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Synthesis of Group 13 Element Metallacarboranes and Related Structure–Reactivity Correlations

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Synthesis, reactivity, and structural characterization studies of a number of group 13 metallacarborane species are described. These include studies of the icosahedral aluminacarborane *closo*-3-Et-3,1,2-$AlC_2B_9H_{11}$ (**1a**). Compound **1a** reacts with Lewis bases to form adducts of the type 2L·**1a** (L = Lewis base). The reaction of **1a** with excess PEt_3 results in the rapid formation of *endo*-10-{$AlEt(PEt_3)_2$}-7,8-$C_2B_9H_{11}$ (**3**). The novel sandwich species *commo*-3,3′-Al[{*exo*-8,9-(μ-H)$_2$-$AlEt_2$-3,1,2-$AlC_2B_9H_9$}(3,1,2-$AlC_2B_9H_{11}$)] (**4**) results from thermal dimerization of **1a**. The related sandwich anions [*commo*-3,3′-Al(3,1,2-$AlC_2B_9H_{11}$)$_2$]$^-$ ([**5**]$^-$) and [*commo*-3,3′-Ga(3,1,2-$GaC_2B_9H_{11}$)$_2$]$^-$ ([**6**]$^-$) have been prepared. The full details of the synthesis and structural characterization of σ-bonded species *nido*-6,9-(μ-AlEt-(OEt_2))-6,9-$C_2B_8H_{10}$ (**8**), [Al(η^2-6,9-$C_2B_8H_{10}$)$_2$]$^-$ ([**10**]$^-$), and [Al(η^2-2,7-$C_2B_6H_8$)$_2$]$^-$ ([**11**]$^-$) are reported. The metallacarboranes **3**, **4**, [**5**]$^-$, [**6**]$^-$, **8**, [**10**]$^-$, and [**11**]$^-$ were characterized by a combination of spectroscopic techniques and by single-crystal X-ray diffraction studies. Crystallographic parameters are as follows: **3**, $P2_1/n$, a = 9.722 (3) Å, b = 16.135 (4) Å, c = 16.984 (5) Å, β = 90.246 (9)°, V = 2652 Å^3, Z = 4, R = 0.064, R_w = 0.082 for 3394 independent reflections with $I > 3\sigma(I)$; **4**, $P2_1/n$, a = 7.122 (2) Å, b = 27.668 (8) Å, c = 11.629 (3) Å, β = 96.246 (5)°, V = 2288 Å^3, Z = 4, R = 0.065, R_w = 0.075, GOF = 2.39 for 2137 independent reflections; Tl[**5**]·$^2/_3C_7H_8$, $P\bar{1}$, a = 11.347 (2) Å, b = 11.748 (2) Å, c = 12.708 (2) Å, α = 92.429 (6)°, β = 90.876 (6)°, γ = 93.343 (5)°, V = 1689 Å^3, Z = 3, R = 0.057, R_w = 0.064, GOF = 1.57 for 1941 independent reflections; Tl[**6**], $P\bar{1}$, a = 6.9564 (6) Å, b = 11.0466 (9) Å, c = 12.0287 (10) Å, α = 102.088 (2)°, β = 95.484 (2)°, γ = 94.687 (3)°, V = 894 Å^3, Z = 2, R = 0.041, R_w = 0.054, GOF = 2.03 for 2733 independent reflections; **8**·$^1/_2C_6H_6$, $A\bar{1}$, a = 13.964 (3) Å, b = 15.966 (4) Å, c = 8.550 (2) Å, α = 92.227 (8)°, β = 86.689 (7)°, γ = 102.060 (8)°, V = 1862 Å^3, Z = 4 (reduced cell: a = 8.552 Å, b = 8.909 Å, c = 13.967 Å, α = 99.172°, β = 93.323°, γ = 116.428°, V = 930.9 Å^3, Z = 2), R = 0.061, R_w = 0.081, GOF = 2.85 for 2338 independent reflections; [$(PPh_3)_2N$][**10**], $P2_1/c$, a = 16.378 (3) Å, b = 18.781 (3) Å, c = 14.806 (3) Å, β = 90.197 (5)°, V = 4554 Å^3, Z = 4, R = 0.078, R_w = 0.088, GOF = 2.0 for 2128 independent reflections; [Na][**11**], $P2_1$, a = 10.035 (2) Å, b = 12.433 (3) Å, c = 11.690 (3) Å, β = 111.019 (7)°, V = 1367 Å^3, Z = 4, R = 0.049, R_w = 0.059, GOF = 2.08 for 2156 independent reflections. The compound Tl[**5**]·$^2/_3C_7H_8$ contains the thallium(I)–arene complex Tl(η^6-MePh). Compounds **1a** and **4** were shown to catalyze the exchange of carborane B–H and arene C–D bonds as well as the polymerization of selected olefins under mild homogeneous conditions. Bonding and the varying degrees of distortion from idealized closo and commo geometries displayed by **3**, **4**, [**5**]$^-$, and [**6**]$^-$ are discussed. Species **8**, [**10**]$^-$, and [**11**]$^-$ contain Al–C σ-bonded aluminum–carborane connectivities. Compound **8** exhibits rapid exchange of aluminum-coordinated ether in solution, and the compound *nido*-6,9-(μ-AlEt-(C_4H_8O))-6,9-$C_2B_8H_{10}$ (**9**) was prepared by ether exchange of **8** in tetrahydrofuran/toluene. Anion [**11**]$^-$ undergoes rapid enantiomer interconversion in solution at room temperature.

Introduction

There has been considerable recent interest in the chemistry of the main-group elements, especially with respect to the occurrence of multihapto bonding involving elements of this classification.[1] Our own interest in this area has prompted us to explore the chemistry of metallacarboranes containing group 13 elements. These studies have revealed an intriguing class of compounds, several members of which exhibit multihapto interactions and apparent π-bonding between the main-group element and carborane cage moieties. The relationship between boron and these other elements makes compounds of this type especially interesting in that the formal replacement of the group 13 metal by a cogeneric boron atom results in the parent carborane compound.

We have previously reported the synthesis and structural characterization of several aluminum- and gallium-containing metallacarborane compounds in a series of papers and preliminary communications.[2-8] These compounds display a range of metal–carborane cage interactions including η^1-, η^3-, and η^5-dicarbollide–metal and bis(η^5-dicarbollide)–metal bonding, as well as carborane carbon–metal σ-bonding. The bis(η^5-dicarbollide)metal compounds represent the first structurally characterized examples of main-group-element sandwich compounds that contain main-group elements in their highest formal oxidation states.[3,7,8]

Aluminacarboranes may also serve as useful reagents for the introduction of carborane cage moieties. While main-group-element metallacarborane derivatives such as the insoluble thallacarboranes[9] are highly valued as reagents in synthesis, the high reactivity of aluminacarborane

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Table I. Interatomic Distances (Å) and Angles (deg) for *endo*-10-{$AlEt(PEt_3)_2$}-7,8-$C_2B_9H_{11}$ (3)

Al(12)–C(01)	1.974 (4)	Al(12)–P(02)	2.554 (2)	Al(12)–P(01)	2.567 (2)
Al(12)–B(10)	2.128 (5)	Al(12)–B(11)	2.448 (5)	Al(12)–B(09)	2.512 (5)
Al(12)–C(07)	2.942 (4)	Al(12)–C(08)	2.976 (4)	C(07)–C(08)	1.555 (6)
C(07)–B(11)	1.631 (6)	C(08)–B(09)	1.612 (7)	B(09)–B(10)	1.776 (7)
B(10)–B(11)	1.788 (7)				

C(01)–Al(12)–B(10)	141.23 (19)	C(01)–Al(12)–B(11)	105.92 (19)
C(01)–Al(12)–B(09)	108.05 (18)	B(10)–Al(12)–B(11)	45.32 (17)
B(10)–Al(12)–B(09)	44.04 (17)	B(11)–Al(12)–B(09)	68.78 (17)
C(08)–B(09)–Al(12)	89.68 (27)	B(04)–B(09)–Al(12)	116.07 (27)
B(10)–B(09)–Al(12)	56.43 (20)	B(03)–B(09)–Al(12)	141.61 (32)
B(04)–B(10)–Al(12)	139.51 (31)	B(05)–B(10)–Al(12)	136.24 (31)
B(09)–B(10)–Al(12)	79.54 (23)	B(11)–B(10)–Al(12)	76.84 (23)
C(07)–B(11)–Al(12)	90.03 (26)	B(05)–B(11)–Al(12)	117.58 (29)
B(10)–B(11)–Al(12)	57.84 (20)	B(06)–B(11)–Al(12)	143.25 (31)
C(02)–C(01)–Al(12)	120.73 (32)	P(01)–Al(12)–P(02)	95.25 (5)
P(01)–Al(12)–C(01)	97.65 (14)	P(02)–Al(12)–C(01)	105.57 (14)
P(02)–Al(12)–B(10)	101.66 (13)		

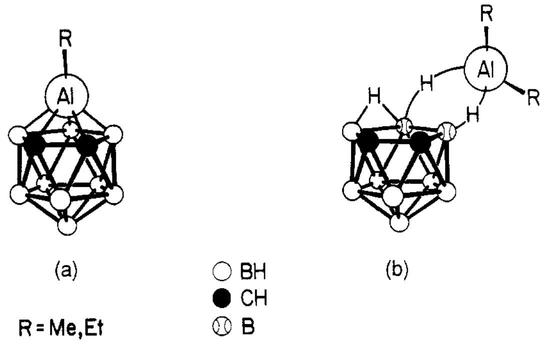

Figure 1. Structures of 3-R-3,1,2-$AlC_2B_9H_{11}$ (R = Et, **1a**; R = Me, **1b**) and *nido*-9,10-(μ-H)$_2$-9,10-AlR_2-7,8-$C_2B_9H_{11}$ (R = Et, **2**; R = Me, **2′**) shown schematically.

compounds coupled with their excellent solubility in organic solvents leads to their potential usefulness as transmetalation reagents. Recently, Jutzi and co-workers have demonstrated the use of this methodology by employing a dicarbollide aluminacarborane derivative in the synthesis of other metallacarborane compounds.[10]

The synthesis and structural characterization of the aluminacarboranes of the type *closo*-3-R-3,1,2-$AlC_2B_9H_{11}$ (R = Et, **1a**; R = Me, **1b**) have been reported previously.[2a,b] The structure of **1a** as determined by an X-ray diffraction study is shown schematically in Figure 1a.[2a,b,d] The icosahedral **1a** is isoelectronic with *closo*-1,2-$C_2B_{10}H_{12}$ and, at the same time, represents an example of η^5-bonding between an aluminum atom and a π-donor ligand. A notable structural distortion exhibited by **1a** is a tilt of the aluminum-bound ethyl group in the direction of the cage carbon atoms at an angle of 19.5° from the normal to the mean of the C_2B_3 plane of the dicarbollide cage.[2d] Synthesis of **1a** and **1b** is accomplished by reaction of *nido*-7,8-$C_2B_9H_{13}$ with the appropriate trialkylaluminum reagent in an aromatic solvent.[2a] These reactions proceed with the initial formation of relatively stable and isolable intermediates of the type *exo-nido*-9,10-(μ-AlR_2)(μ-H)$_2$-7,8-$C_2B_9H_{10}$ (R = Et, **2a**; R = Me, **2b**). The structure of **2b**, as determined by an X-ray diffraction study,[2c] is shown schematically in Figure 1b. Important structural features of **2b** include the presence of a residual B–H–B bridge and the bonding interaction of the cationic dialkylaluminum moiety with the anionic carborane cage via Al–H–B bridges. Compounds **2a** and **2b** exhibit fluxionality in solution, undergoing a rapid interconversion of enantiomeric forms at room temperature.[2b] This process apparently occurs via a "cage walking" mechanism in which the AlR_2 moieties move across the pseudo mirror planes of the cages for each compound. When **2a** or **2b** is heated in aromatic hydrocarbon solvent, elimination of alkane occurs[2a] to produce the corresponding closo compound **1a** or **1b**. A similar alkane elimination reaction was previously employed in the synthesis of *closo*-3-L-3,1,2-$BeC_2B_9H_{11}$, where L is OEt_2 or NMe_3.[11]

Despite the fact that **1a** possesses the 13 skeletal electron pairs required for formal electron precise closo skeletal bonding, this species displays Lewis acid behavior by forming adducts with a variety of bases such as ethers, amines, and nitriles. Preparation of the adduct **1a**·2THF by reaction of $Na_2[7,8\text{-}C_2B_9H_{11}]$ with $AlEtCl_2$ in THF has been reported.[12] The irreversible formation of this adduct by the reaction of **1a** with THF has also been described.[2b] In addition, the monoadducts [3-Et-1,2-Me_2-3,1,2-$AlC_2B_9H_{11}$]·THF and [3-Et-1,2-Me_2-3,1,2-$AlC_2B_9H_{11}$]·OEt_2 have been observed.[10] Structural assignments for all the aluminacarborane–Lewis base adducts have primarily been made on the basis of NMR data alone, and unequivocal structure determinations have not been previously carried out.[2b,10,12]

Results and Discussion

Adduct Formation with 3-Et-3,1,2-$AlC_2B_9H_{11}$ (1a). We have recently examined reactions leading to adduct formation between **1a** and phosphines. Treatment of **1a** with excess triphenylphosphine in benzene solution results in the formation of both 1:1 and 2:1 PPh_3·**1a** adducts as indicated by $^{31}P\{^1H\}$ NMR spectra; however, the formation constants for these adducts are small and adduct instability with respect to dissociation has precluded their isolation. Reaction of **1a** with an excess of the more basic triethylphosphine in benzene solution results in formation of the isolable adduct $2PEt_3$·**1a** (**3**). Species **3** is a colorless, highly air- and moisture-sensitive, crystalline solid that can be isolated only from solutions containing a large excess of triethylphosphine. When crystalline **3** is dissolved in aromatic solvents, rapid dissociation occurs to produce **1a** and free phosphine. Once isolated, **3** is stable indefinitely when stored under dry nitrogen or argon.

The structure of **3** as determined by a single-crystal X-ray diffraction study is shown in Figure 2. Table I lists selected interatomic distances and angles. The two phosphine ligands in **3** may be considered to be coordinated to a highly distorted tetrahedral aluminum center that is displaced with respect to the five-membered face

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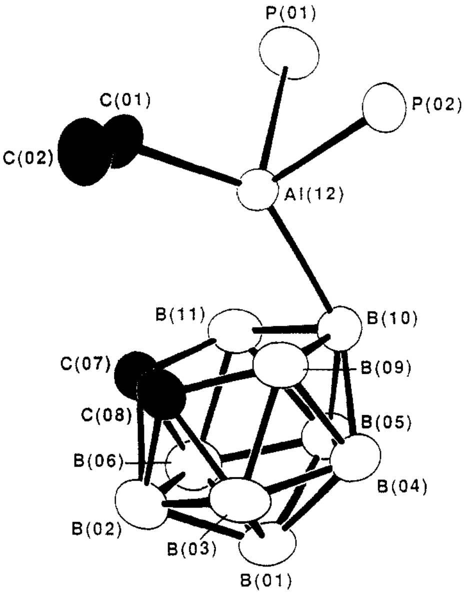

Figure 2. Structure of *endo*-10-{AlEt(PEt_3)$_2$}-7,8-$C_2B_9H_{11}$ (**3**) with hydrogen atoms and ethyl groups attached to phosphorus omitted for clarity.

of the dicarbollide cage in the direction of the unique boron atom B(10). The distance between aluminum and this unique boron is 2.128 (5) Å, while the distances between aluminum and the other two boron atoms of the cage face are nearly equal and average 2.480 (5) Å. The methylene group of the aluminum-bound ethyl group is directed over the two carboranyl carbon atoms of the dicarbollide cage face.

The formation of **3** from **1a** requires extensive changes in the bonding interactions of the aluminum center. In **1a**, the AlEt vertex may be considered to contribute three atomic orbitals and two electrons to skeletal bonding in the icosahedral cluster and one orbital to exopolyhedral bonding with the ethyl group. The slip distortion as well as the formal electron count and geometry of the aluminum center leads to a view of the AlEt(PEt_3)$_2$ moiety in **3** as an endopolyhedral group that is bound in an η^1 fashion to B(10) of the dicarbollide cage. In this bonding mode the dicarbollide cage can be regarded as a formal two-electron donor to the metal center and **3** identified as an endo-substituted tautomer of [*nido*-7,8-$C_2B_9H_{12}$]$^-$, *endo*-10-[EtAl(PEt_3)$_2$]$^{2+}$-7,8-$C_2B_9H_{11}$ (*endo*-H^+ formally replaced by [EtAl(PEt_3)$_2$]$^{2+}$). In contrast to the bonding formalism used for **1a**, the aluminum atom in **3** may be considered to utilize a single hybrid orbital for endo bonding with the η^1-dicarbollide cage. Additional bonding interactions of the aluminum center with B(09) and B(11) cannot be ruled out or confirmed with this information at hand. It is likely that the previously reported[12] adduct 2THF·**1a** is isostructural with **3**.

NMR data acquired for **3** in the presence of excess triethylphosphine indicate that rapid exchange occurs in solution between free and bound phosphine at room temperature. A single concentration-dependent $^{31}P\{^1H\}$ resonance is observed in the 330 K NMR spectrum of samples of **3** in toluene-d_8 in the presence of a 10-fold excess of triethylphosphine. At 240 K a sharp singlet resonance assigned to **3** is observed at δ −20.5 ppm, upfield from the resonance due to free triethylphosphine (δ −20.1 ppm) that is observed simultaneously. The low solubility of **3** precluded the acquisition of spectral data below 240 K.

Aluminacarborane Bis(dicarbollide) Sandwich Compounds. Heating samples of *closo*-3-Et-3,1,2-$AlC_2B_9H_{11}$ (**1a**) in aromatic solvent at 80–90 °C results in the formation of a formally dimeric species, *commo*-3,3′-Al[{*exo*-8,9-(μ-H)$_2$-$AlEt_2$-3,1,2-$AlC_2B_9H_9$}(3,1,2-$AlC_2B_9H_{11}$)] (**4**), which exists in equilibrium with **1a** under these conditions. Formation of **4** can be monitored by ^1H NMR spectroscopy through the appearance of unique ethyl and carboranyl C–H resonances. Characteristic ^1H NMR spectra of a benzene-d_6 solution of **1a** before and after heating at 85 °C for 12 h are shown in Figure 3a,b. Compound **4** persists in solution after cooling to room temperature and can be isolated by removal of solvent in vacuo followed by preferential sublimation of **1a**. The ^1H NMR spectrum of **4** obtained by this procedure is shown in Figure 3c. When **4** is dissolved in benzene or toluene and heated at 80–90 °C, an equilibrium is established with **1a**, as confirmed by ^1H and ^{11}B NMR spectroscopy. A molecular weight determination of **4**, carried out in toluene solution near room temperature by use of vapor pressure osmometry in the absence of air, gave a value of 375 ± 17, indicative of a dimeric formulation in solution (calculated molecular weight 377).

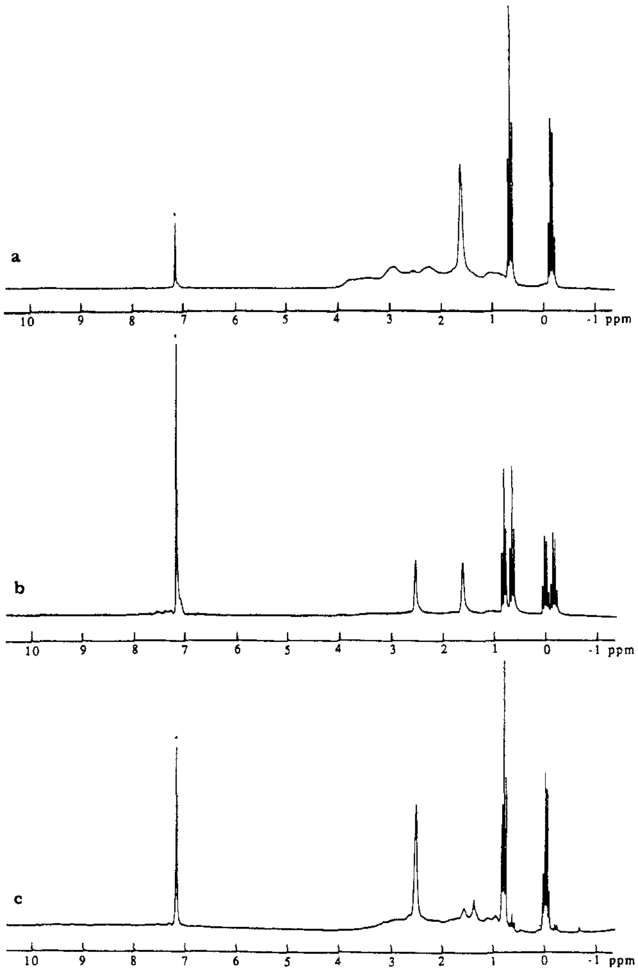

Figure 3. ^1H NMR spectra (25 °C, 200.1 MHz) of 3-Et-3,1,2-$AlC_2B_9H_{11}$ (**1a**) in benzene-d_6 solution (a) before heating and (b) after 12 h at 85 °C and (c) of **4** in benzene-d_6 solution.

The structure of **4**, which is shown in Figure 4, was determined by a single-crystal X-ray diffraction study. Table II lists selected interatomic distances and angles for **4**. The structure of **4** obtained by thermal dimerization is identical with that of a species[3] obtained by carbon monoxide promoted dimerization of **1a**, as confirmed by a second X-ray structure determination. Compound **4** is structurally novel because it represents an example of an aluminum sandwich compound in which an aluminum atom is bound between the nearly parallel and planar

Table II. Interatomic Distances (Å) and Angles (deg) for 4, [5]$^-$, and [6]$^-$

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$_{11}$)] (4)					
Al(03)–C(01)	2.288 (5)	Al(03)–C(01′)	2.240 (4)	Al(03)–C(02)	2.272 (5)
Al(03)–C(02′)	2.254 (5)	Al(03)–B(04)	2.237 (5)	Al(03)–B(04′)	2.174 (5)
Al(03)–B(07)	2.230 (5)	Al(03)–B(07′)	2.164 (5)	Al(3)–B(08)	2.177 (5)
Al(03)–B(08′)	2.130 (5)	Al(20)–B(08)	2.410 (5)	Al(20)–B(09)	2.421 (5)
Al(20)–C(21)	1.909 (5)	Al(20)–C(23)	1.928 (5)	Al(20)–H(08)	1.942
Al(20)–H(09)	1.933	B(08)–H(08)	1.154	B(09)–H(09)	1.146
C(21)–Al(20)–C(23)	130.3 (3)	H(08)–Al(20)–H(09)	98.72	B(08)–Al(20)–B(09)	42.9 (4)
angle between normals to mean bonding planes: 2.6					
Tl[*commo*-3,3′-Al(3,1,2-AlC$_2$B$_9$H$_{11}$)$_2$]·$^2/_3$C$_7$H$_8$ (Tl[5]·$^2/_3$C$_7$H$_8$)					
Anion A					
Al(3)–C(1)	2.30 (2)	Al(3)–C(2)	2.29 (2)	Al(3)–B(4)	2.22 (2)
Al(3)–B(7)	2.24 (2)	Al(3)–B(8)	2.14 (2)		
Anion B					
Al(3)–C(1)	2.28 (2)	Al(3)–C(2)	2.26 (2)	Al(3)–B(4)	2.21 (2)
Al(3)–B(7)	2.19 (2)	Al(3)–B(8)	2.14 (2)		
Anion C					
Al(3)–C(1)	2.24 (2)	Al(3)–C(2)	2.29 (2)	Al(3)–B(4)	2.18 (3)
Al(3)–B(7)	2.29 (2)	Al(3)–B(8)	2.14 (2)		
thallium–arene distances: 3.21, 3.19, 3.18, 3.19, 3.21, 3.22					
[*commo*-3,3′-Ga(3,1,2-GaC$_2$B$_9$H$_{11}$)$_2$]$^-$ ([6]$^-$)					
Ga–C(1)	2.565 (7)	Ga–C(2)	2.591 (8)	Ga–B(4)	2.265 (8)
Ga–B(7)	2.297 (8)	Ga–B(8)	2.083 (8)	Ga–C(1′)	2.481 (7)
Ga–C(2′)	2.492 (7)	Ga–B(4′)	2.253 (8)	Ga–B(7′)	2.251 (8)
Ga–B(8′)	2.095 (8)	Tl–H(12)	2.81 (12)	Tl–H(9)	3.05 (12)
Tl–H(6)	3.06 (12)	Tl–H(10′)	3.08 (11)	Tl–H(5)	3.08 (11)
Tl–H(5′)	3.12 (11)				
B(10)–Ga(3)–B(10′)	170.5 (2)				
Ga–B(10) vector to mean bonding plane normal: 8.7°					
Ga–B(10′) vector to mean bonding plane normal: 7.8°					
angle between normals to mean bonding planes: 5.4					

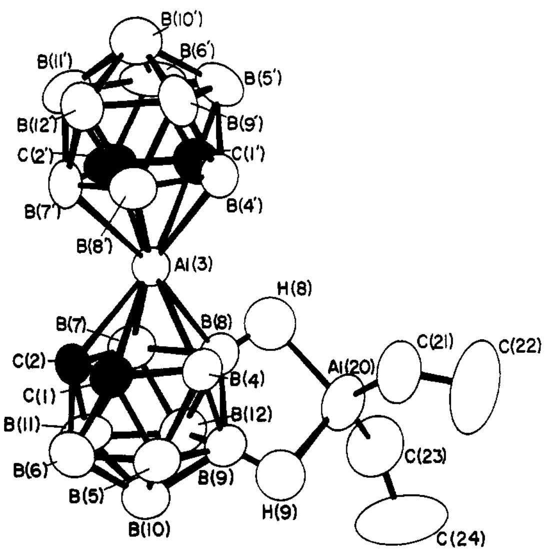

Figure 4. Structure of *commo*-3,3′-Al[{*exo*-8,9-(μ-H)$_2$-AlEt$_2$-3,1,2-AlC$_2$B$_9$H$_9$}(3,1,2-AlC$_2$B$_9$H$_{11}$)] (4) with all hydrogen atoms omitted except those involved in Al–H–B bridge bonding.

bonding faces of two η^5-dicarbollide cages. In addition, a second aluminum atom present as a cationic diethylaluminum moiety is bound to one of the dicarbollide cages by a pair of Al–H–B bridging interactions. The angle between the normals to the mean planes of the C_2B_3 bonding faces of the two dicarbollide cages in 4 is 2.6°. Species 4 can be formally regarded as a zwitterion composed of a [*commo*-3,3′-Al(3,1,2-AlC$_2$B$_9$H$_{11}$)$_2$]$^-$ ([5]$^-$) anion complexed with a [AlEt$_2$]$^+$ cation.

The pair of three-center–two-electron Al–H–B bridging interactions that connect the exopolyhedral Et$_2$Al moiety to atoms B(8) and B(9) of one of the dicarbollide cages in 4 involve hydrogen atoms that were located crystallographically. These interactions are similar to those proposed for 2. In 2, however, the comparable bridging hydrogen atoms were unobserved in the X-ray analysis.[2c] The average bridging B–H and Al–H distances in 4 are 1.1 and 1.9 Å, respectively, and angles around aluminum, including bridging hydrogen atoms, are approximately tetrahedral. It may be noted that the average Al–B distances found in 2 (2.31 Å) and 4 (2.41 Å) are significantly longer than those reported for Al(BH$_4$)$_3$ (2.14 Å).[13,14]

The ^{1}H and ^{11}B NMR spectral analyses of 4 indicate that this species exhibits dynamic solution behavior with respect to cage rotation about the metal–carborane axis as well as a facile intramolecular cage walking of the diethylaluminum moiety about both dicarbollide cages. Intermolecular diethylaluminum group transfer cannot be ruled out on the basis of the NMR spectral data. This fluxional behavior is indicated by the occurrence of a single relatively sharp carboranyl C–H resonance in the ^{1}H NMR spectrum of 4, as well as by the relatively high apparent molecular symmetry suggested by the ^{11}B{^{1}H} NMR spectra. Variable-temperature NMR studies revealed no substantial change in the ^{1}H or ^{11}B NMR spectra of 4 down to −80 °C, the lowest temperature at which spectral data were acquired.

Addition of any one of several alkylaluminum and alkylaluminum chloride reagents to a stirred toluene suspension of Tl[*closo*-3,1,2-TlC$_2$B$_9$H$_{11}$] in a 2:1 mole ratio, respectively, has been found to result in the dissolution

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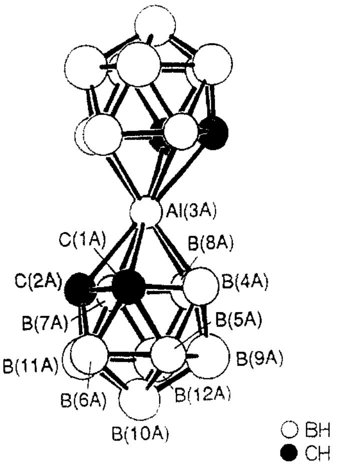

Figure 5. Structure of [*commo*-3,3′-Al(3,1,2-$AlC_2B_9H_{11})_2]^-$ ($[5]^-$) with hydrogen atoms omitted for clarity.

of the carborane salt and formation of the aluminacarborane sandwich anion [*commo*-3,3′-Al(3,1,2-$AlC_2B_9H_{11})_2]^-$ ($[5]^-$). The rate of this reaction is dependent upon the specific aluminum reagent employed. Reactions at room temperature with $AlEt_2Cl$, $AlEtCl_2$, and $AlMe_2Cl$ occur immediately, while reactions with $AlEt_3$ and Al(*i*-$Bu)_3$ require 1 h and several hours, respectively, to reach completion. Mixtures of Tl[*closo*-3,1,2-$TlC_2B_9H_{11}$] and $AlMe_3$ require heating at 60 °C to induce a reaction. The most efficient reagent for this synthesis appears to be $AlMe_2Cl$, which provides a rapid reaction rate and a colorless homogeneous product solution.

It is likely that the formation of $[5]^-$ in these reactions occurs with concomitant formation of thallium aluminate complexes of the type $Tl[AlR_{4-x}Cl_x]$ (R = Me, Et, *i*-Bu; x = 0–3). This is supported by ^{1}H NMR spectra of the reaction mixtures that result from the use of the triethylaluminum and diethylaluminum chloride reagents. These spectra exhibited broadened alkyl resonances characteristic of alkylaluminates.[15] On the basis of this evidence, reactions of AlR_2Cl reagents with Tl[*closo*-3,1,2-$TlC_2B_9H_{11}$] can be postulated to occur according to eq 1. Samples of Tl[**5**] of high purity are difficult to isolate

$$2\mathrm{Tl}[closo\text{-}3,1,2\text{-}\mathrm{TlC_2B_9H_{11}}] + 4\mathrm{AlR_2Cl} \xrightarrow{\text{toluene}} \mathrm{Tl}[commo\text{-}\mathrm{Al(7,8\text{-}C_2B_9H_{11})_2}] + 2\mathrm{Tl[AlR_3Cl]} + \mathrm{Tl[AlR_2Cl_2]} \quad (1)$$

$$\mathrm{R = Me,\ Et,}\ i\text{-}\mathrm{Bu}$$

when not prepared with $AlMe_2Cl$, due to the presence of unstable thallium aluminate byproducts that precipitate metallic thallium during purification. As with **4**, the ^{1}H and ^{11}B NMR spectra of $[5]^-$ in toluene solution at room temperature contain resonances attributable to only one variety of dicarbollide cage.

The $[5]^-$ ion can be readily isolated as the thallium salt by precipitation from the reaction mixture by adding heptane. The resulting salt, $Tl[5]\cdot{}^2/_3C_7H_8$, has been characterized by a combination of spectroscopic techniques and by a single-crystal X-ray diffraction study as reported in a preliminary communication.[7] The unit cell of $Tl[5]\cdot{}^2/_3C_7H_8$ consists of three crystallographically unique aluminacarborane anions, designated $[5A]^-$, $[5B]^-$, and $[5C]^-$, as well as three Tl^+ cations and two toluene solvate molecules. The crystallographically unique anions are very similar in all important aspects. The structure of one representative $[5]^-$ ion is shown in Figure 5, and selected interatomic distances and angles are listed in Table II. Anion $[5C]^-$ was disordered with respect to rotation about the carborane–aluminum pseudo-C_5 axis. The aluminum atom in $[5]^-$ lies at a center of crystallographic symmetry and is thus equidistant from each of the two parallel and nearly planar C_2B_3 bonding faces of the η^5-dicarbollide cages. Interatomic distances between aluminum and the cage face atoms are quite similar in each of the crystallographically unique $[5]^-$ ions, and these distances are also very similar to those found in **4**. A unit cell diagram for $Tl[5]\cdot{}^2/_3C_7H_8$ is shown in Figure 6.

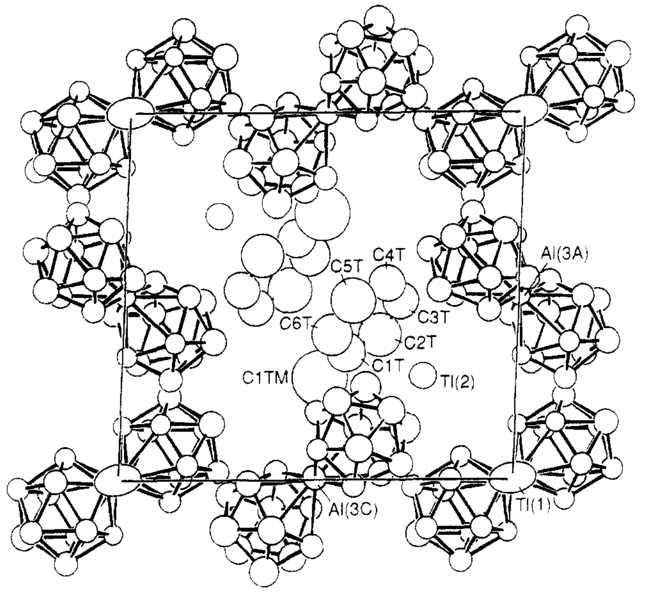

Figure 6. Unit cell diagram for $Tl[5]\cdot{}^2/_3C_7H_8$. The Al(3B) atoms are hidden behind Tl(1) in this view.

Each toluene molecule in $Tl[5]\cdot{}^2/_3C_7H_8$ lies close to a thallium ion, while a third thallium ion lies in a special position closer to one of the $[5]^-$ anions. The two thallium–toluene pairs, which exhibit thallium–arene carbon distances averaging 3.21 Å, can be regarded as thallium(I)–π-arene complexes. Similar thallium–arene complexes have been reported and include those found in $TlAlCl_4\cdot{}^1/_2C_6H_6$ and $TlAlCl_4\cdot 2C_6H_6$.[16] The thallium(I)–η^6-mesitylene complexes $[\{1,3,5\text{-}(CH_3)_3C_6H_3\}_6Tl_4][GaBr_4]_4$[17] and $[TlOTeF_5\{1,3,5\text{-}(CH_3)_3C_6H_3\}_2]_2$[18] have been characterized recently by X-ray diffraction studies and contain thallium–arene interatomic distances that are similar to those found in $Tl[5]\cdot{}^2/_3C_7H_8$. The toluene-coordinated thallium atoms in $Tl[5]\cdot{}^2/_3C_7H_8$ also exhibit six similar nonbonded close approaches to carborane cage hydrogen atoms averaging 2.84 Å. Similar coordination was reported for thallium atoms involved in thallium–mono(mesitylene) interactions in the $[\{1,3,5\text{-}(CH_3)_3C_6H_3\}_6Tl_4]^{4+}$ cation above, which are surrounded by six bromine atoms of nearby $[GaBr_4]^-$ anions. Selected interatomic distances involving thallium in $Tl[5]\cdot{}^2/_3C_7H_8$ are given in Table II.

The reaction of Tl[*closo*-3,1,2-$TlC_2B_9H_{11}$] with excess gallium(III) chloride in toluene solution results in the nearly quantitative formation of a thallium salt of the gallacarborane sandwich anion analogous to $[5]^-$, [*com-*

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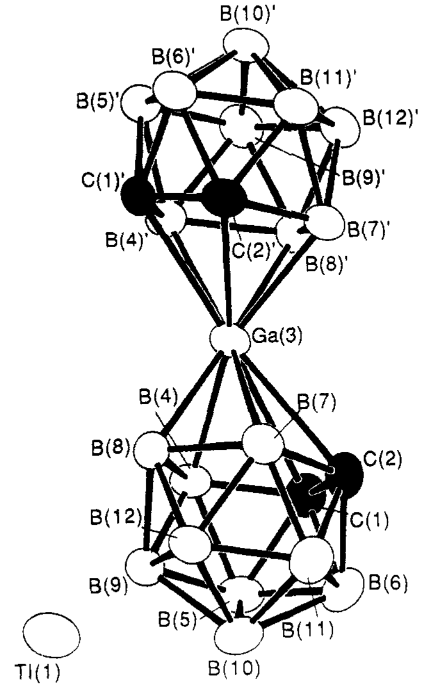

Figure 7. Structure of [*commo*-3,3′-Ga(3,1,2-GaC$_2$B$_9$H$_{11}$)$_2$]$^-$ ([**6**]$^-$) with hydrogen atoms omitted for clarity.

mo-3,3′-Ga(3,1,2-GaC$_2$B$_9$H$_{11}$)$_2$]$^-$ ([**6**]$^-$). The salt Tl[**6**] has been characterized by a single-crystal X-ray diffraction study and has been reported previously in a brief communication.[8] The structure of [**6**]$^-$ is shown in Figure 7. Table II contains interatomic distances and angles for this anion. The structure of [**6**]$^-$ contrasts with that of [**5**]$^-$ in that the former species exhibits a slip distortion, resulting in a situation in which each dicarbollide cage is bound to the metal in essentially an η^3 fashion. In this slipped bonding mode each carborane cage can be regarded as a four-electron donor, contributing a total of eight electrons to complete the valence shell of the formal gallium(III) center.

Anion [**6**]$^-$ also displays an eclipsed conformation of the two dicarbollide cages. While the majority of metallacarborane sandwich compounds adopt a staggered transoid conformation in the solid state with carboranyl carbon atoms on opposing cages as far apart as possible, a rotation of the cages from this typical conformation places the atoms in the opposing cages in the congruent relationship seen in [**6**]$^-$. This conformation has been noted for bis(dicarbollide) metallacarborane sandwich compounds which contain bridging groups that link the two carborane cages and hinder free rotation about the metal carborane axis[19] and in the formal d^6 metallacarborane sandwich compounds *commo*-3,3′-(3,1,2-MC$_2$B$_9$H$_{11}$)$_2$ (M = Ni, Pd).[20] In the case of [**6**]$^-$ this distortion may result from Coulombic interactions of the carborane cage B–H groups with the thallium cation. Each thallium ion in the unit cell was found to be surrounded by five gallacarborane anions, resulting in a total of six B–H interactions involving thallium–hydrogen interatomic distances near 3.0 Å. The angle between normals to the mean planes of the two dicarbollide cages in the [**6**]$^-$ anion is 5.5°.

Thallium tetrachlorogallate was determined to be the only other product formed along with Tl[**6**], as confirmed by mass spectroscopy and X-ray diffraction.[21] The observation of this salt supports the reaction stoichiometry represented by eq 2 for the formation of Tl[**6**]. This

$$2\text{Tl}[closo\text{-}3,1,2\text{-TlC}_2\text{B}_9\text{H}_{11}] + 4\text{GaCl}_3 \xrightarrow{\text{toluene}} \text{Tl}[commo\text{-Ga}(\eta^3\text{-C}_2\text{B}_9\text{H}_{11})_2] + 3\text{Tl}[\text{GaCl}_4] \quad (2)$$

reaction is analogous to those proposed for the formation of Tl[**5**] and represented by eq 1. Attempts to prepare Tl[**6**] by the reaction of alkylgallium reagents with Tl[*closo*-3,1,2-TlC$_2$B$_9$H$_{11}$] were unsuccessful.

The species **4**, [**5**]$^-$, and [**6**]$^-$ represent unusual examples of main-group-element sandwich compounds that contain central atoms in their highest formal oxidation states. Although a variety of main-group-element sandwich compounds of the type M(η^5-C$_5$R$_5$)$_2$, where M is Si, Ge, Sn, and Pb and R is H, Me, and Ph, have been reported,[1,22] these compounds formally involve elements in their +2 oxidation state and can be thought of as 14-interstitial-electron systems. The anion [**5**]$^-$, which formally contains Al(III), is isoelectronic and isostructural with the recently characterized silicon sandwich compound *commo*-3,3′-Si-(3,1,2-SiC$_2$B$_9$H$_{11}$)$_2$,[3b] which formally contains a Si(IV) center. Since each of the dicarbollide ligands is normally considered to donate six electrons to the metal atom when bound in a η^5 fashion, these compounds can also be regarded as 12-interstitial-electron systems. The synthesis and structural characterization of a related series of group 14 element metallacarborane sandwich compounds, including the species *commo*-3,3′-M[1,2-(Me$_3$Si)$_2$-3,1,2-MC$_2$B$_4$H$_4$]$_2$ (M = Si, Ge, Sn), which are electronically and structurally similar to [**5**]$^-$ and the corresponding silicon sandwich compound, have recently been reported.[23,24] These 12-interstitial-electron group 14 element sandwich species contrast with the recently reported formally 14-interstitial-electron silicon(II) sandwich compound Si(C$_5$Me$_5$)$_2$.[25]

Catalytic Reactivity of *closo*-3-Et-3,1,2-AlC$_2$B$_9$H$_{11}$ (1a). The preparation of active Ziegler type catalysts by the reaction of **1a** with TiCl$_4$ has been previously described.[2b] We have recently discovered that the **1a**/**4** equilibrium system catalyzes the exchange of hydrogen between B–H and arene C–H groups as well as the oligomerization of alkenes in the absence of transition metals. When benzene-d_6 or toluene-d_8 solutions of **1a** are heated at 80 °C, exchange of solvent C–D and carborane B–H occurs. When monitored by ^{1}H NMR spectroscopy, this exchange is evidenced by a significant increase in the resonance integral of the residual protons of the deuteriated solvent and by a corresponding decrease in integrals of the broad B–H resonances of the carborane cage, as can be seen in Figure 3a,b. This C–D/B–H exchange is further supported by IR and mass spectral data, which confirm the formation of deuteriated **1a**. Samples of fully boron-deuteriated **1a** and **4** (**1a**-d_9 and **4**-d_{18}), as confirmed by

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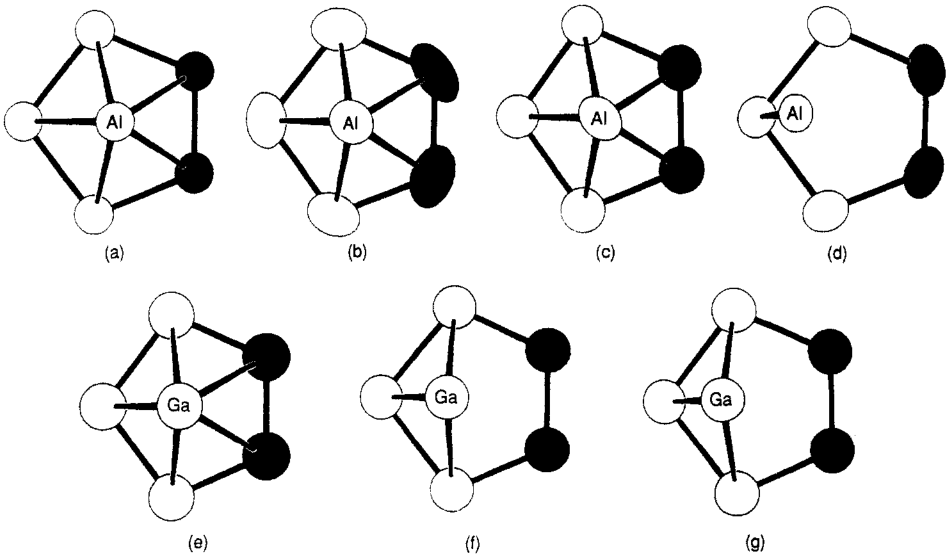

Figure 8. Projections of the metal atoms and the C_2B_3 belt atoms viewed along the normal to the mean plane of the C_2B_3 face of the carborane cage for the aluminacarboranes (a) **1a**, (b) **4**, (c) [**5**]$^-$, and (d) **3** and the gallacarboranes (e) **7**, (f) prime cage of [**6**]$^-$, and (g) nonprime cage of [**6**]$^-$.

IR and mass spectroscopy, can be prepared by heating **1a** in the presence of a large excess of benzene-d_6 followed by the separation of products from the equilibrium mixture. Heating samples of deuteriated **1a** or **4** in a large excess of protio solvent results in the formation of fully protiated **1a** and **4** after equilibrium is established. No exchange of carboranyl or ethyl C–H protons is observed. Exchange of the alkyl C–H of toluene and mesitylene occurs much more slowly than aryl protium exchange. This benzylic protium exchange can be followed by periodic monitoring of the $^{13}C\{^1H\}$ NMR spectrum of samples of concentrated (ca. 0.1 M) toluene or mesitylene solutions of **1a**-d_9 that are heated at 80 °C. These samples show a gradual appearance of deuterium coupling to the benzylic carbons until the expected intensity ratio for statistical H/D scrambling is reached after several days.

The exchange of carborane B–H and arene C–D occurs only very slowly in samples of ca. 0.1 M **1a** in deuterated arene kept at room temperature in sealed NMR tubes. Under these conditions **1a** is by far the predominant species present in solution, as indicated by ^1H NMR spectroscopy. When these samples are heated, the exchange reaction occurs rapidly and accompanies the formation of appreciable amounts of species **4**. Conversely, samples of pure **4** of similar concentration in benzene-d_6 or toluene-d_8 solution show very rapid C–D/B–H exchange at room temperature (conditions under which equilibration with **1a** occurs exceedingly slowly) and achieve approximate isotopic equilibrium within minutes. These observations suggest that **4** may be the active species responsible for the observed catalytic activity.

Dilute toluene solutions of **1a** were found to catalyze the formation of polymers and oligomers at room temperature and atmospheric pressure. For example, 100 mL of a 2.8×10^{-2} M toluene solution of **1a** typically consumes ca. 7.0 g of isobutylene within 4.5 days at 25 °C with the gradual appearance of a dark yellow color. The solution remains visibly homogeneous during the initial stages of alkene uptake; however, precipitation of an oil occurs after 2–3 days. Analysis of the resulting solution by ^1H and ^{13}C NMR spectroscopy and GC–MS revealed 4.9 g of volatile products (70% w/w) consisting of 64% isobutylene dimer (C_8H_{16}) and 36% isobutylene trimer ($C_{12}H_{24}$), as well as 2.1 g of a nonvolatile oil. Elemental analysis of the nonvolatile product provided 84.0% carbon and 13.8% hydrogen. The average molecular weight of this material was found to be 838, corresponding roughly to a C_{60} hydrocarbon, or about 15 isobutylene units. Periodic monitoring of ^1H NMR spectra confirmed that **1a** persists throughout the reaction. Similar experiments which involved propylene and ethylene were carried out which indicated that these alkenes are also polymerized by **1a** under mild temperature and pressure conditions, but at a somewhat slower rate. Typically, a dilute benzene solution of **1a** was found to consume ca. 82% of a 5-fold molar excess of propylene at 60 °C within 82 h. Similar results were obtained for ethylene. Compound **4** was also found to catalyze the polymerization of propylene and isobutylene under the same conditions utilized with **1a**.

Departures of Group 13 Metallacarboranes from Idealized Geometries. It is well-known that metallacarborane compounds containing the [*nido*-7,8-$C_2B_9H_{11}$]$^{2-}$ and [*nido*-2,3-$C_2B_4H_6$]$^{2-}$ ligands and their C-substituted derivatives may exhibit varying degrees of distortion from idealized closo geometry by undergoing a "slipping" of the capping metal across the C_2B_3 cage face in the direction of the unique boron atom. The dicarbollide derivatives discussed herein display "slip distortions" ranging from a minimum for **1a** to a maximum in the case of **3**. The slip distortion has been quantified for metallacarborane dicarbollide derivatives in terms of the slip parameter Δ.[26] This parameter is a measure of the displacement of the metal atom from the normal to the centroid of the lower B_5 plane of the dicarbollide cage. Another useful parameter for describing metallacarborane geometries is the metal–cage distance, which is defined herein as the distance from the metal to the mean plane of the C_2B_3 cage face. The Δ and metal–cage distance parameters for a series of alumina- and gallacarboranes are listed in Table III.

Figure 8 illustrates the slip distortions of these compounds by showing a series of projections of their metal atoms onto the plane of the C_2B_3 pentagonal face of the dicarbollide cage. Compound **1a**, which possesses a slip parameter of 0.11 Å and a metal–cage distance of 1.59 Å, is an essentially undistorted closo cluster. Species **1a**, **4**,

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Table III. Distortion Parameters

compd	slip param Δ/Å[a]	metal-cage dist/Å[b]
1a	0.11	1.59
4		
substituted cage	0.20	1.71
unsubstituted cage	0.21	1.64
[5]$^-$ [c]		
anion A	0.29	1.70
anion B	0.24	1.68
[6]$^-$		
prime cage	0.49	1.75
nonprime cage	0.60	1.79
3	0.96	2.01

[a] Δ is the displacement of the metal from the normal to the centroid of the plane of the lower B_5 ring of the dicarbollide cage. [b] Calculated as the distance of the metal from the mean plane of the upper C_2B_3 ring of the dicarbollide cage. [c] Distortion parameters were not calculated for anion C of [5]$^-$ because of crystallographic disorder.

and **[5]**$^-$ can be considered to possess dicarbollide cages that are bound to aluminum in a η^5 fashion. The aluminacarborane sandwich anion **[5]**$^-$, which was structurally characterized as three crystallographically independent anions, displays a small symmetrical slip distortion averaging 0.26 Å for the two crystallographically ordered anions and a metal–cage distance averaging 1.69 Å. The small differences in Δ values for these anions (see Table V) may be caused by crystal-packing forces. Compound **4** possesses slightly unsymmetrical slip distortions that average 0.20 Å and an average metal–cage distance of 1.68 Å. The gallacarborane anion **[6]**$^-$ exhibits moderate unsymmetrical slip distortions of 0.49 and 0.60 Å and metal–cage distances of 1.75 and 1.79 Å, respectively. The significant difference between the Δ values for these species may result from the unsymmetrical Coulombic interactions of the carborane B–H groups with the thallium cation, as discussed above. The moderate slippage in **[6]**$^-$ results in a situation in which the dicarbollide cages can be regarded as η^3-bonded to the metal. When considered as a 12-vertex species compound, **3** displays an extreme formal slip distortion of 0.96 Å. In better agreement with its structure is the description of **3** as an endo-substituted isomer of [*nido*-7,8-$C_2B_9H_{12}$]$^-$, as described above.

Species **[6]**$^-$ can be compared with another structurally characterized gallacarborane compound, *closo*-3-Me-3,1,2-$GaC_2B_4H_6$ (**7**).[27] Compound **7** displays a similar, although less pronounced, slip distortion when compared with **[6]**$^-$. Since the 2,3-$C_2B_4H_6$ cage does not contain a pentagonal B_5 ring, the usual Δ parameter[26] cannot be calculated for its metallacarborane derivatives. Alternatively, slip distortions for these species can be discussed in terms of the lateral displacement of the metal from the normal to the centroid of the mean plane of the C_2B_3 cage face. In **7** this parameter is 0.24 Å, less than the corresponding unsymmetrical distortions for **[6]**$^-$ of 0.43 and 0.53 Å. Compound **7** also displays a distortion similar to that observed for **1a** in that the Ga–Me vector is tilted away from the normal to the plane of the cage bonding face and toward the cage carbon atoms at an angle of 14.0°. The tilting distortion in **7** has been attributed, in part, to back-bonding from the filled d orbitals of gallium into nonbonding molecular orbitals of the carborane cage.[27] It may be noted, however, that since the comparable aluminacarborane species **1a** also displays an analogous tilting distortion of 19.5°, it seems unlikely that d orbitals play a role in this distortion.[2b,c]

Recent theoretical calculations suggest that the distortions exhibited by **1a**, **4**, **[5]**$^-$, and **[6]**$^-$ result only from an optimization of gallium s- and p-orbital interactions with carborane cage molecular orbitals and require no d-orbital involvement to explain either the slipping or tilting distortions.[28] Any discussions of bonding in the related dicarbollide derivatives presented herein must necessarily be speculative in the absence of detailed molecular orbital studies for these specific compounds. Nonetheless, it appears likely that the comparable distortions seen for **1a**, **4**, **[5]**$^-$, and **[6]**$^-$ may be rationalized in terms of similar considerations involving metal s- and p-orbital interactions with the appropriate dicarbollide cage molecular orbitals.

The aluminacarborane sandwich compounds present an anomaly in formal electron counting. The dicarbollide cage, when bound to metals in the η^5 bonding mode, is considered to be a formal six-electron donor. Compounds **4** and **[5]**$^-$ each possess two dicarbollide ligands bound to their metal centers in a η^5 fashion, resulting in the formal contribution of 12 electrons to aluminum. This situation has previously been rationalized[3a,b] in terms of either the occupation of d orbitals on aluminum or the retention of four electrons in two nonbonding molecular orbitals associated with the dicarbollide ligands. The latter description is presently favored.

Aluminacarborane Compounds Containing Al–C σ Bonds. A number of 11-vertex metallacarborane complexes in which a transition metal is bound to the six-membered open face of isomers of the formal dianionic [*nido*-$C_2B_8H_{10}$]$^{2-}$ ligand have been characterized.[29] These complexes include isomers of the formal Co(III) species *closo*-(η^5-C_5H_5)$CoC_2B_8H_{10}$ and [*commo*-$Co(C_2B_8H_{10})_2$]$^-$. In light of the intriguing structural chemistry exhibited by the aluminacarboranes derived from the dicarbollide ligand, the extension of aluminacarborane chemistry to [*nido*-$C_2B_8H_{10}$]$^{2-}$ and smaller ligand systems was a logical step.

Although **1a** is readily formed by heating triethylaluminum with *nido*-7,8-$C_2B_9H_{13}$ in aromatic hydrocarbon solvent, we were unable to detect analogous reactions for a variety of trialkylaluminum reagents with the less acidic *nido*-5,6-$C_2B_8H_{12}$[30] in toluene or mesitylene at reflux temperature. However, the reaction of the diethyl ether adduct of diethylaluminum chloride with Na[5,6-$C_2B_8H_{11}$][30] in refluxing toluene results in the formation of the aluminacarborane species *nido*-6,9-(μ-AlEt(OEt_2))-6,9-$C_2B_8H_{10}$ (**8**), as described by eq 3. Compound **8** could be isolated

$$\mathrm{Na[5,6\text{-}C_2B_8H_{11}] + AlEt_2Cl{\cdot}OEt_2 \xrightarrow[\text{reflux}]{\text{toluene}}} \\ nido\text{-}\mathrm{6,9\text{-}(\mu\text{-}AlEt(OEt_2))\text{-}6,9\text{-}C_2B_8H_{10} + C_2H_6 + NaCl} \quad (3)$$

in good yield as an extremely air- and moisture-sensitive liquid that could be distilled under vacuum without loss of diethyl ether. Crystals of the air-sensitive benzene solvate **8**·$^1/_2C_6H_6$ (mp 28–30 °C) could be obtained by recrystallization of **8** from benzene/pentane. When sub-

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Table IV. Interatomic Distances (Å) and Angles (deg) for 8, [10]$^-$, and [11]$^-$

		nido-6,9-(μ-AlEt(OEt$_2$))-6,9-$C_2B_8H_{10}$ (8)			
Al–C(6)	2.030 (3)	Al–C(9)	2.025 (3)	Al–B(5)	2.500 (4)
Al–B(7)	2.509 (4)	Al–B(8)	2.499 (3)	Al–B(10)	2.514 (4)
Al–C(1)	1.966 (3)	Al–O(1)	1.909 (2)	Al–C(11)	1.966 (3)
O–C(13)	1.486 (4)	O–C(15)	1.467 (4)	B(1)–B(2)	1.750 (6)
B(1)–B(03)	1.842 (5)	B(1)–B(4)	1.754 (5)	B(1)–B(5)	1.765 (5)
B(1)–B(10)	1.767 (6)	B(2)–C(6)	1.662 (5)	B(2)–B(3)	1.776 (5)
B(2)–B(07)	1.785 (5)	B(3)–B(4)	1.766 (6)	B(3)–B(7)	1.755 (5)
B(3)–B(8)	1.762 (5)	B(4)–B(8)	1.775 (5)	B(4)–C(9)	1.665 (4)
B(5)–C(6)	1.575 (5)	B(5)–B(10)	1.890 (6)	B(7)–C(6)	1.574 (4)
B(7)–B(8)	1.916 (5)	B(8)–C(9)	1.558 (4)	B(10)–C(9)	1.563 (5)
C(11)–C(12)	1.392 (6)	C(13)–C(14)	1.442 (6)	C(15)–C(16)	1.471 (5)
C(18)–C(19)	1.335 (6)	C(18)–C(20)	1.349 (6)	C(19)–C(20)	1.367 (6)
C(6)–Al–C(9)	99.44 (12)	C(11)–Al–O	99.87 (13)	C(13)–O–C(15)	115.88 (25)
C(6)–Al–O	107.96 (11)	C(9)–Al–O	111.08 (11)	B(5)–Al–B(07)	63.97 (13)
B(5)–Al–B(8)	81.17 (12)	B(8)–Al–B(10)	63.57 (12)	C(11)–Al–B(5)	103.79 (15)
C(11)–Al–B(7)	158.15 (15)	C(11)–Al–B(8)	155.42 (15)	C(11)–Al–B(10)	102.92 (14)
B(5)–Al–O	146.47 (13)	B(7)–Al–O	85.64 (11)	B(8)–Al–O	87.13 (10)
B(10)–Al–O	148.68 (12)				
		[*commo*-3,3′-Al(3,1,2-Al$C_2B_9H_{11}$)$_2$]$^-$ ([10]$^-$)			
Al–C(6)	2.06 (2)	Al–C(6′)	2.07 (2)	Al–C(9)	2.05 (2)
Al–C(9′)	2.08 (2)	Al–B(5)	2.53 (2)	Al–B(5′)	2.50 (2)
Al–B(7)	2.55 (3)	Al–B(7′)	2.53 (2)	Al–B(8)	2.53 (2)
Al–B(8′)	2.52 (2)	Al–B(10)	2.51 (2)	Al–B(10′)	2.50 (3)
C(6)–Al–C(9)	98.7 (9)	C(6′)–Al–C(9′)	102.1 (9)	C(6)–Al–C(6′)	114.2 (9)
C(9)–Al–C(9′)	113.6 (9)	C(6)–Al–C(9′)	114.5 (9)		
		[Al(*nido*-2,7-$C_2B_6H_8$)$_2$]$^-$ ([**11a**]$^-$)			
Al(01)–C(2a)	2.018 (5)	Al(01)–C(2b)	2.018 (5)	Al(01)–C(7a)	2.017 (5)
Al(01)–C(7b)	2.020 (5)	Al(01)–B(3a)	2.282 (6)	Al(01)–B(3b)	2.276 (6)
Al(01)–B(6a)	2.501 (5)	Al(01)–B(6b)	2.517 (6)	Al(01)–B(8a)	2.517 (6)
Al(01)–B(8b)	2.511 (6)	C(2a)–B(3a)	1.649 (8)	C(7a)–B(3a)	1.640 (8)
C(2b)–B(3b)	1.644 (8)	C(7b)–B(3b)	1.648 (8)	C(2a)–B(6a)	1.544 (7)
C(2b)–B(6b)	1.568 (8)	C(7a)–B(8a)	1.562 (7)	C(7b)–B(8b)	1.553 (8)
C(2a)–B(1a)	1.669 (7)	C(7a)–B(4a)	1.674 (7)	C(2b)–B(1b)	1.663 (7)
C(7b)–B(4b)	1.659 (7)	Na(1)–H(5b)	2.330	Na(1)–H(4b)	2.394
Na(1)–H(1a)	2.430	Na(1)–H(6b)	2.489		
C(2a)–Al(01)–C(7a)	82.40 (20)	C(2b)–Al(01)–C(7b)	81.88 (20)		
C(2b)–Al(01)–C(7a)	129.34 (20)	C(2a)–Al(01)–C(2b)	112.27 (22)		
C(7a)–Al(01)–C(7b)	130.06 (20)	C(2a)–Al(01)–C(7b)	125.36 (21)		
		[Al(*nido*-2,7-$C_2B_6H_8$)$_2$]$^-$ ([**11b**]$^-$)			
Al(01′)–C(2a′)	2.020 (5)	Al(01′)–C(2b′)	2.026 (5)	Al(01′)–C(7a′)	2.020 (5)
Al(01′)–C(7b′)	2.016 (5)	Al(01′)–B(3a′)	2.288 (5)	Al(01′)–B(3b′)	2.271 (7)
Al(01′)–B(6a′)	2.494 (6)	Al(01′)–B(6b′)	2.509 (6)	Al(01′)–B(8a′)	2.499 (6)
Al(01′)–B(8b′)	2.514 (6)	C(2a′)–B(3a′)	1.621 (8)	C(7a′)–B(3a′)	1.657 (7)
C(2b′)–B(3b′)	1.661 (8)	C(7b′)–B(3b′)	1.647 (8)	C(2a′)–B(6a′)	1.576 (7)
C(2b′)–B(6b′)	1.571 (8)	C(7a′)–B(8a′)	1.563 (7)	C(7b′)–B(8b′)	1.769 (9)
C(2a′)–B(1a′)	1.666 (7)	C(7a′)–B(4a′)	1.675 (7)	C(2b′)–B(1b′)	1.659 (7)
C(7b)–B(4b)	1.656 (7)	Na(1)–H(3a′)	2.538	Na(1)–H(4a′)	2.592
Na(2)–H(5a′)	2.319	Na(2)–H(5b′)	2.511	Na(2)–H(6b′)	2.572
C(2a)–Al(01′)–C(7a)	82.09 (20)	C(2b)–Al(01′)–C(7b)	82.39 (20)		
C(2b)–Al(01′)–C(7a)	121.28 (21)	C(2a)–Al(01′)–C(2b)	111.40 (21)		
C(7a)–Al(01′)–C(7b)	136.63 (23)	C(2a)–Al(01′)–C(7b)	125.55 (23)		

jected to vacuum, these crystals lost benzene of solvation to regenerate liquid 8.

The structure of 8, obtained with use of a single crystal of its benzene solvate, is shown in Figure 9, and selected interatomic distances and angles are listed in Table IV. The structure of 8 consists of a nearly regular octadecahedron in which an aluminum atom resides at the unique vertex and possesses an exopolyhedral ethyl substituent and an aluminum-coordinated diethyl ether molecule. The carboranyl carbon atoms occupy the 6- and 9-positions of the $C_2B_8H_{10}$ cage portion of the cluster. The aluminum atom is nearly equidistant from the four boron atoms in the open face of the carborane cage, with the four similar aluminum–boron interatomic distances averaging 2.51 Å. The aluminum atom is also nearly equidistant from the two carboranyl carbon atoms, with aluminum–carbon interatomic distances averaging 2.03 Å. Angles about aluminum and between carboranyl carbon atoms and the exopolyhedral carbon and oxygen atoms are approximately tetrahedral. The benzene of crystallization was found to be ordered and positioned at a center of symmetry.

Thermal rearrangement of the 5,6-$C_2B_8H_{10}$ ligand to produce the observed 6,9-isomer is not unprecedented; the related cobaltacarborane system *closo*-1-(η^5-C_5H_5)-1-Co-2,4-$C_2B_8H_{10}$ (equivalent to the 5,6-*nido* isomer) is rearranged to the corresponding *closo*-1-(η^5-C_5H_5)-1-Co-2,3-$C_2B_8H_{10}$ isomer (equivalent to the 6,9-*nido* isomer) under similar conditions.[31] Furthermore, this rearrangement is consistent with the general pattern of rearrangements established for neutral, polyhedral carboranes, which in-

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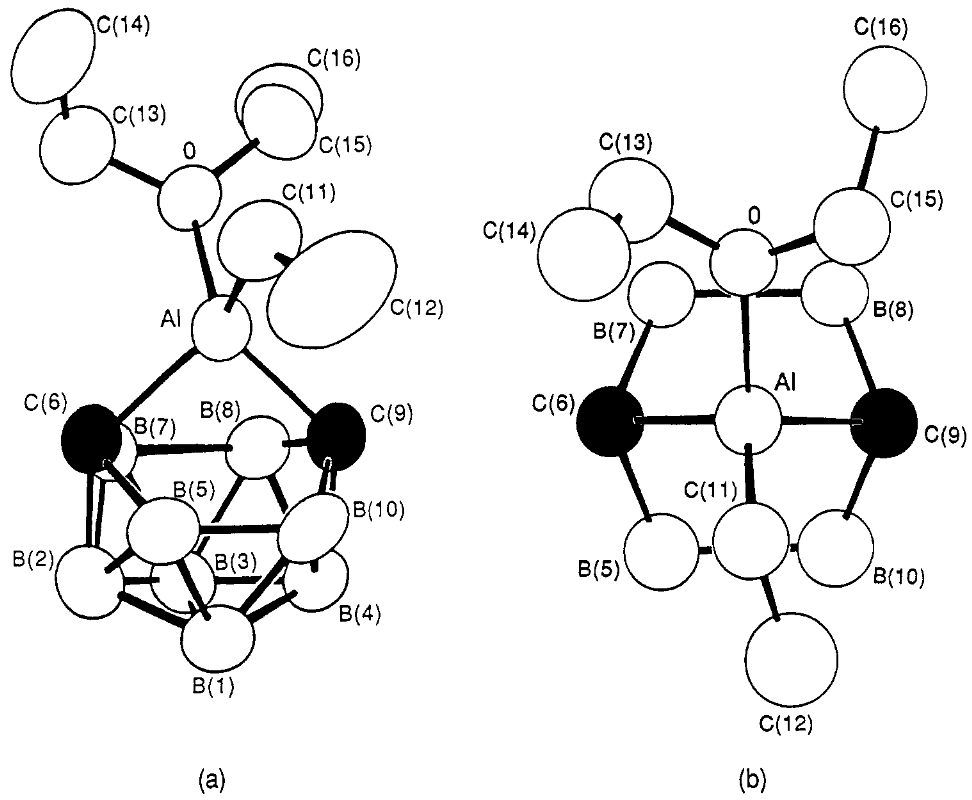

Figure 9. (a) Structure of *nido*-6,9-(μ-AlEt(OEt$_2$))-6,9-$C_2B_8H_{10}$ (8) with hydrogen atoms omitted. (b) View of 8 along the C(6)–Al–C(9) plane with atoms B(1), B(2), B(3), and B(4) and all hydrogen atoms omitted.

volves the migration of carbon atoms to positions that are further separated from one another and are of lower connectivity.[32] It may be noted that this rearrangement also appears to produce the most suitable arrangement of carbon-based orbitals for accommodation of the tetrahedral aluminum center.

The geometry and interatomic distances found in 8 suggest that aluminum–carborane cage bonding can be rationalized by considering the carborane cage as a formally dianionic [*nido*-6,9-$C_2B_8H_{10}$]$^{2-}$ ligand that functions in a η^2 manner by donating four electrons via two carbon-based hybrid orbitals directed toward the approximately tetrahedral formal aluminum(III) center. In this description the aluminum atom and its associated substituents are regarded as a bridging moiety with respect to the carborane cage. The structure of 8 contrasts with that of other known main-group-element-substituted, 11-vertex, 26-electron boron cage compounds, for example, $Me_2M(\eta^4\text{-}B_{10}H_{12})$ (M = Si, Ge, Sn), which adopt nido structures having a single open face that accommodates two bridging hydrogen atoms.[33] Transition-metal complexes of the type 6,9-(μ-ML_2)-6,9-$C_2B_8H_{10}$ (M = Pt, L, = PPh_3, SEt_2; M = Ni, L = *cis*-1,2-$(NH_2)_2C_6H_4$), which are structurally similar to 8 and involve square-planar rather than tetrahedral metal centers, have been reported.[34]

The room-temperature 160.5-MHz ^{11}B NMR spectrum of 8 in toluene-d_8 solution exhibits three doublet resonances in 2:1:1 area ratios that collapsed to singlets upon ^1H decoupling, as shown in Figure 10a. The room-temperature 200.1-MHz ^1H NMR spectrum of 8 in toluene-d_8 solution contains, in the expected intensity ratios, high-field triplet and quartet aluminum-bound ethyl resonances, triplet and quartet diethyl ether resonances, and a single carboranyl C–H and broad B–H resonances characteristic of the $C_2B_8H_{10}$ cage. The apparent C_{2v} symmetry indicated by the ^{11}B NMR spectrum of 8 is attributed to the oc-

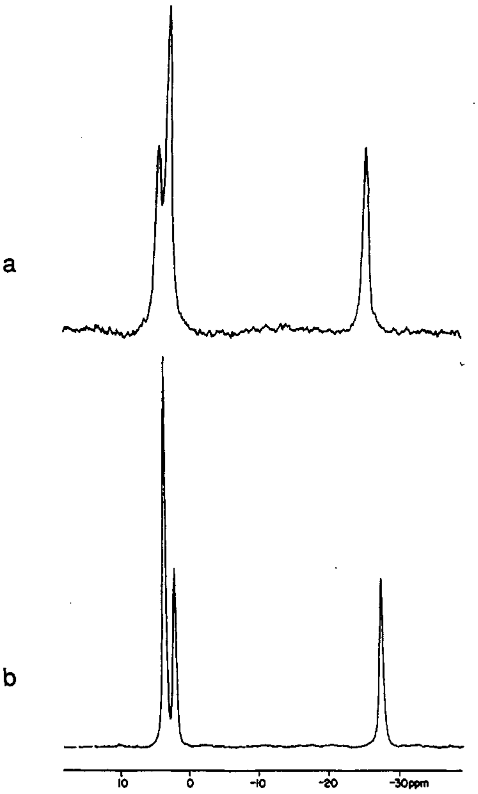

Figure 10. $^{11}B\{^1H\}$ NMR spectra (160.5 MHz) of (a) *nido*-6,9-(μ-AlEt(OEt$_2$))-6,9-$C_2B_8H_{10}$ (8) and (b) [Al(*nido*-6,9-$C_2B_8H_{10})_2$]$^-$ ([**10**]$^-$) in toluene-d_8 solution.

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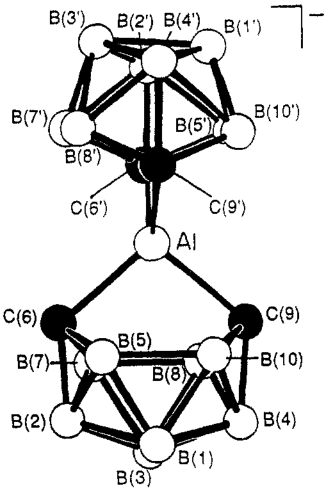

Figure 11. Structure of $[Al(nido\text{-}6,9\text{-}C_2B_8H_{10})_2]^-$ ($[\mathbf{10}]^-$) with hydrogen atoms omitted.

currence of a rapid intermolecular ether exchange process in solution. Only a single set of diethyl ether resonances was observed in the ^{1}H NMR spectrum of a toluene-d_8 solution of **8** to which 1 molar equiv of diethyl ether had been added. These diethyl ether resonances occurred at chemical shift values intermediate between those of free ether and those of **8**, suggesting the occurrence of a rapid exchange of free and bound ether. Variable-temperature NMR studies carried out with toluene-d_8 solutions of **8** showed no significant change in either the ^{1}H or ^{11}B NMR spectra down to −90 °C. In addition, toluene-d_8 solutions of **8** containing added diethyl ether failed to show more than one set of diethyl ether resonances above −90 °C, the lowest temperature at which spectra were acquired.

The kinetic lability of **8** was further demonstrated with the preparation of a THF analogue by ether exchange. Reaction of **8** with THF resulted in facile ether exchange, as observed by ^{1}H NMR spectral monitoring. The THF complex $nido\text{-}6,9\text{-}(\mu\text{-}AlEt(C_4H_8O))\text{-}6,9\text{-}C_2B_8H_{10}$ (**9**) was isolated and characterized by spectroscopic means. This compound was also prepared independently by the reaction of $Na[nido\text{-}5,6\text{-}C_2B_8H_{11}]$ with $Et_2AlCl{\cdot}THF$ in refluxing toluene. Samples of **9** obtained by either route were found to be identical by ^{1}H and ^{11}B NMR and infrared spectroscopy.

The reaction of diethylaluminum chloride with 2 molar equiv of $Na[5,6\text{-}C_2B_8H_{11}]$ in boiling toluene in the absence of diethyl ether or other Lewis bases was found to result in the formation of the aluminacarborane anion $[Al(\eta^2\text{-}6,9\text{-}C_2B_8H_{10})_2]^-$ ($[\mathbf{10}]^-$), in accord with eq 4. Anion $[\mathbf{10}]^-$

$$2Na[nido\text{-}5,6\text{-}C_2B_8H_{11}] + AlEt_2Cl \xrightarrow[\text{reflux}]{\text{toluene}} Na[Al(\eta^2\text{-}nido\text{-}6,9\text{-}C_2B_8H_{10})_2] + 2C_2H_6 + NaCl \quad (4)$$

was initially isolated as the sodium salt, which was converted to the $[(PPh_3)_2N]^+$ salt by metathesis. Although the Na^+ salt of the hydrolytically unstable $[\mathbf{10}]^-$ anion slowly decomposed in moist air, the $[(PPh_3)_2N]^+$ salt was found to be moderately stable to air and moisture. A single-crystal X-ray diffraction study was carried out on $[(PPh_3)_2N][\mathbf{10}]$, and the structure of the anion is shown in Figure 11. Selected interatomic distances and angles for $[\mathbf{10}]^-$ are listed in Table IV.

While the $[(PPh_3)_2N]^+$ cation did not exhibit disorder and no disorder was required by the space group, the aluminacarborane anion was disordered with respect to a 4-fold rotation about the noncrystallographic 2-fold axis of the anion. This disorder resulted in the presence of two crystallographic forms of $[\mathbf{10}]^-$, as major (52.5 (6)%) and minor occupants. Both crystallographic forms of $[\mathbf{10}]^-$ are considered to be identical in a chemical sense and to differ only in their orientation within the unit cell. The overall geometry of $[\mathbf{10}]^-$ is that of two mutually orthogonal octadecahedral cages which share their unique vertices. The aluminum atom resides at the unique position common to both cages and is surrounded by a roughly tetrahedral array of carbon atoms that occupy the 6- and 9-positions of the two $C_2B_8H_{10}$ cages. The four similar aluminum–carbon interatomic distances average 2.06 Å, while the eight similar aluminum–boron distances average 2.53 Å.

The aluminum–carborane cage bonding interactions in $[\mathbf{10}]^-$ appear to be similar to those in **8**. The geometry and interatomic distances in this anion suggest that aluminum participates in four-electron precise bonding interactions with the four nearby carboranyl carbon atoms. In this bonding description each carborane cage in $[\mathbf{10}]^-$ can be regarded as a dianionic $[nido\text{-}C_2B_8H_{10}]^{2-}$ ligand that donates four electrons to the aluminum(III) center via two carbon-based orbitals. The $[\mathbf{10}]^-$ anion can thus be regarded as a spiro aluminate complex.

The 160.5-MHz ^{11}B NMR spectra of both the Na^+ and $[(PPh_3)_2N]^+$ salts of $[\mathbf{10}]^-$ in methylene chloride solution exhibit three doublet resonances in a 2:1:1 area ratio, consistent with the observed solid-state structure. Each doublet resonance collapsed to a singlet upon ^{1}H decoupling, as shown in Figure 10b. The 200.1-MHz ^{1}H NMR spectrum of $[(PPh_3)_2N][\mathbf{10}]$ in toluene-d_8 solution shows a single carboranyl C–H resonance and broad B–H resonances characteristic of the $C_2B_8H_{10}$ cage.

The mechanisms of formation of **8** and $[\mathbf{10}]^-$ are uncertain, but they are obviously similar. These mechanisms most likely involve loss of chloride ion from aluminum followed by elimination of ethane by protolysis of aluminum-bound ethyl groups with carborane bridging hydrogen atoms. As with **8**, migration of the carbon atoms to the 6- and 9-positions of each carborane cage in $[\mathbf{10}]^-$ is the expected thermal rearrangement and results in the most favorable arrangement of carbon-based orbitals for bonding to the tetrahedral aluminum center. Continuous heating at the reflux temperature in toluene solutions of either **8** or $[(PPh_3)_2N][\mathbf{10}]$ for periods of over 3 weeks did not result in decomposition or further rearrangement.

Many transition-metal complexes containing one or more isomeric dicarbazapide ligands ($[nido\text{-}C_2B_7H_9]^{2-}$) have been reported.[35] In an attempt to prepare related aluminacarborane species containing this ligand, the reaction of diethylaluminum chloride with 2 molar equiv of the carborane salt $Na[arachno\text{-}1,3\text{-}C_2B_7H_{12}]{\cdot}OEt_2$[36] in refluxing toluene was carried out. Instead of providing the expected dicarbazapide derivative, this reaction resulted in the formation of an anionic aluminacarborane species containing two $[nido\text{-}2,7\text{-}C_2B_6H_8]^{2-}$ ligands bound to a central aluminum atom. This species, $[Al(\eta^2\text{-}nido\text{-}2,7\text{-}C_2B_6H_8)_2]^-$ ($[\mathbf{11}]^-$), was isolated as the sodium salt and characterized by spectroscopic means, as well as by a single-crystal X-ray diffraction study.

The X-ray structure of $Na[\mathbf{11}]$ revealed the presence of two crystallographically unrelated forms of the alumina-

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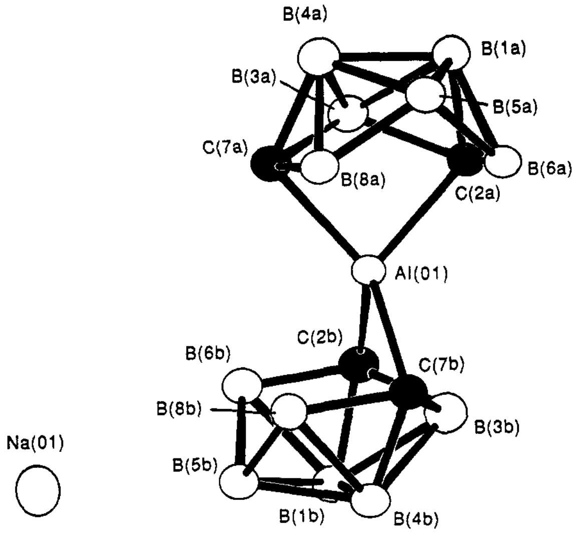

Figure 12. Structure of one enantiomer of Na[Al(*nido*-2,7-$C_2B_6H_8)_2$] (Na[**11**]) with hydrogen atoms omitted for clarity.

carborane anions in the unit cell, designated [**11a**]$^-$ and [**11b**]$^-$. These anions were found to be enantiomerically related, and they will be discussed herein as one species, simply referred to as [**11**]$^-$. The structure of one enantiomer of Na[**11**] is shown in Figure 12. Selected interatomic distances and angles for Na[**11a**] and Na[**11b**] are given in Table IV. The aluminum center in [**11**]$^-$ is surrounded by four carbon atoms of the two 2,7-$C_2B_6H_8$ carborane cages in a distorted-tetrahedral array similar to that seen in [**10**]$^-$. The two metal–ligand C–Al–C angles are similar to one another and average 82.14°. The four Al–C bond lengths are also similar and average 2.02 Å. In addition, two relatively short aluminum–boron interatomic distances averaging 2.28 Å involve the unique boron atoms that lie between the carbon atoms of the open face of each carborane cage (i.e. B(3a), B(3b)). Four more boron atoms (B(6a), B(8a), B(6b), B(8b)) are located at approximately equal distances from the aluminum center, averaging 2.51 Å. Although no discrete coordination geometry about the sodium cations could be discerned, each cation displays one relatively short contact with a B–H group of one of the metallacarborane anions. For [**11a**]$^-$, the shortest such interatomic distance is 2.330 (7) Å for Na···H(6b), and for [**11b**]$^-$, the shortest cation–anion distance is 2.319 (7) Å for Na···H(5a′).

Bonding in [**11**]$^-$ is ostensibly similar to that in **8** and [**10**]$^-$ in that each $C_2B_6H_8$ cage can be regarded as utilizing two carbon-based hybrid orbitals which are directed at an approximately tetrahedral aluminum center to formally donate four electrons to the metal center. The relatively long aluminum–boron distances as well as the coordination geometry suggest that no bonding occurs between these elements in the static structure. As is the case with [**10**]$^-$, [**11**]$^-$ may be thought of as a spiro aluminate complex. In contrast to the case for [**10**]$^-$, however, [**11**]$^-$ possesses only C_1 symmetry and thus displays stereoisomerism of the kind characteristic of a spiro compound having low symmetry. Because of the asymmetry of [**11**]$^-$, this anion would be expected to give rise to six ^{11}B NMR resonances and two carboranyl C–H ^{1}H NMR resonances. However, room-temperature ^{11}B NMR and ^{1}H NMR spectra of Na[**11**] in toluene solution reveal only four ^{11}B NMR resonances, in a 2:1:1:2 area ratio (δ 22.1, 7.6, −13.8, −32.0 ppm), and a single carboranyl C–H ^{1}H resonance (δ 2.96 ppm). The two area 2 ^{11}B NMR resonances were assigned to the two pairs of boron atoms that lie off the local mirror plane of the 2,7-$C_2B_6H_8$ ligand (i.e. B(1), B(4) and B(6), B(8)), and the two area 1 resonances were assigned to the boron atoms that lie on the local mirror plane (i.e. B(3), B(5)). The room-temperature ^{11}B NMR resonances were too broad to exhibit ^{1}H coupling. When toluene solutions of Na[**11**] are warmed, ^{11}B NMR spectra sharpen and at 70 °C the three highest field resonances clearly show ^{1}H coupling. The lowest field resonance remains broad. When these samples are cooled, the ^{11}B NMR resonances broaden and then sharpen again below −80 °C. At −90 °C, the lowest temperature at which suitable spectra could be acquired, ^{11}B{^{1}H} NMR spectra exhibit five resonances in a 2:1:1:1:1 area ratio, the highest field area 2 resonance seen at higher temperatures having been replaced by two area 1 resonances at δ −26.9 and −28.8 ppm. Similarly, low-temperature ^{1}H NMR spectra of these samples revealed two equal-intensity carboranyl C–H resonances at δ 2.63 and 2.93 ppm.

The variable-temperature NMR behavior of Na[**11**] indicates the occurrence of a dynamic process in solution involving the interconversion of the enantiomers [**11a**]$^-$ and [**11b**]$^-$. At −90 °C this process is slow on the NMR time scale, resulting in the nonequivalence of the boron atoms that lie off the local mirror plane of the 2,7-$C_2B_6H_8$ ligand and the appearance of two ^{11}B NMR resonances for one pair of these boron atoms. The large line widths at all temperatures observed for the ^{11}B{^{1}H} NMR resonances of the other pair of presumably nonequivalent boron atoms may obscure the expected asymmetry of these spectra. The reason for this line broadening is not known. The variable-temperature behavior of the carboranyl C–H proton resonances also indicates the occurrence of a fluxional process in solution above −80 °C. Conceptually, the interconversion of the enantiomers of [**11**]$^-$ may occur by rotation of the carborane ligands about the ligand–aluminum axis. Simple rotation of this kind would require a transition state having a square-planar aluminum center and is thus expected to be prohibitively high in energy. Alternatively, this dynamic racemization process may involve a transient η^3 or higher order intramolecular interaction between aluminum and the carborane ligands in solution, or fluxionality within the 2,7-$C_2B_6H_8$ cage framework, which cannot be ruled out on the basis of existing data.

The loss of a single boron vertex from the C_2B_7 polyhedral cage upon metallacarborane formation has been observed previously in the reaction of Na$_2$[*arachno*-1,3-$C_2B_7H_{11}$] with Mn(CO)$_5$Br or Mn$_2$(CO)$_{10}$, resulting in the formation of [*closo*-$C_2B_6H_8$Mn(CO)$_3$]$^-$ ([**12**]$^-$).[37] The mechanism by which the boron vertex is lost upon formation of [**11**]$^-$ and [**12**]$^-$ is not understood. In the case of [**11**]$^-$, the formal elimination of BH$_3$ and a proton from each [*arachno*-1,3-$C_2B_7H_{12}$]$^-$ anion is required to produce the [*nido*-2,7-$C_2B_6H_8$]$^{2-}$ ligand. The examination of crude reaction mixtures by NMR spectroscopy, however, revealed a complex mixture of boron-containing materials, making it impossible to suggest a specific reaction pathway.

Complex [**12**]$^-$ and the previously reported cobaltaborane complex *closo*-$C_2B_6H_8$Co(C_5H_5) (**13**)[38] each contain [*nido*-$C_2B_6H_8$]$^{2-}$ ligands and are closely related to [**11**]$^-$. However, in the closo complexes [**12**]$^-$ and **13**, the carborane ligands exhibit η^5 bonding interactions with the transition metals. Our findings here indicate that the [*nido*-2,7-$C_2B_6H_8$]$^{2-}$ ligand, as is the case with the [*nido*-

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(38) Evans, W. J.; Dunks, D. F.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1973**, *95*, 4565.

Table V. ^{1}H NMR Spectral Data^a

compd	chem shift, δ/ppm (splitting pattern, rel area, assignt)
1a^b	−0.22 (q, 2, CH_2), 0.77 (t, 3, CH_3), 1.63 (br s, 2, carborane C–H)
3^b	0.14 (q, 2, AlEt CH_2), 0.82 (t, 9, PEt_3 CH_3), 0.90 (t, 3, AlEt CH_3), 1.20 (q, 6, PEt_3 CH_2), 2.33 (s, 2, carborane C–H)
4^b	0.17 (q, 2, CH_2), 0.84 (t, 3, CH_3), 2.51 (br s, 2, carborane C–H), ca. 0.0–4.0 (br, B–H)
[**5**]$^{-c}$	2.09 (s, toluene CH_3), 2.84 (br s, carborane C–H), 6.94–7.08 (c, toluene C–H)
[**6**]$^{-c}$	2.72 (br s, carborane C–H)
8^c	−0.38 (q, 3, AlEt CH_2), 0.51 (t, 6, ether CH_3), 0.95 (t, 2, AlEt CH_3), 2.97 (q, 4, ether CH_2), 4.69 (br s, 2, carborane C–H)
9^c	−0.34 (q, 2, ethyl CH_2), 0.82 (t, 3, ethyl CH_3), 1.55 (br, 4, THF CH_2), 3.45 (br, ca. 4, THF CH_2), 4.75 (br s, ca. 2, carborane C–H)
[**10**]$^{-c}$	4.81 (br s, 2, carborane C–H), 0.1–5.1 (br c, B–H)
[**11**]$^{-c}$	2.96 (br s, carborane C–H)

^{a} Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, c = complex. ^{b} In C_6D_6. ^{c} In C_7D_8.

Table VI. $^{11}B\{^1H\}$ NMR Spectral Data

compd	chem shift, δ/ppm (rel area)
1a^a	7.3 (2), 13.5 (1), 15.7 (3), 17.8 (2), 24.0 (1)
3^b	−14.0 (2), −18.2 (4), −28.5 (2), −35.5 (1)
4^b	−12.3 (3), −16.8 (4), −21.6 (1), −31.7 (1)
[**5**]$^{-b}$	12.5 (2), −14.9 (1), −17.9 (3), −19.8 (2), −32.7 (1)
[**6**]$^{-b}$	13.1 (2), −15.4 (1), −17.6 (3), −25.01 (2), −31.2 (1)
8^a	4.3 (1), 2.9 (2), −25.3 (1)
9^b	3.3 (2), 2.4 (1), −25.8 (1)
[**10**]$^{-c}$	2.7 (2), 0.9 (1), −28.7 (1)
[**11**]$^{-c}$	21.6 (ca. 2), 7.1 (ca. 1), −15.0 (ca. 1), −33.2 (ca. 2)

^{a} In benzene. ^{b} In toluene. ^{c} In methylene chloride.

Table VII. Characteristic Infrared Spectral Data^a

compd	freq/cm^{-1} (assignt)
4	3223 (m, C–H str), 2578 (s, B–H str), 2532 (s, B–H str), 1094 (m), 988 (m), 656 (m)
Tl[5]·$^2/_3C_7H_8$	3035 (m, C–H str), 2510 (s, B–H str), 1030 (m), 746 (m), 657 (m)
Tl[6]	2522 (s, B–H str), 1094 (w), 1023 (w), 980 (w)
8	2943 (vs), 2793 (m), 2548 (vs, B–H str), 1468 (s), 1392 (s), 1327 (m), 1287 (m), 1192 (s), 1150 (s), 1090 (s), 1053 (m), 1012 (vs), 953 (m), 890 (s), 833 (m), 770 (s)
Na[10]	2543 (vs, B–H str), 1092 (m), 1064 (s), 723 (s), 693 (s)
Na[11]	3040 (w, carborane C–H), 2525 (vs, B–H str), 1466 (m), 1392 (m), 1125 (m), 1092 (m), 1060 (s), 1013 (s), 932 (m), 872 (s), 834 (m), 762 (m), 740 (m), 702 (m), 632 (m)

^{a} Abbreviations: w = weak, m = medium, s = strong, vs = very strong, str = stretch.

6,9-$C_2B_8H_{10}]^{2-}$ ligand, may function as a four-electron σ-donor, as in [**11**]$^-$, or a six-electron π-donor, as in [**12**]$^-$ and **13**, depending upon the electronic requirements of the metal to which it is coordinated. The variable electron donation abilities of these carborane cages may be compared with that of the [*nido*-7,8-$C_2B_9H_{11}]^{2-}$ ligand, which has been shown, in part by the studies described above, to be formally capable of either two-, four-, or six-electron donation to metal centers.

Experimental Section

General Considerations. Standard glovebox, Schlenk, and vacuum line techniques were employed for all manipulations of air- and moisture-sensitive compounds.[39] Reaction solvents were reagent grade and were distilled from appropriate drying agents under nitrogen before use. Benzene and toluene were distilled from potassium and sodium, respectively; tetrahydrofuran and methylene chloride were distilled from sodium benzophenone ketyl and phosphorus pentoxide, respectively. Deuteriated solvents were obtained from Cambridge Isotope Laboratories in sealed ampules under argon and were used without further purification. The preparation of *closo*-3-Et-3,1,2-$AlC_2B_9H_{11}$ (**1a**) was carried out in a single-step modification of the method described previously[2b] without isolation of the intermediate **2**. The carborane salt Na[*nido*-5,6-$C_2B_8H_{11}$] was prepared by deprotonation of *nido*-5,6-$C_2B_8H_{12}$[30] with NaH in diethyl ether followed by filtration and removal of solvent in vacuo. The reagent $AlEt_2Cl{\cdot}OEt_2$ was prepared by adding 1 molar equiv of OEt_2 to a stirred 0.5 M solution of $AlEt_2Cl$ in toluene. The insoluble reagent Tl[3,1,2-$TlC_2B_9H_{11}$] was prepared by a literature method.[9] Sodium hydride (Aldrich) and bis(triphenylphosphoranylidene)ammonium chloride ([$(Ph_3P)_2N$]Cl, Aldrich) were used as received. Triphenylphosphine (Aldrich) was recrystallized from absolute ethanol and dried in vacuo. Triethylphosphine (Alfa) was obtained in sealed ampules and was used without further purification. Gallium trichloride (Alfa) was sublimed in vacuo prior to use. Elemental analyses of Tl[**6**] were performed by Galbraith Laboratories, Knoxville, TN. The aluminacarboranes as a class cannot be analyzed well. Melting points were observed in sealed tubes and are uncorrected.

Spectral Data. NMR spectra were recorded on Bruker AF 200 (^{1}H, ^{13}C), WP 200 (^{1}H, ^{31}P, ^{13}C), WB 500 (^{11}B, ^{1}H; Southern California Regional Magnetic Resonance Facility), and AM 500 (^{11}B, ^{1}H, ^{13}C; UCLA) spectrometers, as well as on a JEOL FX 90Q (^{31}P) instrument. Chemical shift values for ^{11}B and ^{31}P NMR spectra were referenced relative to external $BF_3{\cdot}OEt_2$ and H_3PO_4, respectively. Chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced to $SiMe_4$ and measured with respect to residual protons in deuteriated solvents. Resonances observed upfield of the references were assigned negative chemical shift values in all cases. The ^{1}H and ^{11}B NMR spectral data for the compounds described herein are given in Tables V and VI, respectively. Infrared spectra were obtained as Nujol mulls or neat samples between NaCl plates and were recorded on a Beckman FT-1100 instrument. Infrared data for the compounds described herein are listed in Table VII. Electron impact mass spectra were obtained on an AEI Ltd. Model MS-902 sector-filled, double-focusing spectrometer, and xenon FAB mass spectra were obtained on an AEI Ltd. Model MS-9 spectrometer.

Syntheses. *endo*-10-{AlEt$(PEt_3)_2$}-7,8-$C_2B_9H_{11}$ (3). To 0.25 g (1.3 mmol) of **1a** and 3 mL of toluene in a Schlenk tube having a constriction was added 1.3 mL of PEt_3 (10.1 mmol). The mixture was freeze–pump–thaw-degassed on a vacuum line and sealed in vacuo. Slow cooling to −20 °C resulted in crystallization of **3**. The tube was opened in a glovebox, and the crystals were washed with *n*-pentane, resulting in 0.52 g (94%) of **3** (mp 28–31 °C). In the case of the NMR experiments, the same procedure was followed on a smaller scale, with use of sealed 5- and 10-mm NMR tubes. The reaction of **1a** with PEt_3 is quite rapid.

***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$_{11}$)] (4).** In a dry nitrogen-filled glovebox, a Carius tube was charged with 2.0 g of **1a** and 30 mL of toluene. The resulting solution was freeze–pump–thaw-degassed on a vacuum line and the tube sealed. The tube was partially immersed in an oil bath and heated at 85 °C for ca. 24 h to establish monomer–dimer equilibrium. The tube was then cooled and opened in a glovebox and the solution transferred to a vacuum sublimator with a magnetic spin bar. Solvent was removed in vacuo at room temperature to give a mixture of **1a** and **4**. The cold finger of the sublimator was then cooled to 0 °C, and **1** was sublimed from the mixture in vacuo at 80 °C with occasional stirring with the spin bar. The solid remaining after complete sublimation of **1a** (0.98 g, mp >300 °C) was nearly pure **4** and contained only a trace of **1a** as contaminant, as determined by subsequent IR and NMR analysis. In the case of the NMR experiments, samples of **1a** and deuteriated solvent were added to 5- and 10-mm NMR tubes in a glovebox and the tubes were sealed after freeze–pump–thaw degassing on a vacuum line.

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(39) Shriver, D. F. *The Manipulation of Air-Sensitive Compounds*; McGraw-Hill: New York, 1969.

[*commo*-3,3′-Al(3,1,2-AlC$_2$B$_9$H$_{11}$)$_2$]$^-$ ([5]$^-$). To a stirred suspension of 500 mg (0.92 mmol) of Tl[3,1,2-TlC$_2$B$_9$H$_{11}$] in 75 mL of toluene under argon was added 2.0 mL (2.0 mmol) of a 1.0 M solution of AlMe$_2$Cl in toluene. The suspended yellow Tl[3,1,2-TlC$_2$B$_9$H$_{11}$] immediately dissolved to produce a clear, colorless solution. Addition of 150 mL of *n*-heptane resulted in the precipitation of 220 mg of Tl[**5**]·2C$_7$H$_8$ (96%), which was isolated by Schlenk filtration as a white microcrystalline solid.

[*commo*-3,3′-Ga(3,1,2-GaC$_2$B$_9$H$_{11}$)$_2$]$^-$ ([6]$^-$). To a solution of GaCl$_3$ (325 mg, 1.85 mmol) in ca. 100 mL of toluene under argon was added 500 mg (0.92 mmol) of Tl[3,1,2-TlC$_2$B$_9$H$_{11}$]. The solution became homogeneous and colorless after stirring for 1 h. The product was isolated by fractional crystallization from toluene with use of heptane counter solvent. Product purity was monitored by infrared and mass spectroscopy noting the disappearance of Tl[GaCl$_4$]. When Tl[GaCl$_4$] was no longer observable, the product was washed with heptane, yielding 136 mg (55%) of Tl[**6**] as a white crystalline solid. Anal. Calcd for TlGaC$_4$B$_{18}$H$_{22}$: C, 8.92; H, 4.08; B, 36.12; Tl, 37.94; Ga, 12.94. Found: C, 8.06; H, 3.71; B, 35.20; Tl, 38.18; Ga, 13.20.

***nido*-6,9-(μ-AlEt(OEt$_2$))-6,9-C$_2$B$_8$H$_{10}$ (8).** To a stirred 0 °C suspension of 1.2 g (8.3 mmol) of freshly prepared Na[*nido*-5,6-C$_2$B$_8$H$_{11}$] in 200 mL of toluene in a 500-mL Schlenk flask was added 17.0 mL of a 0.5 M solution of AlEt$_2$Cl·OEt$_2$ (8.5 mmol). The resulting mixture was stirred at room temperature and then refluxed for 16 h. The mixture was cooled to room temperature, filtered through a medium glass frit to remove precipitated NaCl, and concentrated in vacuo. Addition of *n*-pentane resulted in separation of crude **8** as a pale yellow oil. Further purification was accomplished by distillation at 60 °C to a 0 °C U-trap under a running high vacuum to give 1.6 g (77%) of **8** as a colorless oil. Crystalline **8**·$^1/_2$C$_6$H$_6$ (mp 28–30 °C) was obtained by carefully layering a benzene solution of **8** with *n*-pentane.

***nido*-6,9-(μ-AlEt(OC$_4$H$_8$))-6,9-C$_2$B$_8$H$_{10}$ (9).** The same procedure was followed as in the synthesis of **8** with 1.0 g (6.9 mmol) of Na[*nido*-5,6-C$_2$B$_8$H$_{11}$] and 14.0 mL of a 0.5 M solution of AlEt$_2$Cl·C$_4$H$_8$O (7.0 mmol) to yield 1.27 g (74%) of purified **9** as an air-sensitive, colorless oil.

Na[Al(η^2-*nido*-6,9-C$_2$B$_8$H$_{10}$)$_2$] (Na[10]). The Na[*nido*-5,6-C$_2$B$_8$H$_{11}$] used in this experiment was ground to a fine powder in a glovebox and heated at 40 °C in vacuo for ca. 12 h to remove residual OEt$_2$. To a 0 °C suspension of 1.18 g (8.16 mmol) of Na[*nido*-5,6-C$_2$B$_8$H$_{11}$] in 200 mL of toluene in a 500-mL Schlenk flask was added 4.10 mL of a 1.0 M solution of AlEt$_2$Cl in hexane. The mixture was stirred at room temperature for 1 h and then refluxed for 16 h. The solution was cooled and filtered through a medium glass frit to remove precipitated NaCl. After the solution volume was reduced under vacuum, addition of 200 mL of *n*-pentane resulted in precipitation of Na[**10**]. Further purification by recrystallization from methylene chloride/*n*-pentane resulted in 0.98 g (81%) of microcrystalline Na[**10**] (mp >300 °C). Xe-FAB mass spectrum: parent ion observed *m/e* 271, [^{12}C$_4$^{11}B$_{16}$H$_{20}$^{27}Al]$^+$.

[(PPh$_3$)$_2$N][Al(η^2-*nido*-6,9-C$_2$B$_8$H$_{10}$)$_2$] ([(PPh$_3$)$_2$N][10]). To a suspension of 0.50 g (1.72 mmol) of Na[**10**] in 500 mL of methylene chloride under nitrogen was added 0.99 g (1.72 mmol) of [(PPh$_3$)$_2$N]Cl. After it was stirred for 24 h at room temperature, the mixture was filtered through a medium frit. The filtered solid was washed with three 75-mL portions of methylene chloride. Addition of *n*-heptane to the combined filtrate after the volume was reduced in vacuo resulted in 1.39 g (96%) of [(PPh$_3$)$_2$N][**10**] as a white, crystalline solid.

Na[Al(η^2-*nido*-2,7-C$_2$B$_6$H$_8$)$_2$] (Na[11]). All manipulations were carried out under an atmosphere of dry N$_2$. To a stirred suspension of 0.5 g of NaH in 50 mL of OEt$_2$ was slowly added a solution of 1.0 g (8.9 mmol) of *arachno*-1,3-C$_2$B$_7$H$_{13}$ in 50 mL of OEt$_2$, the evolved hydrogen being allowed to escape through a bubbler. After it was stirred for 15 min, the solution was filtered into a 500-mL Schlenk flask and the solvent removed in vacuo to yield solid Na[*arachno*-1,3-C$_2$B$_7$H$_{12}$] as the diethyl ether solvate. This solid was heated at 60 °C under running vacuum for ca. 6 h. Proton NMR data obtained for samples of carborane salt prepared in this manner indicated that this salt has the approximate formula Na[*arachno*-1,3-C$_2$B$_7$H$_{12}$]·OEt$_2$. To the flask containing this salt was added 200 mL of toluene followed by 4.5 mL (4.5 mmol) of a 1.0 M solution of AlEt$_2$Cl in hexane. The mixture was stirred for 1 h and then refluxed for 16 h. The solution was cooled and filtered to remove precipitated NaCl. Reduction of the filtrate volume in vacuo followed by addition of heptane resulted in precipitation of crude Na[**11**]. Further purification by three recrystallizations from toluene/heptane resulted in 0.46 g (42%) of Na[**11**] (mp >300 °C). Xe-FAB mass spectrum: parent ion observed *m/e* 223, [^{12}C$_4$^{11}B$_{12}$H$_{16}$^{27}Al]$^+$.

General Methods of Crystallographic Analyses. All data were collected on an automated diffractometer in the θ–2θ scan mode with Mo Kα radiation. Data for **3**, **4**, **8**·$^1/_2$C$_6$H$_6$, [(Ph$_3$P)$_2$N][**10**], and Na[**11**] were collected on a modified Picker FACS-1 diffractometer, and data for Tl[**5**]·$^2/_3$C$_7$H$_8$ and Tl[**6**] were collected on a Huber diffractometer. All calculations were performed by using the DEC VAX 11/750 computer of the J. D. McCullough Crystallographic Laboratory and the UCLA crystallographic programs listed in ref 40. Data were corrected for Lorentz and polarization effects. Tl[**5**]·$^2/_3$C$_7$H$_8$ and Tl[**6**] were also corrected for absorption. Structures of **3**, **4**, **8**·$^1/_2$C$_6$H$_6$, [(Ph$_3$P)$_2$N][**10**], and Na[**11**] were solved with use of statistical methods (MULTAN80, MAGEX, and SHELX76). Structures of Tl[**5**]·$^2/_3$C$_7$H$_8$ and Tl[**6**] were solved with use of heavy-atom methods. Remaining atoms were located by use of difference electron density maps. In the course of refinement all cage C and B atoms were initially assigned scattering factors for boron. After refinement, carboranyl carbon atom positions could be distinguished by their anomalously low temperature factors and by shorter interatomic distances. Reported R and R_w values are defined as $R = [\sum(|F_o| - |F_c|)/\sum|F_o|]$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2(F_o)$, and "goodness of fit" is defined by $[\sum w|F_o| - |F_c|)^2/(N_{obsd} - N_{variable})]^{1/2}$. Scattering factors for hydrogen were obtained from Stewart et al.,[41] and those for other atoms were taken from ref 42. Details of the individual data collections are given in Table VIII.

X-ray Analysis of 3. A colorless crystal obtained by slowly cooling a toluene solution of **3** was sealed in a capillary. Systematic absences were found for reflections $0k0$, $k = 2n + 1$, and $h0l$, $h + l = 2n + 1$. Unit cell parameters were determined from a least-squares fit of 19 accurately centered reflections (9.5° < 2θ < 20°). Three intense reflections (2,2,–7, 212, 224) were monitored every 97 reflections to check stability. Intensities of these reflections fluctuated only slightly, ca. ±6%, during the course of the experiment. Anisotropic thermal parameters were refined for all non-hydrogen atoms. All carboranyl H atoms were kept in located positions. All other hydrogen atoms were kept in calculated positions with assigned B values of 5 (carboranyl), 7 (CH$_2$), and 10 (CH$_3$) Å^2. Anomalous dispersion terms were applied to the scattering of P. A final difference electron density map was essentially featureless; the maximum and minimum peaks were ca. 0.3 e Å^{-3}.

X-ray Analysis of 4. Colorless parallelepipeds were grown from toluene/heptane. Data were collected for a 0.43 × 0.46 × 0.41 mm crystal sealed in a nitrogen-filled capillary. Intensities of standard reflections 283, 2,4,–3, and 0,2,–5 fluctuated a maximum of ±3% with decay less than 4% during the course of the experiment (48.5 h). Unit cell parameters were determined from a least-squares fit of 26 centered reflections (9.3° < 2θ < 20.3°). Systematic absences were found for reflections $0k0$, $k = 2n + 1$, and $h0l$, $h + l = 2n + 1$. Anisotropic thermal parameters were refined for all non-hydrogen atoms. All carboranyl H atoms were kept in located positions. All other H atoms were kept in calculated positions with assigned B values of 7 (carboranyl), 10 (CH$_2$), and 13 (CH$_3$) Å^2. A final difference electron density map was essentially featureless, with maximum peaks of 0.5 e Å^{-3}.

X-ray Analysis of Tl[5]·$^2/_3$C$_7$H$_8$. Crystals were grown from toluene/*n*-pentane. Data were collected for a clear, colorless 0.32

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(40) Programs: CARESS (Broach, Coppens, Becker, and Blessing), peak profile analysis, Lorentz and polarization corrections; ORFLS (Busing, Martin, and Levy), structure factor calculation and full-matrix least-squares refinement; MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declerq, and Woolfson), direct methods; SHELX76 (Sheldrick), structure analysis; MAGEX (Hull, Viterbo, Woolfson, Zhang), direct methods; ORTEP (Johnson), figure plotting.

(41) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(42) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table VIII. Details of Crystallographic Data Collections[a]

	3[b]	**4**[c]	Tl[**5**]·$^2/_3C_7H_8$[d]	Tl[**6**][e]	**8**·$^1/_2C_6H_6$[f]	[(PPh$_3$)$_2$N][**10**][g]	[Na][**11**][h]
temp/K	298	297	298	298	298	178	128
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$A\bar{1}$	$P2_1/c$	$P2_1$
a/Å	9.722 (3)	7.122 (2)	11.347 (2)	6.9564 (6)	13.964 (3)	16.378 (3)	10.035 (2)
b/Å	16.135 (4)	27.668 (8)	11.748 (2)	11.0466 (9)	15.966 (4)	18.781 (3)	12.433 (3)
c/Å	16.984 (5)	11.629 (3)	12.708 (2)	12.0287 (10)	8.550 (2)	14.806 (3)	11.690 (3)
α/deg			92.429 (6)	102.088 (2)	92.227 (8)		
β/deg	90.246 (9)	96.246 (5)	90.876 (6)	95.484 (2)	86.689 (7)	90.197 (5)	111.019 (7)
γ/deg			93.343 (5)	94.687 (3)	102.060 (8)		
V/Å^3	2652	2288	1689	894	1862	4554	1367
Z	4	4	3	2	4	4	4
ρ(calcd)/g cm^{-3}	1.54	1.10	1.64	2.0	1.03	1.18	1.19
μ/cm^{-1}	2.45	1.17	72.8	105.7	0.95	1.40	1.19
scan width/deg							
below Kα_1	1.3	1.3	1.3	1.3	1.3	1.2	1.6
above Kα_2	1.4	1.3	1.6	1.6	1.4	1.2	1.6
scan rate/deg min^{-1}	6	4.5	6	3	6	6	3
no. of unique rflns	5807	4013	4420	3145	3273	5909	2507
no. of obsd ($I > 3\sigma(I)$) rflns	3394	2137	1941	2733	2338	2128	2156
2θ(max)/deg	54	50	45	50	50	45	50
data collected	$h,k,\pm l$	$h,k,\pm l$	$h,\pm k,\pm l$	$h,\pm k,\pm l$	$h,\pm k,\pm l$	$h,k,\pm l$	$h,k,\pm l$
no. of params refined	253	253	215	283	190	303	260
R	0.064	0.065	0.057	0.041	0.061	0.078	0.049
R_w	0.082	0.075	0.064	0.054	0.081	0.088	0.059
GOF	2.46	2.39	1.57	2.03	2.85	2.0	2.08

[a] Conditions: radiation (graphite monochromator), Mo Kα; wavelength, 0.7107 Å. [b] $C_{14}H_{41}B_9AlP_2$. [c] $C_8H_{32}B_{18}Al_2$. [d] $C_{18}H_{38}B_{18}AlTl$. [e] $C_4H_{22}B_{18}GaTl$. [f] $C_{14}H_{31}OB_8Al$. [g] $C_{40}H_{50}B_{18}NP_2Al$. [h] $C_4H_{16}B_6AlNa$.

× 0.13 × 0.13 mm parallelepiped (with normals to 100, 0,−1,0, and 001, respectively) sealed in an argon-filled capillary. Unit cell parameters were determined from a least-squares fit of 25 accurately centered reflections (8.0° < 2θ < 18.1°). Three intense reflections (1,−2,1, 202, 220) were monitored every 97 reflections. Intensities of these reflections fluctuated a maximum of ±3% with no decay during the course of the experiment. Absorption corrections were applied (maximum, minimum, average 0.6603, 0.4659, 0.5957). Anisotropic thermal parameters were refined for Tl, Al, and the phenyl carbon atoms of toluene. Toluene was refined as two rigid groups, C_6H_5 and CH_3. Carboranyl H atoms were included in located positions with U = 0.09 (carboranyl), 0.2 (phenyl), and 0.35 (methyl) Å^2. One of the three crystallographically different $[Al(C_2B_9H_{11})_2]^-$ anions was disordered in such a way that only one atom could be assigned as C. The two adjacent atoms of the bonding face were treated as half C and half B. Such a disorder is fairly common for metallacarborane dicarbollide complexes.[43] Anomalous dispersion terms were applied to the scattering of Tl. The largest peaks on the final difference electron density map were in the vicinity of Tl and were ±0.3 e Å^{-3}.

X-ray Analysis of Tl[6]. Colorless crystals were grown from a toluene/mesitylene solution of Tl[**6**] by layering with heptane. Data were collected for a 0.08 × 0.15 × 0.32 mm parallelepiped (with normals to 010, 001, and 1,1,−1) sealed in an argon-filled glass capillary. Unit cell parameters were determined from a least-squares fit of 24 accurately centered reflections (10.1° < 2θ < 20.4°). Three intense reflections (004, 1,−3,1, 221) were monitored every 97 reflections. Intensities of reflections decayed less than 7% during the course of the experiment (56.4-h exposure). A ψ-scan absorption correction was applied. Anisotropic thermal parameters were refined for all non-hydrogen atoms. Positional parameters were refined for all hydrogen atoms. The thermal parameter B for all H atoms has the assigned value 4.0 Å^2. Anomalous dispersion terms were applied to the scattering of Tl and Ga. The larger peaks on a difference electron density map, 1.2–0.6 e Å^{-3}, were all near Tl.

X-ray Analysis of 8·$^1/_2C_6H_6$. Crystals were grown by layering a benzene solution of **8** with *n*-pentane. Data were collected for a colorless crystal of irregular shape sealed in a nitrogen-filled capillary. Unit cell parameters were determined from a least-squares fit of 18 centered reflections (9.3° < 2θ < 20.0°). Three intense reflections (1,0,−2, 131, and 213) were monitored every 97 reflections. Intensities of these reflections decayed less than 2% over the course of the experiment (57.1 h). Anisotropic thermal parameters were refined for all non-hydrogen atoms. Hydrogen atoms were kept in located positions, with B = 5 (carboranyl, CH_2), 10 (CH_3 ether), and 15 (CH_3 ethyl) Å^2.

X-ray Analysis of [(PPh$_3$)$_2$N][10]. Crystals were grown from toluene/*n*-pentane. Data were collected from a crystal fragment in an argon-filled capillary. Unit cell parameters were determined from a least-squares fit of 31 accurately centered reflections (9.7° < 2θ < 20.0°). Three intense reflections (2,−3,2, −2,−3,2, 2,5,−1) were monitored every 97 reflections and showed no decay during the course of the experiment (49.8 h). Systematic absences were found for $0k0$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$. All phenyl groups of the $[(Ph_3P)_2N]^+$ cation were constrained to be rigid, with C–C = 1.395 Å, C–H = 1.0 Å, and 120° angles; thermal parameters for H were assigned to be U = 0.063 Å^2. The anion is disordered. In order to model this disorder, which corresponds to two anions with occupancies 0.53 and 0.47 rotated 90° with respect to one another about an axis through the two C_2B_8 moieties and Al, all like distances were constrained to be equal with a single thermal parameter for each type. For example, distances Al–C(6), Al–C(6′), Al–C(9), Al–C(9′), Al(2″)–C(6C), Al(2″)–C(6D), Al(2″)–C(9C), and Al(2″)–C(9D) were constrained to be equal. Only 29 of 40 carboranyl H atoms were located. The largest peaks on a final difference electron density map were in the vicinity of the cation and were less than 0.5 e Å^{-3}. With the exception of N, P, and C of two phenyl groups, all non-hydrogen atoms were refined isotropically (SHELX76). Anomalous dispersion terms were applied to the scattering of P.

X-ray Analysis of Na[11]. Crystals were grown from toluene/*n*-pentane. Data were collected on a colorless crystal fragment in a sealed argon-filled capillary. Unit cell parameters were determined from a least-squares fit of 22 accurately centered reflections (9.6° < 2θ < 20.6°). Systematic absences were found for $0k0$, $k = 2n + 1$. Three intense reflections (312, 2,2,−1, 3,−3,−1) were monitored every 97 reflections. Intensities of these reflections fluctuated a maximum of ±3%, and there was no decay during the course of the experiment (47.1 h). Only Al and Na were refined anisotropically. Only positional parameters were refined for H (assigned B = 2.36 Å^2). Anomalous dispersion terms were included for Na. The largest peak on a final difference electron density map corresponded to 0.8 e Å^{-3}.

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(43) For example, see: Hardy, G. E.; Callahan, K. P.; Strouse, C. E.; Hawthorne, M. F. *Acta Crystallogr.* **1976**, *B32*, 264.

gional NMR Facility (Grant No. CHE-79-16324). We also thank Andrea Owyeung for the illustrations.

Supplementary Material Available: Tables of positional and thermal parameters and complete interatomic distances and angles for 3–6, 8, 10, and 11 (62 pages); tables of observed and calculated structure factors (81 pages). Ordering information is given on any current masthead page. Tables of crystallographic data for the compounds 4,[3] $\mathrm{Tl}[5]\cdot{}^2/_3\mathrm{C_7H_8}$,[7] Tl[6],[8] $8\cdot{}^1/_2\mathrm{C_6H_6}$,[4] $[(\mathrm{PPh_3})_2\mathrm{N}][10]$,[5] and Na[11][6] were supplied with the now-published initial preliminary communications pertaining to these structures.

Molecular Structures and Reactivities of Digermiranes and Azadigermiridines

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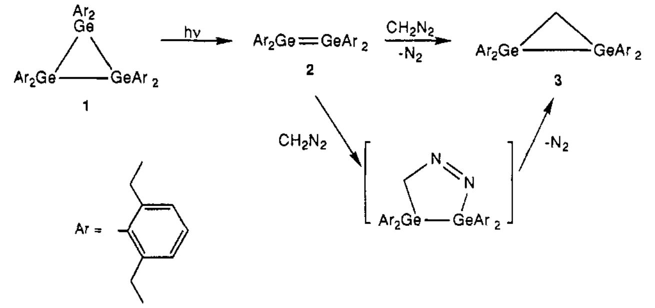
Reaction of tetrakis(2,6-diethylphenyl)digermene (2) with diazomethane produces 1,1,2,2-tetrakis(2,6-diethylphenyl)digermirane (3). The photolysis of 3 with a high-pressure mercury lamp yields germene 13 and germylene 14. The digermirane 3 reacts with pyridine *N*-oxide, sulfur, and selenium to yield the insertion products of O, S, and Se into the germanium–germanium bond. 2,2,3,3-Tetrakis(2,6-diethylphenyl)-1-phenylazadigermiridine (5) is also prepared by the reaction of 2 with phenyl azide. The structures of the digermirane 3 and the azadigermiridine 5 have been determined by X-ray crystal analyses. Both 3 and 5 have relatively short germanium–germanium bond distances of 2.379 (1) Å and nearly planar arrangements of $\mathrm{C_{Ar}}$, $\mathrm{C_{Ar}}$, and Ge atoms around each germanium.

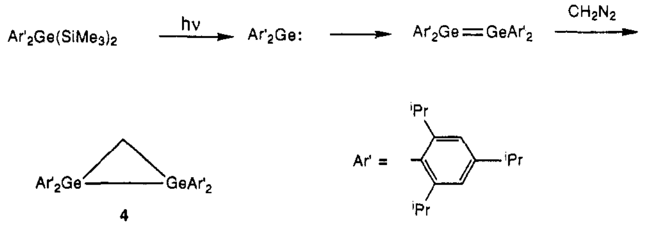
Introduction

In recent years the chemistry of metal group 14 three-membered heterocycles has progressed rapidly, owing to the synthesis of a variety of small-ring systems involving group 14 elements.[2-10] Especially, the synthesis of small-ring systems involving a germanium–germanium bond has received considerable attention because of interest in the reactivity of the reactive germanium–germanium bonds in the ring.[7-10] Recently, we prepared thia- and selenadigermiranes by the reactions of digermene with sulfur and selenium, demonstrating that this method was useful for the preparation of three-membered cyclogermanes containing a germanium–germanium bond.[6a,8] Masamune prepared three-membered Ge–Ge ring compounds from the cycloaddition reaction of the Ge=Ge double bond, but the chemical reactivities are not well-known.[10a] In this paper we report the first synthesis of digermiranes and azadigermiridines from the reactions of digermenes with diazomethane and phenyl azide, including the crystal structures of a digermirane and an azadigermiridine and some of the chemical properties of these.[9,10a]

Scheme I



Scheme II



Results and Discussion

Preparation of Digermiranes and Azadigermiridines. Irradiation of a cyclohexane solution of hexakis(2,6-diethylphenyl)cyclotrigermane (1)[7b,c] at room temperature with a low-pressure mercury lamp afforded tetrakis(2,6-diethylphenyl)digermene (2) in good yields, as

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