carborane faces seem to be planar. Since the slippages were small, it was not possible to establish what effect, if any, this type of slippage would have on the structure of the carborane cage. In our investigation of the structures of the "carbons adjacent" pentagonal bipyramidal main group metallacarboranes we found that the gallacarboranes were characterized by large slip distortions and ring folding.⁸ Therefore, we have initiated a structural investigation of the "carbons apart" gallacarboranes, of which this is the first report. The structure of the 1-(C₈H₆N₄)(*t*-CMe₃)Ga-2,4-(SiMe₃)₂-2,4-C₂B₄H₄ (**1**) complex, described herein, has caused us to reexamine the relationship between slip distortion and cage folding.

RESULTS AND DISCUSSION

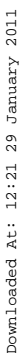
TABLE I

Selected bond distances in 1-(C₈H₆N₄)(*t*-CMe₃)Ga-2,4-(SiMe₃)₂-2,4-C₂B₄H₄ (**1**)

Bond Distances (Å)			
Ga(1)–Cnt(1)	2.244	Ga(2)–Cnt(2)	2.432
Ga(1)–B(2)	3.019 (17)	Ga(2)–B(32)	3.309 (18)
Ga(1)–B(4)	2.185 (19)	Ga(2)–B(34)	2.226 (16)
Ga(1)–B(5)	2.198 (17)	Ga(2)–B(35)	2.225 (17)
Ga(1)–C(1)	2.808 (13)	Ga(2)–C(31)	2.974 (13)
Ga(1)–C(3)	2.771 (13)	Ga(2)–C(33)	2.987 (13)
Ga(1)–C(13)	1.988 (22)	Ga(2)–C(43)	1.943 (17)
Ga(1)–N(17)	2.153 (12)	Ga(2)–N(47)	2.064 (14)
Ga(1)–N(24)	2.152 (11)	Ga(2)–N(54)	2.116 (10)



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TABLE II
Selected bond angles in 1-(C₈H₆N₄)(*t*-CMe₃)Ga-2,4-(SiMe₃)₂-2,4-C₂B₄H₄ (**1**)

Bond Angles (°)			
Cnt(1)–Ga(1)–C(13)	113.0	Cnt(2)–Ga(2)–C(43)	147.5
Cnt(1)–Ga(1)–N(24)	130.1	Cnt(2)–Ga(2)–N(54)	108.3
Cnt(1)–Ga(1)–N(17)	125.4	Cnt(2)–Ga(2)–N(47)	87.9
C(13)–Ga(1)–N(24)	103.6	C(43)–Ga(2)–N(54)	103.7
C(13)–Ga(1)–N(17)	103.4	C(43)–Ga(2)–N(47)	105.1
N(17)–Ga(1)–N(27)	73.9	N(47)–Ga(2)–N(54)	77.2

Per unit cell, there are two crystallographically independent molecules of 1-(C₈H₆N₄)(*t*-CMe₃)Ga-2,4-(SiMe₃)₂-2,4-C₂B₄H₄ (**1a** and **1b**), which are shown in Figures 1 and 2, respectively. Table I lists some important bond distances, and Table II some bond angles.¹¹ Both structures show that the gallium resides above the C₂B₃ open face of the carborane, but is severely slip distorted away from the unique boron atom in each cage, B(2) and B(32), respectively, to the extent that the metal is best described as being η²-bonded to the carborane ligand. In **1b** the gallium is outside of the face, while in **1a**, which is less slip distorted, the metal is still within the frame of the cage. The net result is that, while the Ga(1)–B(4,5) distance of 2.19 Å is about the same as the Ga(2)–B(34,35) distance of 2.22 Å, the distances between the Ga and other facial atoms in **1b** are longer than the corresponding ones in **1a**, the relevant distances are: Ga(2)–B(32) = 3.309 Å; Ga(2)–C(31,33) = 2.980 Å; Ga(1)–B(2) = 3.019 Å; and Ga(1)–C(1,3) = 2.89 Å. Other than the difference in slippage, the two molecules differ in the relative orientations of the two *exo*-polyhedral ligands (the *t*-Bu and the bipyrimidine) with the pseudo-mirror plane of the carborane.¹² In **1a** these two groups reside almost in the mirror plane, with the dihedral angle between the mirror plane and the one defined by atoms C(13), Ga(1), and the C(22)–C(23) midpoint being 11.1°, while in **1b** the groups are almost at right angles to the mirror plane; the analogous dihedral angle is 41.4°. In **1a** the electron rich C₈H₆N₄ group is more removed from the carborane than it is in **1b**, so that the rotation of the C₈H₆N₄ closer to the carborane in going from **1a** to **1b** could account for the larger slip distortion in **1b**. In both molecules the Ga atoms reside in the mirror plane of the particular carborane. The Ga–(*t*-Bu) and Ga–C₈H₆N₄ distances in **1a** and **1b** are about the same as those found in the corresponding "carbons adjacent" isomer, 1-(C₈H₆N₄)(*t*-Bu)Ga-2,3-(SiMe₃)₂-2,3-C₂B₄H₄; the bond distances equivalent to the Ga(1)–C(13) and Ga(1)–N(17,24) are 2.019 Å and 2.176 Å, respectively.⁸ Because of the different directions of the slip distortions and different placements of the C₂B₃

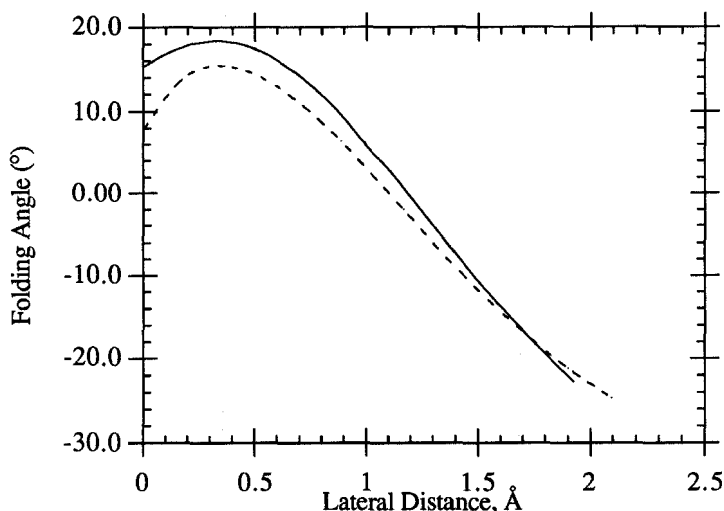


FIGURE 3 Folding angle as a function of lateral distance for 1-Sn-2,4-C₂B₄H₆ (solid line) and 1-Sn-2,3-C₂B₄H₆ (dashed line).

atoms, a comparison of the Ga-C₂B₃ atom distances is not particularly useful.

A striking structural feature of both molecules of **1** is that the C₂B₃ bonding face is not planar, but is folded away from the apical boron such that the unique boron, B(2) or B(32) in Figures 1 and 2, respectively, resides above the plane of the other facial atoms. The extent of this ring folding can be ascertained from the folding angle, which is defined as the acute dihedral angle between the planes C(3)-B(4)-B(5)-C(1) and C(3)-B(2)-C(1), with a positive value indicating a displacement of the unique boron toward the capping metal, as found in **1**, and a negative value meaning a displacement of the unique boron away from the metal. The folding angle in **1a** is 8.5° while that in **1b** is 7.7°. These folding angles can be compared to the value of -8.7° found in the "carbons adjacent" gallacarborane isomer.⁸ Compound **1** provides the first unequivocal example of a positive folding angle. The structures of several "carbons apart" stanna-¹⁰, lithia-, and nickelacarboranes¹³ show that ring folding is not inherent in the particular carborane ligand. The following analysis shows that the position of the gallium in **1** dictates this distortion. An experimental correlation between ring folding and metal slip distortion has long been noted in metallocarboranes containing both transition metals^{14,15} and main group metals.⁶⁻⁸ However, these data have been obtained almost exclusively on the "carbons adjacent" carborane ligands, where metal slippage has been toward the unique boron, which is opposite from that found in **1**. In the transition metal complexes, it has been suggested that interactions between filled metal *d* orbitals and vacant carborane

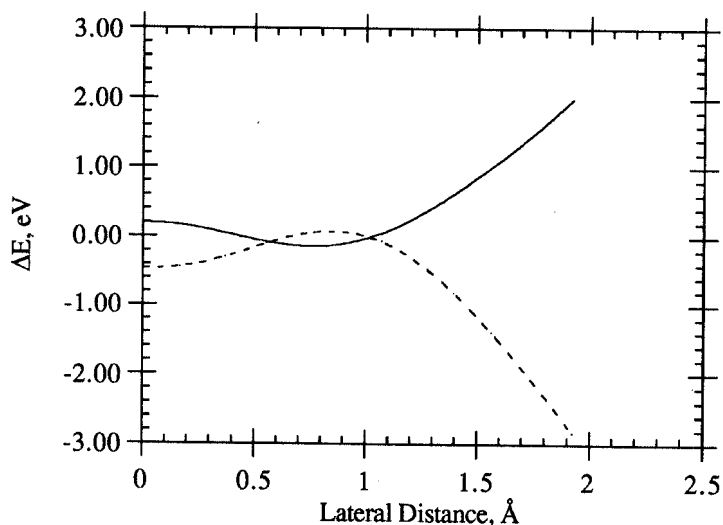


FIGURE 4 Plot of the difference in total tin energy (dashed line) and total carborane energy (solid line) between fixed and free carborane cages in 1-Sn-2,4-C₂B₄H₆ as a function of lateral distance.

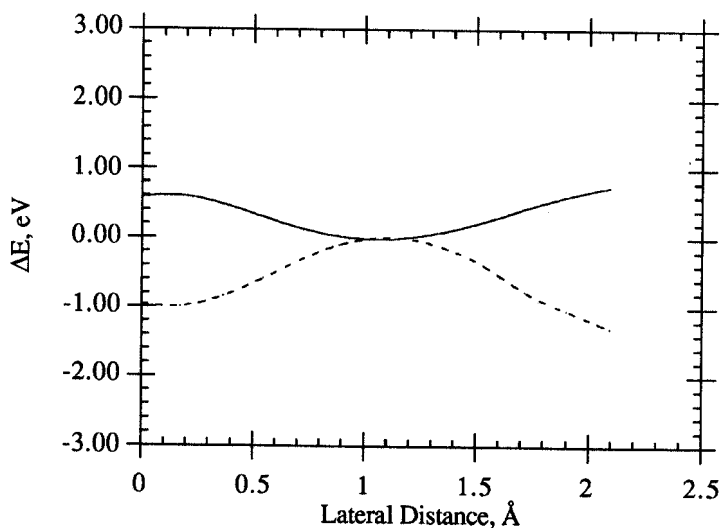


FIGURE 5 Plot of the difference in total tin energy (dashed line) and total carborane energy (solid line) between fixed and free carborane cages in 1-Sn-2,3-C₂B₄H₆ as a function of lateral distance.

orbitals could give rise to these distortions.¹⁶ However, their presence in the main group metallocarboranes indicates that other interactions are important. We have found that MNDO semiempirical molecular orbital calculations on the model compound 1-Sn-2,3-C₂B₄H₆ and its Lewis base adducts could provide insight into the factors dictating slip distortions in the stannacarboranes.^{8,17} Because of this success and the fact that such calculations predicted a ring folding accompanying the slippages of the tin,¹⁷ we have carried out additional calculations on the model compounds 1-Sn-2,4-C₂B₄H₆ (**2**) and 1-Sn-2,3-C₂B₄H₆ (**3**), giving careful attention to the relationship between ring folding and slippage of the capping metal. Figure 3 shows plots of the MNDO¹⁸ predicted ring folding-metal slippage relationship for these complexes, as a plot of the folding angle versus the lateral displacement, in Å, of the metal from the facial atoms that are opposite the unique boron; in **2** these are boron atoms equivalent to B(4) and B(5) in Figure 1, while in **3**, they are the cage carbons.¹⁹ In the optimized structure of **2** the tin is slipped slightly away from the unique boron, at a lateral displacement of 1.02 Å, and the folding angle is 5.0°. On the other hand, the optimized structure of **3** shows the tin to be slipped more toward the unique boron, at a lateral distance of 1.16 Å, and the corresponding folding angle is -1.9°.²⁰ Thus, the calculations show that the carborane cage is flexible and the planarity of the C₂B₃ bonding face is a function of the position of the metal above this face. For both of the model compounds the folding angle goes from positive to negative as the metal moves across the bonding face of the carborane, toward the unique boron; it is zero, that is, the face is planar, when the metal is centered above the bonding face.²⁰ This parallels what is found experimentally. In analyzing the slip distortions of the stannacarboranes by MNDO,^{7,10,17} it was found useful to partition the total electronic energy, *E*, of the molecules as the sums of one-center, *E_A*, and two-center, *E_{AB}*, terms such that²¹

$$E = \sum_A E_A + \sum_{A < B} E_{AB}$$

E_{AB} has been found to provide a good quantitative measure of the A-B bond strength. A large negative value of *E_{AB}* indicates bonding between atoms A and B, while a positive value implies antibonding.²² The present calculations and previous ones on several "carbons adjacent" and "carbons apart" stannacarboranes, and their Lewis base adducts, show that the driving force for metal slippage is an increase in intracarborane bonding, at the expense of tin-carborane bonding, as the tin moves away from the cage carbons, irrespective of their placement in the C₂B₃ bonding face.^{7,10,17} In the base-stannacarborane complexes, tin-base bonding, which increases with metal slippage, also tends to compensate for the loss of tin-carborane

bonding, resulting in increased slip distortions. In order to ascertain the role of ring folding in stabilizing slip distorted metallacarboranes, the total energy, E , was divided into those tin containing one- and two-center terms, called the "total tin energy", and those terms involving only the carborane atoms, called the "total carborane energy". These "total" energies were determined as a function of the lateral tin distance for **2** and **3**, under conditions where the carborane cage folding angle was fixed at its original MNDO optimized position and when it was allowed to vary. The difference between these two differently calculated tin and carborane energies, ΔE , should reflect the added stability introduced by ring folding. Plots of ΔE versus lateral tin displacement in **2** and **3** are shown in Figures 4 and 5, respectively. The subtraction was such that a negative ΔE indicates gained stability on ring folding. As can be seen in the Figures, ring folding stabilizes metal-carborane rather than intracarborane interactions. The major contribution of ring folding is that it allows for stronger bonding of the metal to the facial atoms on either side of the unique boron (boron atoms in **2** and cage carbon atoms in **3**) as the lateral distance increases. This increase is such that it may be better to ascribe ring folding to a dislocation of these two facial atoms toward the metal, such that they are lifted above the bonding face, rather than the unique boron being depressed. This is the same conclusion reached by Mingos for the slip distorted icosahedral metallacarboranes.¹⁴ On the other hand, increased metal-B_{unique} bonding is responsible for folding in the opposite direction found for small lateral distances. Therefore, it seems that, while increased intracarborane bonding is the dominant driving force in metal slip distortions, increased metal-carborane bonding dictates the magnitude, and direction, of carborane ring folding.

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