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BRIDGE INSERTION REACTIONS OF THE 2,3-$C_2B_4H_7^-$ ION WITH ALUMINUM, GALLIUM AND TRANSITION METAL REAGENTS

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Summary

The reaction of lithium or sodium salts of the 2,3-$C_2B_4H_7^-$ anion with organometallic reagents of aluminum, gallium, rhodium, gold and mercury effects insertion of the metal atom into a bridging position on the base of the pyramidal carborane cage, with the metal apparently linked to the cage by a B—M—B three-center, two-electron bond. μ-Dimethylaluminum-2,3-*nido*-dicarbahexaborane(8) is extremely unstable in solution or in the liquid phase with respect to decomposition to 2,3-$C_2B_4H_8$, but in the gas phase forms $CH_3AlC_2B_4H_6$. The gallium-bridged analog is thermally stable but reacts readily with HCl to generate $C_2B_4H_8$ and $(CH_3)_2GaCl$; however, under no conditions studied did this material rearrange to the previously characterized *closo*-gallacarborane, 1-CH_3-1,2,3-$GaC_2B_4H_6$. The compounds μ-$[(C_6H_5)_3P]_3RhC_2B_4H_7$ and μ-$[(C_6H_5)_3P]AuC_2B_4H_7$ were prepared and characterized as moderately air-sensitive crystalline solids, and a partially characterized, unstable material believed to be μ-$C_6H_5HgC_2B_4H_7$ was obtained.

Introduction

The *nido*-carborane 2,3-$C_2B_4H_8$ [dicarbahexaborane(8)] is easily bridge-deprotonated by reaction with hydride ion, generating the 2,3-$C_2B_4H_7^-$ anion [1]. This ion has one remaining bridge proton on its pentagonal base, but the "bare" B—B bond on the base is highly reactive toward electrophilic reagents which can accept a pair of electrons and form bridge-substituted products containing a three-center, two-electron B—M—B bond as illustrated in Fig. 1. Bridge insertions of this type have been demonstrated with a variety of silicon, germanium, tin and lead reagents on the parent $C_2B_4H_7^-$ species [2-4], and with silicon, germanium and boron reagents on the *C,C'*-$(CH_3)_2C_2B_4H_5^-$

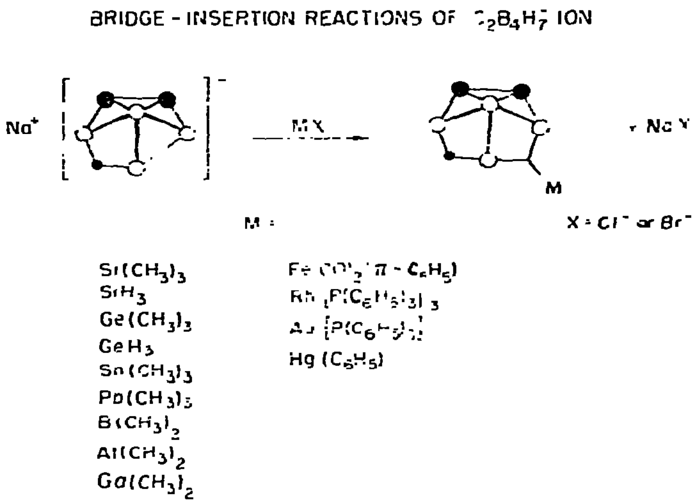


Fig. 1. Schematic diagram of $C_2B_4H_7^-$ bridge-insertion reactions, including those previously reported (see text). Open circles are BH groups and large solid circles are CH, except for the $B(CH_3)_2$-bridged species in which the solid circles represent C-CH_3. The bridged structure of the $Al(CH_3)_2$ compound is assumed but has not been confirmed; bridge-substitution in the other species is indicated from ^{11}B NMR data.

ion [5, 6]. In addition, an iron-bridged species, μ-$[(\eta\text{-}C_5H_5)Fe(CO)_2]C_2B_4H_7$ has been prepared and converted photolytically to closed polyhedral ferracarboranes by the loss of two mol equivalents of CO [7, 8]. However, bridge insertions of $C_2B_4H_7^-$ with metals other than iron and the Group IV elements have not previously been described, and it was of particular interest to determine whether the insertion of transition metals into a bridging position is a generally applicable technique. In this report we summarize our findings on reactions of the $C_2B_4H_7^-$ ion with reagents of aluminum, gallium, rhodium, mercury and gold, and compare the results with earlier data.

Results and discussion

Aluminum and gallium derivatives

Attempts to effect reactions of trimethylaluminum, triethylaluminum, and dimethylaluminum chloride with the sodium salt of $C_2B_4H_7^-$ in tetrahydrofuran (THF), solutions of which are conveniently prepared [1-4], led to extensive polymer formation which was evidently induced by the solvent (in a control experiment, $(CH_3)_3Al$ and THF readily formed a solid polymer). Accordingly, a suspension of the lithium salt [2] in n-hexane was treated with dimethylchloroalane, forming a clear, slightly volatile liquid which was characterized as $[(CH_3)_2Al]C_2B_4H_7$ (I) from its electron impact and chemical ionization mass spectra. In the liquid phase or in solution, this material proved

$$LiC_2B_4H_7 + (CH_3)_2AlCl \xrightarrow[0^\circ,\ 3\ h]{C_6H_{14}} \underset{(I)}{[(CH_3)_2Al]C_2B_4H_7} + LiCl$$

highly unstable with respect to decomposition to $C_2B_4H_8$ and $[HAl(CH_3)_2]_2$, and NMR spectra were not obtained. In the absence of ^{11}B NMR data the position of aluminum attachment to the cage could not be confirmed, but bridge substitution is probable in view of the precedent established in the previously cited reactions of $C_2B_4H_7^-$ or its dimethyl derivative with Si, Ge, Sn, Pb, B, and Fe reagents. Spontaneous rearrangement of an initially formed μ-$[(CH_3)_2Al]C_2B_4H_7$ to a terminally *B*-substituted species is possible but unlikely since the facile conversion of I to $C_2B_4H_8$ is typical of a bridged, rather than a terminally-attached, derivative [4].

The extreme instability of I in dried CS_2, THF, ether or hydrocarbon solvents, or in neat liquid form, prevented all but the most cursory examination of its chemistry. Pyrolysis of I at 100° in the vapor phase produced a small amount of a more volatile compound, II, whose infrared and mass spectra are consistent with a *closo*-$CH_3AlC_2B_4H_6$ species analogous to the previously characterized 1-CH_3-1,2,3-$GaC_2B_4H_6$ [9, 10]. The aluminum compound, however, is far less stable than the gallium analog, and like I decomposed rapidly as a neat liquid or in solution, yielding $C_2B_4H_8$ and the dimer of CH_3AlH_2. Both I and II are stable indefinitely in the gas phase at ambient temperature.

The reaction of dimethylchlorogallane with sodium dicarbahexaborate in THF produced the expected gallium-bridged species μ-$[(CH_3)_2Ga]C_2B_4H_7$ (III) as a slightly volatile clear liquid which was retained in a —12° trap on vacuum fractionation. The mass spectrum displays a typical 4-boron pattern and a cutoff at *m/e* 161 corresponding to the $CH_3GaC_2B_4H_7^+$ ion with a loss of one methyl group from the parent species, and an intensity pattern corresponding to that calculated for a GaB_4 species based on natural isotope distribution [9, 10]. The ^{11}B NMR spectrum consists of two doublets in a 3/1 area ratio, confirming that the $(CH_3)_2Ga$ group is bridge-bonded (see Experimental section). The expected non-equivalence of the basal borons is not apparent from the ^{11}B spectrum, a phenomenon frequently observed in both bridge- and terminally-substituted $C_2B_4H_8$ derivatives [2-8].

The pyrolysis of III was expected to generate the known [9, 10] compound *closo*-1-CH_3-1,2,3-$GaC_2B_4H_6$, but this was not observed, although the *closo* species is evident during electron-impact mass spectrometry of III. Heating III at 100° in the vapor phase and in CS_2 solution produced mainly solids and $C_2B_4H_8$, while ultraviolet irradiation of III gave only nonvolatile solid products. The pyrolysis in CS_2 solution was carefully monitored at intervals via its ^{11}B NMR spectrum but no evidence of 1-CH_3-1,2,3-$GaC_2B_4H_6$ was detected. Since the latter *closo* compound is thermally quite stable (and moreover forms readily from $C_2B_4H_8$ and $(CH_3)_3Ga$ at 215° in the vapor phase [9,10]) the failure of III to convert to the *closo* species is not explainable on the basis of relative thermodynamic stability. Kinetic factors which favor the formation of solid polymer from III undoubtedly play an important role.

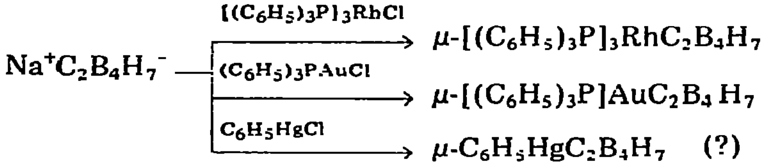
The treatment of III with hydrogen chloride readily produced $C_2B_4H_8$, analogous to the behavior of the μ-$(CH_3)_3MC_2B_4H_7$ species [4] in

$$\mu\text{-}(CH_3)_2GaC_2B_4H_7 + HCl \rightarrow C_2B_4H_8 + (CH_3)_2GaCl$$

which M = Si, Ge, Sn or Pb. The rapid reaction of the gallium-bridged compound, however, is more reminiscent of the tin and lead derivatives than the germanium and silicon analogs whose interaction with HCl is sluggish [4].

Transition metal-bridged derivatives

The reaction of $(\eta\text{-}C_5H_5)Fe(CO)_2I$ with $C_2B_4H_7^-$ ion to generate $\mu\text{-}[(\eta\text{-}C_5H_5)Fe(CO)_2]C_2B_4H_7$, mentioned earlier, suggested that the insertion of transition metals into a bridging location on the carborane cage might be a general reaction with suitable attacking groups. Accordingly, reactions of $C_2B_4H_7^-$ with several commercially available transition metal organometallic reagents containing ionic halide were examined, as summarized below.



$$Na^+C_2B_4H_7^- \xrightarrow{[(C_6H_5)_3P]_3RhCl} \mu\text{-}[(C_6H_5)_3P]_3RhC_2B_4H_7$$
$$Na^+C_2B_4H_7^- \xrightarrow{(C_6H_5)_3PAuCl} \mu\text{-}[(C_6H_5)_3P]AuC_2B_4H_7$$
$$Na^+C_2B_4H_7^- \xrightarrow{C_6H_5HgCl} \mu\text{-}C_6H_5HgC_2B_4H_7 \quad (?)$$

Each reaction was conducted at room temperature in THF solution and gave the desired bridge-substituted species, as indicated by the absence of singlets (which would indicate terminal attachment of the metal group) in the ^{11}B NMR spectrum. The yellow rhodium compound, obtained in approximately 10% yield, is moderately air-sensitive but survives brief exposure to the atmosphere. The gold derivative, a red solid which also exhibited some sensitivity to air, was isolated in 60% yield. A probable phenylmercury-bridged species was obtained as a yellowish-white solid which decomposed in air, releasing elemental mercury.

The air-sensitivity of all of the known metal-bridged $C_2B_4H_8$ derivatives, including the previously reported iron, germanium, tin and lead species and the compounds reported herein, is attributed to the reactivity of the B—M—B unit with water vapor. In the compounds of the Group III and IV elements the main boron product obtained on exposure to atmospheric H_2O is $C_2B_4H_8$, indicating a pronounced tendency for the bridging group to be replaced by a hydrogen atom.

The bridged derivatives of $C_2B_4H_8$ are structural analogs of transition metal-substituted complexes of B_6H_{10} [hexaborane(10)] [11], and of Group IV-bridged derivatives of the $B_5H_8^-$ ion [12, 13]. In all three species, $C_2B_4H_7^-$, B_6H_{10} and $B_5H_8^-$, the basal B—B bond is the reactive site with respect to metal electron-acceptor reagent groups. Other such borane and carborane species are expected to form similar bridged complexes; indeed, the reaction of $2\text{-}CH_3\text{-}2,3,4\text{-}C_3B_3H_5^-$ ion (a structural analog of B_6H_{10} and $C_2B_4H_8$) with $BrMn(CO)_5$ yields an unstable red intermediate which loses 2 CO to form the *closo*-metallocarborane $(CO)_3Mn(CH_3)C_3B_3H_5$ [14]. Although this intermediate was assumed at the time to be a metal—carbon σ-bonded species, it now seems likely that it contains a $(CO)_3Mn$ moiety linked to the C_3B_3 cage by a B—Mn—B three center bond. The remaining members of the pyramidal $C_nB_{6-n}H_{10-n}$ series [15] (n = 0-4), CB_5H_9 and $C_4B_2H_6$, may also conceivably form metal-bridged complexes; CB_5H_9 would require prior deprotonation to the $CB_5H_8^-$ ion, and $C_4B_2H_6$, which has a C_4B basal ring, could accept a bridging substituent only via formation of a B—M—C three-center bond, a presently unknown structural feature.

Experimental section

Materials. Commercial reagent grade chemicals were used as received in all cases, except where otherwise stated. Triethylaluminum, trimethylaluminum, dimethylaluminum chloride and ethylaluminum dichloride were purified by fractionation on the vacuum line prior to use. Dicarba-*nido*-hexaborane(8) ($C_2B_4H_8$) was prepared as described elsewhere [16]. Tetrahydrofuran, diglyme, and carbon disulfide were dried over lithium aluminum hydride prior to use.

Spectroscopy. ^{11}B NMR spectra at 32.1 MHz and ^1H NMR spectra at 100 MHz were obtained on a Varian HA-100 spectrometer; IR spectra were recorded on a Beckman IR-8 spectrometer, using either a 9 cm gas cell or a 0.1 mm, 9 μl NaCl cavity cell. Mass spectra were obtained on Hitachi—Perkin—Elmer RMU-6 and AEI MS-902 instruments.

Gas chromatography and analysis. The GLPC apparatus used has been described in earlier papers [2, 14]. Analyses were obtained either by wet-chemical methods (Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.), or from mass spectral data by comparison with calculated spectra.

General procedures. All experiments were performed either in a Pyrex vacuum line with greaseless stopcocks under high vacuum conditions, under a dry nitrogen atmosphere in a glove box, or under a flowing dry nitrogen atmosphere in a glove bag. Gas phase reactions were carried out in round-bottom Pyrex flasks equipped with thick capillary necks which were sealed off after the reactants were introduced and condensed (liquid nitrogen) and with break-off seals which were under vacuum to allow the removal of volatile products. Solid-gas reactions were run in the same apparatus. Gas-liquid reactions were conducted in an evacuated 20 cm Pyrex tube, wrapped with a Variac-controlled heating tape.

Lithium dicarbahexaborate (1—). n-Butyllithium in hexane (1 ml) was transferred by syringe into a 100 ml round-bottom flask with a stopcock and vacuum line attachment in a nitrogen filled dry bag, and the closed apparatus was reattached to the vacuum line and pumped out. $C_2B_4H_8$ (1.0 mmol) was added and the mixture warmed slowly to 0°, during which time the solution turned yellow. The solution of $LiC_2B_4H_7$ was used immediately in subsequent reactions without filtering, in order to minimize the decomposition which invariably occurred during filtration.

Reaction of lithium dicarbahexaborate (1—) and dimethylaluminum chloride. A 25% hexane solution of $(CH_3)_2AlCl$ (4.0 mmol) was added to $LiC_2B_4H_7$ (2.0 mmol in ≈ 1 ml of hexane) in an evacuated 100 ml reactor containing a sidearm which could be closed off with a greaseless stopcock, and the solution was stirred at 0° for 3 h. The solution was transferred into the sidearm, which was then cooled in a —12° bath and the volatiles distilled into a —196° trap on the vacuum line. The —196° condensate was fractionated through a —63° trap, which retained $(CH_3)_2AlCl$. The material passing —63° was hexane containing a small quantity of $C_2B_4H_8$, identified from its IR spectrum. The material retained at —12° exhibited an electron-impact mass spectrum with a cutoff at m/e 76 and a characteristic 4-boron pattern corresponding to $C_2B_4H_8^+$, as well as intense peaks at m/e 58 and 43 corresponding to $(CH_3)_2AlH^+$ and CH_3AlH^+, respectively; the $(CH_3)_2AlC_2B_4H_7^+$ parent ion was not observed. However, the chemical ionization (CI) mass spectrum obtained in methane did exhibit a weak cutoff at m/e 133 corresponding to the protonated parent ion, as well as strong groupings with local cutoffs at m/e 119 and 105 arising from the successive loss of two methyl groups, each grouping having an intensity pattern corresponding to a 4-boron species (the patterns are not affected by aluminum, which is monoisotopic, and the ^{13}C contributions are minor due to the small number of carbons). Only a weak and basically uninformative infrared spectrum was obtained, and all attempts to record the ^{11}B NMR spectrum of $(CH_3)_2AlC_2B_4H_7$ gave only signals corresponding to $C_2B_4H_8$ [2], which formed by decomposition of $(CH_3)_2AlC_2B_4H_7$ at 25° in carefully dried solvents and in neat liquid form.

Pyrolysis of μ-$(CH_3)_2AlC_2B_4H_7$ at 100°. A sample of μ-$(CH_3)_2AlC_2B_4H_7$ was heated at 100° for six hours, during which time H_2 was formed. Volatile materials were passed through a —23° cold trap, but no material was retained. Materials passing through —23° contained a strong BH stretch at 2605 cm^{-1} in the infrared spectrum. The volatile material was chromatographed on Kel-F at 41°, and the mass spectrum of the fraction with a 5 min retention time at 60° exhibited a 4-boron pattern at m/e 76 and peaks at m/e 41, $Al(CH_2)^+$; 43, $Al(CH_3)H^+$; and 57, $Al(CH_3)_2^+$. Chemical ionization mass spectrometry disclosed 4-boron groupings with local cutoffs at m/e 105, $H_2AlC_2B_4H_8^+$; 103, $HAlC_2B_4H_7^+$; 77, $C_2B_4H_8H^+$; and single peaks at m/e 42, $AlCH_3^+$; 43, $(CH_3)AlH^+$. The gas phase IR spectrum contained absorptions at 3020 w (cage CH stretch), 2960 s and 2940 s (methyl CH stretch), 2607 s (terminal BH stretch), 1520 w, 1470 w, 1310 s, 1300 s, 1210 w, 1190 w, 1160 s, 1150 s, 1070 w, 970 w, 680 m, and was characteristic of a closed-cage metallocarborane [9, 10], consistent with the assigned structure of $CH_3AlC_2B_4H_6$. The fraction with retention time of 1 min at 60° contained mass spectral peaks at m/e 41, $(CH_2)Al^+$ and m/e 43, $(CH_3)AlH^+$, and was identified as $[H_2Al(CH_3)]_2$.

The pyrolysis was repeated and the products chromatographed on Apiezon. In addition to the two fractions separated on Kel-F, a small amount of $C_2B_4H_8$ was recovered.

Dimethylgallium chloride. A 4.6 mmol quantity of $(CH_3)_3Ga$ and an equimolar amount of HCl were condensed with a —196° cold trap into an evacuated 100 ml flask with a stopcock. With the stopcock closed, the reaction mixture was allowed to warm to room temperature and a white crystalline solid was formed immediately. The reaction mixture was frozen to —196° and pumped on to remove the methane. The remaining material was identified as pure $(CH_3)_2GaCl$ from its mass spectrum.

Reaction of sodium dicarbahexaborate (1—) with dimethylgallium chloride. In the same reaction vessel described in the $LiC_2B_4H_7/(CH_3)_2AlCl$ reaction above, $(CH_3)_2GaCl$ (4.6 mmol) was added to $NaC_2B_4H_7$ (4.6 mmol) in THF and allowed to react at 0° for three hours. Precipitation of a white solid from solution indicated a reaction, but no H_2 was evolved. The solution was placed in the sidearm, and with a —12° cold trap on the latter, the volatiles were distilled into a

—196° cold trap on the vacuum line. The volatile materials were fractionated through a —45° cold trap, and the material passing through —45° was identified as THF from its IR spectrum. A clear liquid, III, was retained in the sidearm, which was filled with N_2 gas and opened to the atmosphere. The liquid was removed by a capillary pipette, flushed out with N_2 into a solid mass spectrum probe enclosed in an N_2-filled jar, and transferred to the mass spectrometer with minimal exposure to air. The mass spectrum at 70 eV ionizing voltage is described above. The ^{11}B NMR spectrum in CS_2 solution contains symmetrical doublets at δ —2.72 ppm relative to $BF_3 \cdot O(C_2H_5)_2$ (J = 138 Hz) and +51.9 (182) with relative areas of 3 and 1. The absence of a singlet resonance confirms that all borons retain their terminal hydrogens and thus supports the bridged μ-$[(CH_3)_2Ga]C_2B_4H_7$ structure of III. The bridged geometry is also supported by a split B—H stretching absorption (2500-2600 cm^{-1}) in the infrared spectrum, a feature characteristic [2, 4, 6] of silicon-, germanium-, tin- and lead-bridged $C_2B_4H_8$ derivatives. The IR spectrum in CS_2 solution vs. CS_2 contained bands (cm^{-1}) at 2970 s, 2900 s, 2600 s, 2520 s, 1940 m (br), 1210 s, 1070 s, 1030 s, 960 s, 910 s, 760 (sh), and 740 s.

Reaction of hydrogen chloride with μ-$[(CH_3)_2Ga]C_2B_4H_7$. In a vacuum line trap, 0.16 mmol of HCl was allowed to react with an approximately equimolar quantity of μ-$[(CH_3)_2Ga]C_2B_4H_7$ without solvent. After 50 min, the volatile materials were fractionated through a trap at —128°; the condensate consisted of a mixture of $(CH_3)_2GaCl$ and $C_2B_4H_8$ (identified from the mass spectrum) which were not separated.

Pyrolysis of μ-$[(CH_3)_2Ga]C_2B_4H_7$. Samples of the compound were pyrolyzed under a variety of conditions, including sealed-bulb experiments for 1 h at 100° and passage over Pyrex glass wool at 145°, but in all cases the only volatile boron product was $C_2B_4H_8$; no volatile gallium products were detected. In a sequence monitored by ^{11}B NMR spectroscopy, a 75% solution of μ-$[(CH_3)_2Ga]C_2B_4H_7$ in CS_2 was sealed into a 5 mm diameter NMR tube. No significant change in the spectrum was noted after 48 h at room temperature, but after 25 min at 100° the larger (low field) doublet became slightly asymmetric. During an additional 80 min period at 120-127° the colorless solution became yellowish, solids appeared in the NMR tube, and the spectrum changed to a broad hump centered at approximately δ —1.0. Subsequent GLPC analysis disclosed the presence of a small quantity of $C_2B_4H_8$ but no gallium-containing volatile products.

Ultraviolet irradiation of μ-$[(CH_3)_2Ga]C_2B_4H_7$ *in THF*. A quantity of μ-$[(CH_3)_2Ga]C_2B_4H_7$ was pipetted into a 100 ml quartz reactor, 5 ml of THF was added, and the vessel was evacuated and irradiated by sun lamp for one hour. Polymeric material was noted on the reaction flask, but no material containing a BH band in the infrared was recovered. In another experiment the irradiation was conducted in pentane solution, with formation of polymer and a trace of $C_2B_4H_8$.

μ-$[(C_6H_5)_3P]_3RhC_2B_4H_7$. A solution of $Na^+C_2B_4H_7^-$ was prepared by allowing 1.21 mmol of $C_2B_4H_8$ to react with 2.0 mmol of NaH (56% in mineral oil dispersion) in THF solution in vacuo. After 20 min the solution was filtered in a glove bag and added to a pressure-equalizing dropping funnel. The carborane solution was dropped under nitrogen into a THF solution of tris(triphenylphosphine)rhodium chloride (1.11 mmol in 7 ml). After 30 min the reactor was opened to the air and the THF removed. The residue was applied to a 2.25 × 50 cm liquid phase chromatographic column packed with 70-230 mesh silica gel, and eluted with benzene. The yellow product was recrystallized under nitrogen from methylene chloride/hexane, giving 103.3 mg (0.107 mmol, 9.7% yield). Analysis found: C, 66.70; H, 5.74; B, 5.67; Rh, 10.50; P, 9.24. $C_{56}H_{52}B_4P_3Rh$ calcd.: C, 69.74; H, 5.44; B, 4.49; P, 9.64; Rh, 10.68%. IR spectrum (cm^{-1}, CH_2Cl_2 vs. CH_2Cl_2): 3030 m, 2580 s, 1970 w, 1910 w, 1820 w, 1780 w, 1675 w, 1590 w, 1575 w, 1482 s, 1430 m, 1190 m, 1120 m, 1110 m, 1090 s, 1070 w, 1060 w, 1030 m, 1000 m, 850 w. ^1H NMR (100 MHz, CH_2Cl_2): δ -6.82 ppm rel to $(CH_3)_4Si$ (triphenylphosphine resonance); -4.42 (cage CH); $+10.50$ (bridge proton); cage/bridge area ratio is 2/1. ^{11}B NMR (32.1 MHz, CH_2Cl_2): broad singlets at δ -8.3, $w_{1/2} = 550$ Hz, area ≈ 3; $+35.5$, $w_{1/2} = 240$ Hz, area $\sim$ 1. The width of the peaks and the absence of splitting from B—H coupling may be due to traces of a paramagnetic species in solution.

μ-[$(C_6H_5)_3P$]$AuC_2B_4H_7$. A solution of 3.0 mmol of $Na^+C_2B_4H_7^-$ in 25 ml of THF, prepared as described in the previous synthesis, was taken into a dry box, filtered and transferred to a pressure-equalized addition funnel. The carborane solution was added dropwise to a solution of 3.0 mmol of triphenylphosphine gold chloride in 20 ml of THF. After stirring at room temperature overnight, the red solution was filtered and solvent removed. Since the red solids seemed to be somewhat air sensitive, the material was purified by thin layer chromatography employing benzene as the eluent in a nitrogen atmosphere glove bag to give 95 mg ($\approx$ 60% yield) of the red crystalline product. The mass spectrum contained a cutoff at *m/e* 535 corresponding to the $^{13}C^{12}C_{19}{}^{11}B_4{}^1H_{22}{}^{31}P^{197}Au^+$ parent ion, with intensities closely matching the calculated pattern. IR spectrum (cm^{-1}, CH_2Cl_2 vs. CH_2Cl_2): 3020 m, 2930 s, 2855 m, 2570 vs, 2480 s, 1965 w, 1895 w, 1818 w, 1770 w, 1670 w, 1590 w, 1485 s, 1435 m, 1335 m, 1315 w, 1295 m, 1185 m, 1100 s, 1065 m, 1050 w, 1030 m, 1000 m, 962 m, 890 m, 855 m, 840 w, 805 w, 670 w, 615 w. ^1H NMR ($CDCl_3$ solution): singlets at δ -7.36 and -7.30 (phenyl); -6.11 and -5.93 (carborane CH); area ratio of phenyl to carborane CH, 15/1/1. ^{11}B NMR (THF): doublets at δ -3.9 ($J = 150$); $+0.94$ (145); $+49.8$ (162); 1/2/1 area ratio.

Attempted preparation of μ-(C_6H_5)$HgC_2B_4H_7$. A solution of $Na^+C_2B_4H_7^-$ in THF, prepared as described above from 2.16 mmol of $C_2B_4H_8$, was added via a dropping funnel under nitrogen to a solution of 1.88 mmol of phenylmercury chloride in THF and allowed to react for 3 h. The solution was filtered and concentrated, methylene chloride was added and the solution was refiltered in air, during which a gray precipitate slowly formed. Evaporation of the filtrate under vacuum gave a yellowish-white solid product. The mass spectrum exhibited a grouping from *m/e* 348 to 356 corresponding to the parent ion, $C_8B_4H_{12}Hg^+$, which was partly overlapped by diphenylmercury peaks at *m/e* 358 to 352. A strong grouping corresponding to $C_2B_4H_7^+$ with local cutoff at *m/e* 75 was also present. ^{11}B NMR (THF solution): doublets at δ -3.8 ($J = 146$); 0 (166); and $+52.2$ (186), area ratio 2/1/1.

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