Alkylaluminum and Alkylgallium Derivatives of $(3)\text{-}1,2\text{-}B_9C_2H_{13}$

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Abstract: The reaction of trialkylaluminum and -gallium with $(3)\text{-}1,2\text{-}B_9C_2H_{13}$ has been shown to produce two series of derivatives: $1,2\text{-}B_9C_2H_{12}MR_2$ and $1,2\text{-}B_9C_2H_{11}MR$ ($M = Al$, $R = CH_3$, C_2H_5; $M = Ga$, $R = C_2H_5$). The former have been shown to be tautomeric nido compounds containing bridging MR_2 groups, presumably attached through B–H–M bridges. The latter series of derivatives is composed of closo compounds, substituted homologs of the icosahedral $1,2\text{-}B_{10}C_2H_{12}$ carborane. The thermal rearrangement of the latter compounds to the corresponding 1,7 derivatives, degradation, catalytic properties, and derivative chemistry are discussed.

Since the discovery by Wiesboeck and Hawthorne[1,2] of $(3)\text{-}1,2\text{-}$ and $(3)\text{-}1,7\text{-}B_9C_2H_{12}^-$ and their derived $B_9C_2H_{11}^{2-}$ ions, a large number of transition metal[3] and main-group[4] derivatives of these ions have been reported. In these derivatives the icosahedral geometry of the original carborane, $1,2\text{-}B_{10}C_2H_{12}$ or $1,7\text{-}B_{10}C_2H_{12}$, was restored by an insertion reaction into the open face of the $(3)\text{-}1,2\text{-}$ or $(3)\text{-}1,7\text{-}B_9C_2H_{11}^{2-}$ ion. Using this route a boron atom has also been inserted, thus restoring the original dicarba-*closo*-dodecaborane(12) structure.[5] Another synthetic route to this type of derivative has recently been discovered which employed the acidic carborane $(3)\text{-}1,2\text{-}B_9C_2H_{13}$.[1] Dimethylberyllium etherate reacted with the two acidic protons in the open pentagonal face of this derivative liberating 2 mol of methane. The derivative, 3-trimethylamino-3-beryl-1,2-dicarba-*closo*-dodecaborane(12), was isolated upon addition of trimethylamine.[6,7]

Using this synthetic route we recently reported a series of alkyl-substituted aluminocarboranes and the crystallographic characterization of two of them, $1,2\text{-}B_9C_2H_{11}Al(C_2H_5)$[8] and $1,2\text{-}B_9C_2H_{12}Al(CH_3)_2$.[9] We now wish to report the preparation and characterization of these and related compounds in greater detail and the results of similar syntheses of the gallium homologs.

Results and Discussion

Reaction of Aluminum and Gallium Trialkyls with $(3)\text{-}1,2\text{-}B_9C_2H_{13}$. Triethylaluminum and $(3)\text{-}1,2\text{-}B_9C_2H_{13}$ reacted under mild conditions in benzene solution. Ethane (1 mol equiv) was liberated, producing 7,8-μ-diethylalumino-1,2-dicarba-*nido*-undecaborane(13) (I) in high yield. Trimethylaluminum and triethylgallium both reacted similarly and formed the 7,8-μ-dimethylalumino and 7,8-μ-diethylgallo derivatives II and III, respectively. Melting points, yields, and analyses for the complexes are given in Table I.

Table I. Melting Points, Yields, and Elemental Analyses of the Aluminum and Gallium Complexes

	Compound	Mp, °C[a]	Yield, %	Analyses, %[b]				
I	$1,2\text{-}B_9C_2H_{12}Al(C_2H_5)_2$	34.5–35.5	79	Calcd:	B, 44.53;	C, 32.98;	H, 10.15;	Al, 12.35
				Found:	B, 41.36;	C, 33.90;	H, 11.92;	Al, 10.88
II	$1,2\text{-}B_9C_2H_{12}Al(CH_3)_2$	120–122	83	Calcd:	B, 51.09;	C, 25.22;	H, 9.53;	Al, 14.17
				Found:	B, 48.52;	C, 24.98;	H, 9.52;	Al, 15.42
III	$1,2\text{-}B_9C_2H_{12}Ga(C_2H_5)_2$		81	Calcd:	B, 37.24;	C, 27.58;	H, 8.49;	Ga, 26.69
				Found:	B, 40.88;	C, 25.59;	H, 8.40;	Ga, 27.55
IV	$1,2\text{-}B_9C_2H_{11}Al(C_2H_5)$	97–99	72	Calcd:	B, 51.63;	C, 25.49;	H, 8.56;	Al, 14.32
				Found:	B, 51.14;	C, 25.52;	H, 8.84;	Al, 14.30
V	$1,2\text{-}B_9C_2H_{11}Al(CH_3)$	97–100	9	Calcd:	B, 55.78;	C, 20.66;	H, 8.09;	Al, 15.74
				Found:	B, 52.07;	C, 20.89;	H, 8.51;	Al, 13.14
VI	$1,2\text{-}B_9C_2H_{11}Ga(C_2H_5)$	114–115	80	Calcd:	B, 42.09;	C, 20.78;	H, 6.98;	Ga, 30.16
				Found:	B, 40.22;	C, 21.28;	H, 7.10;	Ga, 30.26
VII	$1,7\text{-}B_9C_2H_{11}Al(C_2H_5)$	100–102	85	Calcd:	B, 51.63;	C, 25.49;	H, 8.56;	Al, 14.32
				Found:	B, 53.40;	C, 24.39;	H, 8.49;	Al, 13.51
IX	$B_9C_2H_{11}Al(C_2H_5)\cdot 2THF$	119–120	46	Calcd:	B, 29.28;	C, 43.30;	H, 9.62;	Al, 8.10
				Found:	B, 28.16;	C, 42.13;	H, 9.93;	Al, 7.48
	$(3)\text{-}1,2\text{-}B_9C_2H_{13}$	110 dec	88					

[a] Melting points are uncorrected in a sealed capillary. [b] Because of the extreme air sensitivity of these compounds, good analyses were difficult to obtain.

A single-crystal X-ray diffraction study of II has recently been completed.[9] The structure determination was carried out with a single crystal of the enantiomer illustrated in Figure 1, and the aluminum atom was found to reside in a bridging position. Because of the great similarity of the various spectra of I, II, and III, an analogous structure is assumed for all three.

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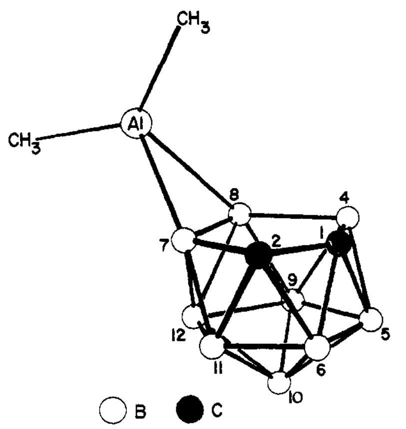

Figure 1. Schematic representation of the reported[9] crystallographic structure of 7,8-μ-dimethylalumino-1,2-dicarba-*nido*-undecaborane(13), II.

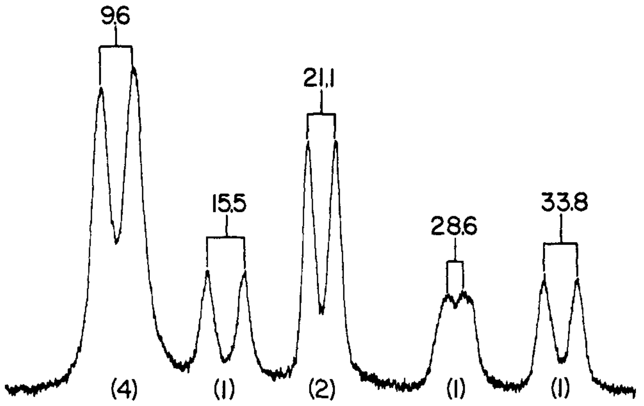

Figure 2. ^{11}B nmr spectrum (80 Mcps) of II in CH_2Cl_2 solution at 25°; chemical shifts in parts per million from $BF_3 \cdot O(C_2H_5)_2$ are indicated.

Of particular interest in the structure of II is the fact that the aluminum atom resides considerably outside of the cage face, near the positions normally occupied by terminal H atoms on B_7 and B_8 in (3)-1,2-$B_9C_2H_{13}$ or (3)-1,2-$B_9C_2H_{12}^-$. The dihedral angle between the planes B_7–Al–B_8 and B_7–B_8–B_4–C_1–C_2 is 129.5°. Also, the angle B_7–Al–B_8 is very small (47°) for a tetrahedral geometry about aluminum and the Al–B_7 and Al–B_8 bond lengths are somewhat long, 2.33 and 2.28 ± 0.02 Å, respectively. These considerations together with other data (*vide infra*) lead us to conclude that the aluminum atom is bound to B_7 and B_8 by two hydrogen bridge bonds similar to those present in $Al(BH_4)_3$, in which the Al–B bond length was reported to be 2.14 Å.[10,11] These two bridging H atoms probably occupy positions near the original terminal hydrogen atoms on B_7 and B_8 in (3)-1,2-$B_9C_2H_{13}$. If one assumes an idealized geometry in which the two bridging H atoms are equidistant between the aluminum and boron atoms and the H–Al–H angle is tetrahedral, 109°, the Al–H and B–H distances would be 1.34 Å. The corresponding distances in $Al(BH_4)_3$ are 1.80 and 1.28 Å, respectively.

Although the structure determination of II failed to locate the hydrogen atom positions, it is clear that six hydrogen atoms are associated with the cage face. The 250-Mcps proton nuclear magnetic resonance spectrum of II at 25° in toluene solution exhibited a broad resonance at τ 13.6 (half-band width 171 Hz) which integrated correctly for one proton when compared to the resonances of the two cage C–H protons and six methyl protons[12] (Table III). We have assigned this signal to a bridging H atom between B_4 and B_8. No proton nmr evidence for the proposed Al–H–B bridge H atoms was observed at this temperature.

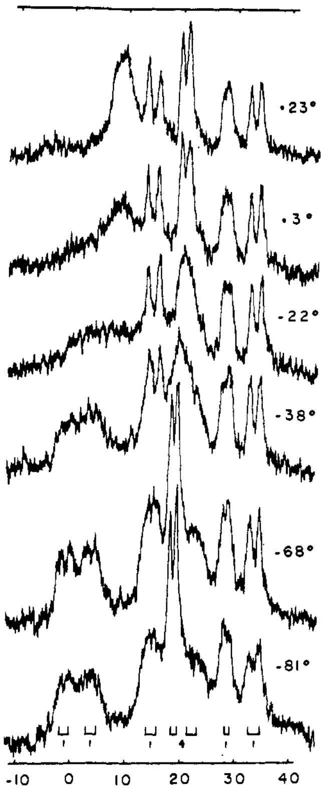

Figure 3. ^{11}B nmr spectra (80 Mcps) of II in toluene-*n*-hexane solution; temperatures and chemical shifts in parts per million from $BF_3 \cdot O(C_2H_5)_2$ are indicated.

The 80-Mcps ^{11}B nmr spectra of I, II, and III all exhibited a temperature dependence and the averaged spectrum obtained from a concentrated solution of II in methylene chloride at 25° is presented in Figure 2. This spectrum is essentially identical with that obtained from a toluene or benzene solution at 75°, with the observed difference in tautomeric rates perhaps being due to a weak association of the aromatic solvents with the aluminum atom.

The low-temperature spectra of II were obtained from a dilute sample in a solvent consisting of one part toluene and two parts *n*-hexane to minimize viscosity effects (Figure 3 and Table II).

We presently believe that the tautomeric process involves the exchange of bridging positions between the dialkylaluminum (or gallium) moiety and proton H_b as shown in Figure 4. This scheme would account for the temperature-independent τ 13.6 resonance of H_b in II with no exchange with protons H_4, H_7, or H_8 and in ad-

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(12) For comparison the bridging protons in (3)-1,2-$B_9C_2H_{13}$ and Cs^+(3)-1,2-$B_9C_2H_{12}^-$ gave a broad resonance at τ 12.3 (2 H) and 12.8 (1 H), respectively. The terminal protons occur as a series of overlapping quartets centered at τ 7, with a width of approximately 4 ppm.

Table II. Boron Nmr Spectra (80 Mcps) of the Aluminum and Gallium Complexes

Compound	Conditions	Chemical shift, δ^a	J, Hz	Rel intensity
I 1,2-$B_9C_2H_{12}Al(C_2H_5)_2$		7.7	138	3.8
		12.8	160	1.0
	d, e	18.0	107	2.0
		26.2	59	1.0
		31.7	142	1.0
II 1,2-$B_9C_2H_{12}Al(CH_3)_2$		9.6	134	4.0
		15.5	170	1.1
	e, f	21.1	97	2.0
		28.6	58	1.0
		33.8	143	1.0
		−1.1	150	1.2
		3.5	140	1.1
		15.5[b]		1.2
	g	18.7[b]	90	4.1
		22.4[b]		
		28.6	60	1.0
		33.8	140	1.0
III 1,2-$B_9C_2H_{12}Ga(C_2H_5)_2$		9.8	134	4.1
		15.4	145	1.0
	d, e	19.7	109	2.0
		28.7	74	1.0
		33.2	141	1.0
IV 1,2-$B_9C_2H_{11}Al(C_2H_5)$		7.3	146	2.0
		13.5[b]	150	1.0
	d	15.7[b]	150	2.9
		17.8[b]	152	1.9
		24.0	152	1.0
V 1,2-$B_9C_2H_{11}Al(CH_3)$		8.5	154	2.1
		14.7[b]	150	1.0
	d	17.0[b]	151	2.8
		19.2[b]	147	2.0
		25.5	151	1.0
VI 1,2-$B_9C_2H_{11}Ga(C_2H_5)$		9.5	140	2.0
		17.1[b]	150	3.0
	d	19.2[b]	145	3.0
		23.0	143	1.0
VII 1,7-$B_9C_2H_{11}Al(C_2H_5)$		8.6	154	2.0
		15.5[b]	149	3.1
	d	18.5[b]	151	2.0
		20.6[b]	146	1.1
		25.9	146	1.0
1,2-$B_9C_2H_{13}$		−3.0	160	2.0
		5.3	145	2.0
	d	17.6[b]	167	2.0
		28.1[c]	140, 48	3.0

[a] Parts per million of centers of doublets relative to external $BF_3 \cdot O(C_2H_5)_2$, in benzene solution. [b] Overlapping doublets. [c] Doublet of doublets. [d] Benzene solution, 25°. [e] Averaged spectrum of tautomeric species. [f] Toluene solution, 75°, or CH_2Cl_2 solution, 25°. [g] 1:2 toluene:*n*-hexane solution, −65°.

dition provide a rationale of the observed ^{11}B nmr spectra.

The higher temperature averaged spectrum of II (Figure 2) would thus be rationalized as follows: the 33.8-ppm signal is assigned most probably to B_6 in close proximity to C_1 and C_2, with a normal terminal coupling constant (143 Hz); the 28.6-ppm signal is assigned to B_8, with only bridge-proton coupling (58 Hz) observed; the 21.1-ppm signal is assigned to B_4 and B_7, with a proton coupling constant (97 Hz) intermediate between the bridge and normal terminal values; the 15.5-ppm signal is assigned to B_{10}, with a large terminal coupling constant (170 Hz); and the 9.6-ppm signal is assigned to B_5, B_9, B_{11}, and B_{12}, with normal terminal proton coupling constants (average 134 Hz).

On cooling the sample (Figure 3) the 33.8-, 28.6-, and 15.5-ppm signals appeared to remain unchanged except for viscosity effects. The 21.1- and 9.6-ppm signals broaden and reemerge. The 9.6-ppm signal reappears at −1.1 and 3.5 ppm (one boron atom each) and in the 17–19-ppm region (two boron atoms), theoretically centered about 18.0 ppm. The 21.1-ppm signal also reappears in this region, perhaps associated with the unusually sharp signal at 18.7 ppm (J = 90 Hz). This resonance could perhaps be assigned to the B, shown as B_7 in Figure 1, coupled only to one Al–H–B bridging H atom. These assignments are only postulates at the present time. However, given the assumed relationship between the 9.6-, −1.1-, and 3.5-ppm signals and the observed coalescence temperature of −22 ± 5°, it is possible to calculate the rate and corresponding free energy $\Delta F^{\ddagger}$.[13] These were found to be 3.0×10^3 sec^{-1} at −22° and 10.6 ± 0.5 kcal/mol, respectively.

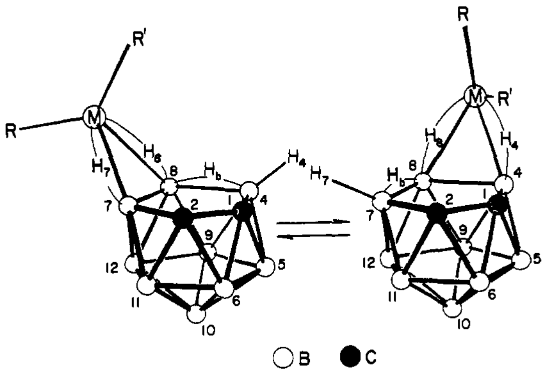

Figure 4. Proposed mechanism for the tautomeric process in the *nido*-dialkylaluminum and -gallium complexes I, II, and III.

The proton nmr spectra of I, II, and III gave typical resonances for the carborane C–H, aluminum alkyl, and gallium alkyl protons (Table III).

Upon cooling the samples in deuteriotoluene solution, no changes in the proton resonances except for viscosity broadening were observed down to −75°. Under these conditions the bridging and terminal alkyl resonances of trialkylaluminum dimers have been resolved, the chemical shift differences being about 1 ppm.[14] This observation, together with the fact that II is monomeric in the crystalline state leads us to believe that I, II, and III are monomeric in solution. However, when II was cooled to −84°, it was possible to observe the splitting of the τ 10.23 methyl resonance into two methyl signals at τ 10.20 and 10.26. The coalescence temperature was observed to be −75° ± 5°. This corresponds to a rate of 3.7×10^1 sec^{-1} and a free energy of activation, $\Delta F^{\ddagger}$, of 10.0 ± 0.5 kcal/mol, in good agreement with that calculated from the ^{11}B nmr spectra.

We believe the two methyl signals represent the methyl groups exo and endo relative to the cage face, respectively. The carborane C–H resonance was too broad at these temperatures to observe a possible chemical shift difference due to the asymmetric position of the dialkylaluminum group.

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Table III. Proton Nmr Data of the Aluminum and Gallium Complexes

	Compound	Feature	Chemical shift, τ	Rel intensity	Assignment
I	$1,2\text{-}B_9C_2H_{12}Al(C_2H_5)_2$	Br s	7.39[a]	1.8	Two carborane C–H protons
		“Triplet” of A_2B_3 pattern	8.82	6.0	Six methyl protons
		“Quartet” of A_2B_3 pattern $J_{AB} = 7.5$ cps	9.61	3.9	Four methylene protons
II	$1,2\text{-}B_9C_2H_{12}Al(CH_3)_2$	Br s	7.44[a]	1.8	Two carborane C–H protons
		Sh s	10.23[e]	6.0	Six methyl protons
		Br s	13.6[f]	1.0	One bridging B–H–B proton
III	$1,2\text{-}B_9C_2H_{12}Ga(C_2H_5)_2$	Br	7.32[a]	2.0	Two carborane C–H protons
		Overlapped “triplet” and “quartet” of A_2B_3 pattern	8.80[b]	10.1	Ten methyl and methylene protons
IV	$1,2\text{-}B_9C_2H_{11}Al(C_2H_5)$	Br s	7.90[a]	1.7	Two carborane C–H protons
		“Triplet” of A_2B_3 pattern	8.95	3.0	Three methyl protons
		“Quartet” of A_2B_3 pattern $J_{AB} = 7.5$ cps	9.66	1.8	Two methylene protons
V	$1,2\text{-}B_9C_2H_{11}Al(CH_3)$	Br s	8.09[a]	2.0	Two carborane C–H protons
		Sh s	10.42	2.8	Three methyl protons
VI	$1,2\text{-}B_9C_2H_{11}Ga(C_2H_5)$	Br s	7.80[a]	2.0	Two carborane C–H protons
		Sh s	8.92[c]	5.0	Five methyl and methylene protons
VII	$1,7\text{-}B_9C_2H_{11}Al(C_2H_5)$	Br s	8.23[a]	1.8	Two carborane C–H protons
		“Triplet” of A_2B_3 pattern	8.87	3.0	Three methyl protons
		“Quartet” of A_2B_3 pattern $J_{AB} = 8$ cps	9.53	1.9	Two methylene protons
VIII	$1,7\text{-}B_9C_2H_{11}Ga(C_2H_5)$	Br s	8.28[a]	2.0	Two carborane C–H protons
		Sh s	8.95	11[d]	Methyl and methylene protons
	$(3)\text{-}1,2\text{-}B_9C_2H_{13}$	Br s	7.33[a]	2.0	Two carborane C–H protons
		Br s	12.3[f]	2.0	Two bridging B–H–B protons

[a] Benzene solution. [b] At 250 Mcps this band was resolved into a “triplet” and “quartet” of an A_2B_3 pattern at τ 8.71 and 8.90, respectively. [c] At 250 Mcps this band was resolved into an A_2B_3 pattern in which the chemical shift difference was on the order of magnitude of the coupling constant. [d] This band is overlapped with one from the methyl and methylene protons of VI in the mixture of VIII and VI; see text. [e] At −84° in deuteriotoluene solution this band was split into two resonances at τ 10.20 and 10.26; see text. [f] Observed in benzene solution at 250 Mcps; see text.

Table IV. Infrared Spectra of the Aluminum and Gallium Complexes

	Compound	Absorptions, cm^{-1}
I	$1,2\text{-}B_9C_2H_{12}Al(C_2H_5)_2$	*a* 3053 vw, 2943 s, 2898 m, 2864 s, 2775 vw, 2730 vw, 2554 vs, 2511 sh, 2475 sh, 2368 s, 2288 sh, 2215 sh, 1461 m, 1446 m, 1397 m, 1374 m, 1261 m, 1222 m, 1191 m, 1115 w, 1082 m, 1035 w, 1018 s, 984 s, 949 s, 926 s, 883 s, 860 m, 842 w, 790 w, 773 w,748 m, 740 m, 726 w, 707 m, 672 vs, 608 s
II	$1,2\text{-}B_9C_2H_{12}Al(CH_3)_2$	*b* 2719 vw, 2571 vs, 2520 vs, 2472 s, 2379 s, 2283 m, 2212 w, 1851 vw, 1294 vw, 1256 w, 1187 s, 1119 w, 1079 w, 1033 m, 1014 s, 970 m, 946 m, 921 m, 912 sh, 902 sh, 879 m, 854 w, 841 sh, 784 sh, 751 sh, 732 s, 715 vs, 672 sh, 634 m, 616 m
		c 3037 m, 2933 m
III	$1,2\text{-}B_9C_2H_{12}Ga(C_2H_5)_2$	*a* 3052 m, 2949 vs, 2930 sh, 2899 vs, 2869 vs, 2736 w, 2573 vs, 2543 vs, 2506 sh, 2466 sh, 2388 s, 2299 s, 2158 w, 1867 w, 1705 w, 1556 w, 1475 sh, 1457 s, 1446 s, 1409 s, 1376 s, 1261 s, 1230 m, 1196 s, 1190 sh, 1082 s, 1016 vs, 1001 vs, 962 w, 945 s, 922 m, 878 s, 850 m, 840 sh, 788 m, 748 s, 737 w, 720 w, 701 w, 661 vs, 629 s, 610 w, 600 w, 575 vs
IV	$1,2\text{-}B_9C_2H_{11}Al(C_2H_5)$	*b* 3033 s, 2737 vw, 2621 s, 2568 vs, 2532 m, 2496 vs, 1990 vw, 1922 vw, 1222 w, 1197 w, 1155 w, 1148 m, 1091 m, 1047 m, 1021 s, 1003 s, 993 m, 968 s, 950 w, 916 w, 900 s, 877 m, 862 s, 774 m, 746 w, 730 m, 705 m, 688 vs, 625 s, 620 s
		c 3025 s, 2935 m, 2890 m, 2864 m, 1452 m, 1443 m, 1388 m, 1374 m
V	$1,2\text{-}B_9C_2H_{11}Al(CH_3)$	*b* 3019 s, 2610 s, 2580 vs, 2528 vs, 2095 vw, 1992 vw, 1934 vw, 1296 w, 1211 w, 1188 w, 1144 w, 1088 m, 1042 w, 1016 s, 1000 s, 964 m, 912 m, 897 s, 876 m, 861 s, 767 w, 753 w, 738 m, 725 m, 715 vs, 696 s, 681 s
VI	$1,2\text{-}B_9C_2H_{11}Ga(C_2H_5)$	*b* 3044 s, 2611 s, 2560 vs, 2528 vs, 2506 vs, 2462 sh, 2088 w, 1927 w, 1407 m, 1234 w, 1224 w, 1209 sh, 1197 m, 1187 sh, 1146 m, 1085 m, 1043 s, 1012 s, 996 m, 963 m, 942 w, 929 w, 910 w, 891 m, 876 w, 856 m, 845 w, 775 w, 765 w, 742 m, 726 m, 701 m, 659 s, 636 m
		c 2969 sh, 2949 m, 2925 m, 2898 sh, 2468 m, 1445 m, 1376 w
VII	$1,7\text{-}B_9C_2H_{11}Al(C_2H_5)$	*b* 2555 vs, 2530 vs, 1982 vw, 1396 w, 1221 w, 1190 w, 1154 w, 1101 m, 1049 s, 995 s, 972 s, 911 w, 890 s, 867 m, 854 w, 776 s, 747 w, 723 m, 701 s, 683 s, 640 m, 620 s
		c 3002 w, 2937 m, 2924 m, 2893 m, 2860 m, 1454 m, 1444 sh, 1394 m, 1373 m
IX	$B_9C_2H_{11}Al(C_2H_5)\cdot 2THF$	*b* 2726 vw, 2572 s, 2503 vs, 2480 sh, 2432 sh, 1420 w, 1349 m, 1323 w, 1298 w, 1250 m, 1228 vw, 1187 sh, 1175 m, 1088 w, 1040 m, 997 s, 970 w, 956 w, 916 m, 890 w, 857 s, 837 vs, 792 w, 745 w, 732 w, 689 m, 637 s, 624 s, 604 s, 579 s
		c 3009 sh, 2974 m, 2943 m, 2905 m, 2870 m, 1472 sh, 1458 sh, 1440 m
	$(3)\text{-}1,2\text{-}B_9C_2H_{13}$	*b* 3055 w, 2587 vs, 2550 sh, 1961 w, 1855 vw, 1300 vw, 1263 m, 1190 w, 1165 w, 1150 w, 1088 s, 1028 s, 966 s, 938 m, 927 m, 909 m, 885 s, 826 w, 808 w, 777 m, 753 vs, 719 w, 699 w

[a] Neat film. [b] Nujol mull. [c] Fluorolube mull.

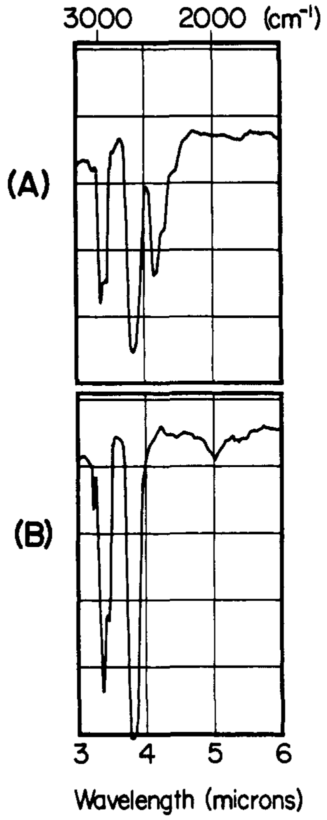

Figure 5. Infrared spectra of I (A) and (3)-1,2-$B_9C_2H_{13}$ (B) in the 3–6-μ range, Nujol mulls.

At −84° the bridging proton signal at τ 13.6 had sharpened to a half-band width of 52 Hz. No evidence of the proposed Al–H–B bridging protons was observed in this region at this temperature. However, these resonances could have been obscured in the complex terminal B–H signals at lower field or unobserved due to coupling with the aluminum nucleus. For example, Ogg and Ray[15] have reported the proton nmr spectra of $Al(BH_4)_3$. The Al–H–B bridging proton signal had a half-band width of 11.3 ppm at 30 Mcps and a chemical shift of about τ 10.

Compounds I, II, and III all exhibit normal strong infrared bands (Table IV) near 2550 cm^{-1} assigned to the terminal B–H stretching modes. In addition, they display rather intense bands near 2400 cm^{-1} which are intermediate in value between B–H terminal stretching values and the B–H–Al stretching mode, 2154 cm^{-1}, reported for $Al(BH_4)_3$.[11] Figure 5 presents representative infrared spectra of this region for both I and (3)-1,2-$B_9C_2H_{13}$. The B–H–B stretching absorption is found at 1961 cm^{-1} in (3)-1,2-$B_9C_2H_{13}$.[1]

Thermal Closing to the Icosahedral Skeleton. Further heating of I in dry benzene solution slowly released a second molar equivalent of ethane and produced IV, 3-ethyl-3-alumino-1,2-dicarba-*closo*-dodecaborane(12) in good yield. Figure 6 presents the previously reported[8] structure of IV. The aluminum atom is coordinated to all five atoms in the cage face, the mean distances being Al–B, 2.137 ± 0.008 and Al–C, 2.173 ± 0.007 Å.

Compounds II and III were similarly closed forming 3-methyl-3-alumino and 3-ethyl-3-gallo derivatives V and VI. The gallium homolog VI was formed under essentially the same conditions as IV. The formation of V required more severe conditions which resulted in lower yields.

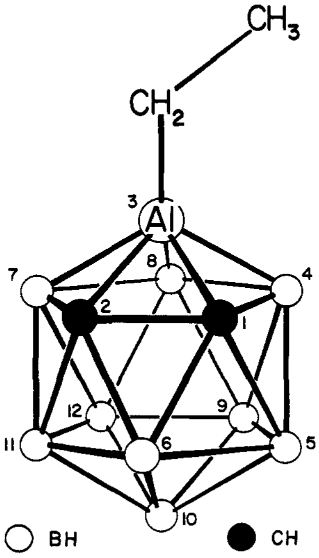

Figure 6. Schematic representation of the reported[8] structure of 3-ethyl-3-alumino-1,2-dicarba-*closo*-dodecaborane(12), IV.

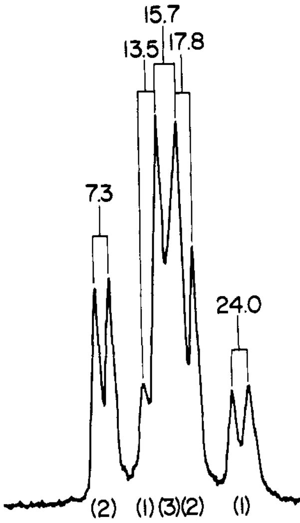

Figure 7. ^{11}B nmr spectrum of IV in benzene solution at 80 Mcps, chemical shifts in parts per million from $BF_3 \cdot O(C_2H_5)_2$ are indicated.

IV, V, and VI may be considered to be analogs of 1,2-$B_{10}C_2H_{12}$ in which a BH group neighboring the two CH groups has been replaced by a heavier group IIIa alkyl-substituted metal. In addition, VI is analogous to the proposed structure of $CH_3GaC_2B_4H_6$ prepared from trimethylgallium and 2,3-dicarba-*nido*-hexaborane(8) by Grimes and Rademaker.[16]

The infrared spectra of these compounds show normal terminal B–H stretching modes similar to those of 1,2-$B_{10}C_2H_{12}$. The absence of B–H–Al bridge H absorptions observed in the nido complexes is indicative of the formation of the closo species.

The ^{11}B nmr spectra exhibited resonances with typical terminal B–H coupling constants; Figure 7

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(15) R. A. Ogg, Jr., and J. D. Ray, *Discuss. Faraday Soc.*, No. 19, 239 (1955).

(16) R. N. Grimes and W. J. Rademaker, *J. Amer. Chem. Soc.*, 91, 6498 (1969).

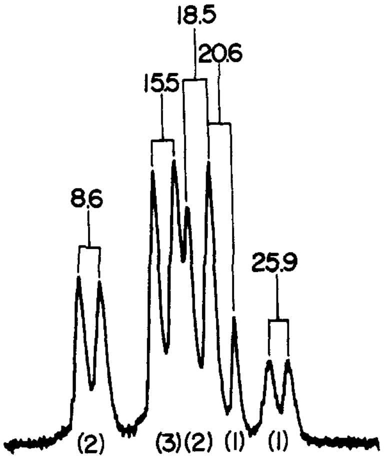

Figure 8. ^{11}B nmr spectrum of VII in benzene solution at 80 Mcps; chemical shifts in parts per million from $BF_3 \cdot O(C_2H_5)_2$ are indicated.

illustrates that of IV. We are unable to assign these resonances with certainty at this time.

Table III presents the proton nmr spectra of these compounds, and normal methyl and ethyl resonances for these groups bound to aluminum and gallium were observed along with typical carborane C–H resonances. Upon cage closure, I → IV, II → V, and III → VI, the carborane C–H resonances were observed to shift to higher field by about 0.5 ppm. A corresponding shift of about 0.13 ppm was observed in the alkyl resonances. We attribute this observation to a greater electron density in the closed cage as compared to the open system. The proton nmr spectra of IV and V were investigated in toluene solution at temperatures down to −95° and no changes in the spectra, except for viscosity broadening, were observed. Thus we believe that these compounds are monomeric in solution as well as in the crystalline state.

Thermal Rearrangement of the Icosahedral Skeleton. Compound IV underwent thermal rearrangement in the vapor phase at elevated temperatures. Sublimation of IV through a glass-wool-filled hot tube at 350° under high vacuum produced only unchanged starting material, but at 410° pure 3-ethyl-3-alumino-1,7-dicarba-*closo*-dodecaborane(12) (VII) (*vide infra*) was produced in high yield. We believe this compound to have the same structure as IV with C–H groups at positions 1 and 7. The use of quartz-wool tube packing and temperatures up to 650° produced no new isomers; only smaller yields of VII were obtained due to associated decomposition reactions.

Similarly, the gallium homolog VI was recovered unchanged at 350°. At 400° a mixture of products was obtained which proved to be 9% unchanged VI, 74% $B_9C_2H_{11}$, and 7% of a compound which we believe to be 3-ethyl-3-gallo-1,7-dicarba-*closo*-dodecaborane(12) (VIII) (*vide infra*). Fractional sublimation of this mixture separated $B_9C_2H_{11}$ which was identified by its characteristic infrared spectrum.[17] The remaining mixture of VI and VIII was not separated; however, VIII was tentatively identified by comparison of the proton nmr spectra of this mixture with those of the aluminum homologs IV and VII.

At temperatures above 400°, lower yields of $\mathbf{B_9C_2H_{11}}$ containing trace amounts of VI and VIII were recovered. It is interesting to note that no trace of $B_9C_2H_{11}$ was found in the aluminum product VII under these conditions.

The selective formation of the 1,7 isomer is similar in behavior to 1,2-$B_{10}C_2H_{12}$,[18] which rearranges to 1,7-$B_{10}C_2H_{12}$ at 400–500°, but is in contrast to the behavior of the metal-substituted derivatives Ni[π-(3)-1,2-B_9H_9-$C_2(CH_3)_2$]$_2$ and Pd[π-(3)-1,2-$B_9H_9C_2(CH_3)_2$]$_2$.[19]

The latter series of compounds was found to undergo rearrangements in which the products contained carbon atoms in the 1 and 6 positions.

The infrared and proton nmr spectra of the 1,7 isomers were similar to those of 1,2 isomers. There was a shift of about 0.4 ppm to higher field in the carborane C–H resonances upon separation of these centers by a B–H group. Similar results were reported for the anions (3)-1,2- and (3)-1,7-$B_9C_2H_{12}^{2-}$.

The ^{11}B nmr spectrum of VII is presented in Figure 8.

Mass spectral data were obtained for compounds I, II, III, IV, VI, and VII (Table V). The observed parent ion patterns were in accord with predicted values of *m/e*.

Table V. Mass Spectral Data of Some Aluminum and Gallium Complexes

	Compound	Isotopic species	Mass	*m/e*[a]	*m/e*[b]
I	1,2-$B_9C_2H_{12}Al(C_2H_5)_2$	$^{11}B_9{}^{12}C_6{}^{1}H_{22}{}^{27}Al_1$	220	221	217
II	1,2-$B_9C_2H_{12}Al(CH_3)_2$	$^{11}B_9{}^{12}C_4{}^{1}H_{18}{}^{27}Al_1$	192	193	191
III	1,2-$B_9C_2H_{12}Ga(C_2H_5)_2$	$^{11}B_9{}^{12}C_6{}^{1}H_{22}{}^{69}Ga_1$	262	264	261
IV	1,2-$B_9C_2H_{11}Al(C_2H_5)$	$^{11}B_9{}^{12}C_4{}^{1}H_{16}{}^{27}Al_1$	190	191	189
VI	1,2-$B_9C_2H_{11}Ga(C_2H_5)$	$^{11}B_9{}^{12}C_4{}^{1}H_{16}{}^{69}Ga_1$	232	234	231
VII	1,7-$B_9C_2H_{11}Al(C_2H_5)$	$^{11}B_9{}^{12}C_4{}^{1}H_{16}{}^{27}Al_1$	190	191	189

[a] Largest *m/e* observed in parent-ion pattern. [b] Most intense *m/e* peak observed in parent-ion pattern.

Aqueous Degradation of the Aluminum and Gallium Complexes in Air. Since these compounds explosively hydrolyzed upon contact with water, they were first exposed to moist air for several hours by slow diffusion. After adding water to the resulting product the anionic species present were precipitated with trimethylammonium chloride and recrystallized. Compounds I, II, III, IV, V, and VI were found to yield (3)-1,2-$B_9C_2H_{12}^{-}(CH_3)_3NH^{+}$ and compound VII gave (3)-1,7-$B_9C_2H_{12}^{-}(CH_3)_3NH^{+}$, which were identified by their characteristic infrared spectra.[2]

This reactivity contrasts markedly with that of B-substituted carboranes. It has been postulated that the removal of the phenyl-substituted boron atom from the cage by a "frontside" attack of hydroxide ion upon 3-phenyl-1,2-$B_{10}C_2H_{11}$ is blocked by the phenyl group.[5] Apparently the availability of aluminum and gallium d orbitals provides a pathway for nucleophilic attack.

Further Reactions of the ***nido-*** **and** ***closo*****-Alkylaluminumcarboranes.** When IV was dissolved in tetrahydrofuran (THF) and excess solvent removed, a microcrystalline product was obtained and identified as 1,2-$B_9C_2H_{11}Al(C_2H_5) \cdot 2THF$ (IX). This compound was also prepared from (3)-1,2-$B_9C_2H_{11}^{2-}$ and

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(17) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 90, 869 (1968).

(18) S. Papetti and T. L. Heying, *ibid.*, **86**, 1874 (1964).

(19) L. F. Warren, Jr., and M. F. Hawthorne, *ibid.*, **92**, 1157 (1970).

$Al(C_2H_5)Cl_2$ in THF, a synthesis independently discovered and reported by Mikhailov and Potapova.[20] The ability of IV to form a THF adduct parallels the behavior of trialkylaluminums.[21] The reaction of IV with stronger Lewis bases led only to degradation reactions from which (3)-1,2-$B_9C_2H_{12}^-$ was isolated.

The reaction of IV with anhydrous HCl in benzene solution regenerated the starting nido carborane, (3)-1,2-$B_9C_2H_{13}$, in quantitative yield.

Attempts at reaction of I with a second molar equivalent of (3)-1,2-$B_9C_2H_{13}$ in benzene solution failed to produce any product in which two carborane cages were coordinated to the same aluminum atom. It was possible to observe the thermal conversion of I to IV in the presence of excess (3)-1,2-$B_9C_2H_{13}$, which was subsequently recovered unchanged.

The addition of either I or IV to a solution of $TiCl_4$ in *n*-heptane produced dark red precipitates similar to those described by Ziegler for various trialkylaluminum compounds.[22] Subsequent exposure of these solutions to ethylene catalytically produced high-molecular-weight polyethylene at ambient temperature and pressure. Bestian and Clauss[23] have reported that methyltitanium trichloride will undergo a slow growth reaction with ethylene in polar inert solvents at low temperatures. Recently, Giannini and Zucchini[24] have reported that benzyltitanium compounds will polymerize ethylene. Thus it would appear that I and IV, as well as trialkylaluminum, may generate titanium alkyl groups which could be responsible for the observed polymerization catalysis.

Experimental Section

Physical Measurements. Infrared spectra were obtained on a Perkin-Elmer Model 421 spectrophotometer. Proton nmr spectra were obtained on a Varian Associates Model A-60D spectrometer at 60 Mcps and on a 250-Mcps instrument constructed by Professor F. A. L. Anet of this department. ^{11}B nmr spectra were obtained at 80 Mcps on the latter instrument. Mass spectra were obtained on an Associated Electrical Industries Model MS-9 spectrometer. Reported melting points are uncorrected. Elemental analyses were made by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. All reactions were carried out under an inert atmosphere.

Materials. Trimethyl- and triethylaluminum were obtained from Texas Alkyls Inc., Houston, Texas; no further purification was necessary. Benzene, toluene, and *n*-hexane were freshly distilled from calcium hydride under nitrogen and tetrahydrofuran from lithium aluminum hydride. Triethylgallium was prepared as reported by Eisch.[25]

Preparation of (3)-1,2-$B_9C_2H_{13}$. The preparation of (3)-1,2-$B_9C_2H_{13}$ has been described previously.[1,17] The most convenient preparation, however, consisted of merely dissolving the dry potassium salt of (3)-1,2-$B_9C_2H_{12}^-$,[2] in excess 85% phosphoric acid under nitrogen at room temperature. The product was then extracted three times from the acid with dry benzene. The benzene extracts were combined and evaporated to dryness, leaving the crude product which was then sublimed at 40° under high vacuum, yield 88.0%.

Preparation of the Aluminum and Gallium Complexes. (A) **1,2-$B_9C_2H_{12}Al(C_2H_5)_2$ (I).** In a typical preparation 3.20 g (0.0238 mol) of freshly sublimed (3)-1,2-$B_9C_2H_{13}$ was dissolved in 60 ml of dry benzene under nitrogen. This solution was stirred at room temperature while another solution consisting of 2.72 g (0.0238 mole) of triethylaluminum in 50 ml of dry benzene was slowly added. After stirring for 1 hr 305 cm³ of ethane had been liberated. The solution was then warmed to 50° for 1 hr. Upon cooling to room temperature the total volume of ethane liberated was 490 cm³ (0.0228 mol).[26] The benzene was then pumped off, leaving an essentially quantitative yield of colorless, microcrystalline crude product. Recrystallization from dry, cold *n*-hexane gave large colorless crystals of pure product, yield 4.09 g, 79.0%. Compound I could be sublimed under high vacuum at 50°.

(B) **1,2-$B_9C_2H_{12}Al(CH_3)_2$ (II).** In the same manner as described for the preparation of I, 3.90 g (0.0290 mol) of (3)-1,2-$B_9C_2H_{13}$ in 80 ml of benzene was allowed to react with 2.09 g (0.0290 mole) of trimethylaluminum in 80 ml of benzene. Very little methane was liberated at room temperature. The solution was warmed to 50° and stirred for 3 hr, during which time 620 cm³ (0.0276 mol) of methane was released. The solution was then filtered through a medium frit under nitrogen, pumped down to 40-ml volume, and chilled. The product was obtained as small clear crystals after decanting the mother liquor and rinsing with *n*-hexane, yield 4.59 g, 83%. II could be sublimed at 50° under high vacuum.

(C) **1,2-$B_9C_2H_{12}Ga(C_2H_5)_2$ (III).** Using the procedure described for the preparation of I, 5.77 g (0.0430 mol) of (3)-1,2-$B_9C_2H_{13}$ in 70 ml of benzene was allowed to react with 6.73 g (0.0430 mol) of triethylgallium in 50 ml of benzene. After heating and stirring the solution at 50° for 1 hr, 820 cm³ (0.0366 mol) of ethane was released. The benzene was removed leaving a colorless heavy oil. Attempts to crystallize the product failed and the oil was then sublimed at 50° (10 μ), yield 9.15 g, 81.3%.

(D) **1,2-$B_9C_2H_{11}Al(C_2H_5)$ (IV).** A 5.00-g (0.0229 mol) sample of I was dissolved in 20 ml of dry benzene under nitrogen and heated at 79° for 25 hr. During this time 485 cm³ (0.0216 mol) of ethane was released. The solution was then cooled to room temperature and the benzene pumped off, leaving an essentially quantitative yield of clear, microcrystalline crude product. This was then dissolved in a little dry benzene, filtered through a medium frit under nitrogen, and diluted with *n*-hexane. Upon cooling the solution, the product was obtained as clear, medium-size crystals, yield 3.11 g, 72.0%. It was also possible to convert I to IV by heating the neat melted liquid I. However, the yields were lower than those obtained in benzene solution. It was possible to sublime IV under high vacuum at 80°.

(E) **1,2-$B_9C_2H_{11}Al(CH_3)$ (V).** A 4.96-g (0.0261 mol) sample of II was dissolved in 80 ml of dry toluene under nitrogen. This solution was heated at 110° for 103 hr and the progress of the conversion was monitored periodically by nmr spectroscopy. Gas evolution exceeded the theoretical amount due to associated decomposition. The solution was then pumped free of toluene and the product sublimed at 90° (10 μ), yield 0.40 g, 8.8%.

(F) **1,2-$B_9C_2H_{11}Ga(C_2H_5)$ (VI).** In a manner analogous to the preparation of IV, 8.18 g (0.0314 mol) of III was dissolved in 50 ml of benzene and heated at 79° for 76 hr. The progress of the conversion was monitored by nmr spectroscopy. The benzene was removed leaving a colorless, microcrystalline product which was rinsed with *n*-hexane and sublimed at 90° (10 μ), yield 5.77 g, 79.5%.

(G) **1,7-$B_9C_2H_{11}Al(C_2H_5)$ (VII).** A 1.29-g sample of IV was placed in an apparatus consisting of a 50-ml quartz flask joined to a 20-cm long, 2-cm diameter quartz tube fitted with a cold finger condenser at the other end. The tube was next filled with dry glass wool under nitrogen and the apparatus evacuated to 20 μ. The tube was first heated to 410° and then the flask and sample were heated to 120–130°. After several hours, the product was obtained as a white sublimate on the cold finger, yield 1.09 g, 84.5%.

(H) **1,7-$B_9C_2H_{11}Ga(C_2H_5)$ (VIII).** Using the same apparatus and method described for the preparation of VII, 0.70 g (0.0030 mol) of VI was sublimed through glass wool at 400°. White sublimate (0.41 g) was collected. According to proton nmr investigation, this product proved to be 74% $B_9C_2H_{11}$, 9% unchanged VI, and 7% of what we assign to be VIII, analogous to VII. It was possible to remove the $B_9C_2H_{11}$ by fractional sublimation at 30° (20 μ). This compound was then identified by its Nujol infrared spectrum.[17] The separation of the mixture of VI and VIII was not achieved.

(I) **1,2-$B_9C_2H_{11}Al(C_2H_5)$. 2THF(IX).** Compound IV was dissolved in dry tetrahydrofuran under nitrogen and the excess THF pumped off under high vacuum. A Nujol mull of the microcrystal-

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line product was made and the infrared spectrum taken. IX was made as reported[20] from $Al(C_2H_5)Cl_2$ and $(3)\text{-}1,2\text{-}B_9C_2H_{11}^{2-}$ in THF, yield 46.0%. A Nujol infrared spectrum of this product was found to be identical with that obtained from the THF adduct of IV.

Polymerization of Ethylene. Ziegler-type catalysts were prepared from compounds I and IV in a manner similar to that originally described for triethylaluminum.[21] Solutions were made under nitrogen of 0.50 g of I in 50 ml of dry heptane and 0.50 g of IV in 20 ml of dry benzene mixed with 30 ml of heptane. To these solutions was added 0.50 ml of $TiCl_4$, which immediately produced dark red-brown precipitates. These mixtures were then evacuated to the solvent vapor pressures and exposed to dry ethylene gas with stirring. Over several hours the mixtures became warm and viscous as ethylene was periodically added to maintain 1 atm of pressure. Finally they were cooled and hydrolyzed with 2-propanol; the polyethylene was filtered off and washed with methanol and water. After 6 hr of exposure to ethylene gas at 1 atm, 3.5 g of white, amorphous polyethylene had been produced. An infrared spectrum of a pressed disk confirmed its identity. In both cases it was possible to isolate $(3)\text{-}1,2\text{-}B_9C_2H_{12}^{-}N(CH_3)_3H^+$ from the hydrolyzed catalyst upon addition of trimethylammonium chloride.[2]

Acknowledgment. The authors wish to express their gratitude to Professor F. A. L. Anet and Dr. Craig Bradley of this department for the 250-Mcps proton and the 80-Mcps boron nmr spectra and to the Office of Naval Research for support of this research.

Effects of Solvent on the Rate and Mechanism of Exchange of Methyl Groups in the Systems Dimethylcadmium, Dimethylzinc–Trimethylindium, and Dimethylcadmium–Trimethylgallium Determined by Proton Magnetic Resonance Spectroscopy

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Received February 8, 1971

Abstract: The self-exchange of $Cd(CH_3)_2$ in diethyl ether, the exchange of $Cd(CH_3)_2$ with $Ga(CH_3)_3$ in cyclopentane and in toluene, and the exchange of $Zn(CH_3)_2$ with $In(CH_3)_3$ in diethyl ether and in triethylamine have been investigated. The activation energies and rate constants for each of these systems have been determined. These data show that the rate of reaction is dependent on the coordinating ability of the solvent and the nature of the metal atom. Strongly coordinating solvents have been shown to enhance the exchange rate between derivatives of group II metals, but decrease the exchange rate when one of the species is from group III. These effects are discussed in detail.

The exchange of ligands between alkyl derivatives of group II metals and between group II and group III metals has been under investigation for sometime. These studies have shown that "rapid" self-exchange occurs in dimethylcadmium[2,3] and in divinyl- and methylvinylcadmium.[4] They have also shown that rapid exchange of alkyl groups occurs between cadmium and zinc[3,5] and between zinc or cadmium and magnesium derivatives.[6] It has also been suggested that self-exchange occurs in zinc derivatives, as evidenced by lack of ^{13}C coupling across the C–Zn–C system[7] and by the appearance of an AX_4 spectrum in diallylzinc.[8] Exchange has been observed under a variety of conditions for magnesium derivatives.[9] Several research groups have demonstrated that groups such as alkoxide and halide,[2a] as well as the studies already cited on unsaturated organic derivatives,[4,8,10] tend to catalyze exchange in these systems and permit, in some cases, establishment of equilibria similar to the Schlenk equilibrium observed in Grignard reagents.[11]

Studies have been reported on the exchange between group II and group III derivatives, with the emphasis placed on the reactions of aluminum alkyls.[2a,3,12] These studies are limited, however, in the sense that the dominant feature is the stability of the bridge bond in aluminum trimethyl, which governs the rate of reaction. Limited studies have been reported on the exchange of other group III derivatives with group II compounds,

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