sumably containing sulfate or bisulfate) were rather unstable and were never obtained pure. When, however, air was bubbled through an acetone solution of $[Fe(Et_2dtc)_3]$ acidified with sulfuric acid and containing hexafluorophosphate ion, a stable hexafluorophosphate salt, $[Fe(Et_2dtc)_3]PF_6$, could be obtained analytically pure. It appears that the anion affects the stability of these iron(IV) complexes.

Conditions under which the $[Fe(R_2dtc)_3]BF_4$ complexes are prepared must be carefully controlled or other products may be obtained. Thus, when $[Fe(i\text{-}Pr_2dtc)_3]$ was treated with excess boron trifluoride, a new compound which analyzed as "$Fe(i\text{-}Pr_2dtc)_2BF_3$" was formed. This complex is distinct from $[Fe(i\text{-}Pr_2dtc)_3]BF_4$ but resembles it and the other tetrafluoroborates in its physical properties. The magnetic moment is low, 2.61 BM, and may indicate weak antiferromagnetic coupling within the complex. It most likely contains iron(IV) also. The "BF_3" may be present as the ion F_3BO^{2-},[22] derived from F_3BOH_2 (there is considerable doubt about the existence of this ion[23]), although the analytical data are not in very good accord. *Anal.* Calcd for $Fe(i\text{-}Pr_2dtc)_2BF_3$: C, 35.30; H, 5.92; N, 5.88; S, 26.93; B, 2.27; F, 11.97. Calcd for $Fe(i\text{-}Pr_2dtc)_2OBF_3$: C, 34.16; H, 5.67; N, 5.63; S, 26.05; B, 2.19; F, 11.57. Found: C, 35.35; H, 5.29; N, 6.08; S, 26.84; B, 2.20; F, 12.12. Further speculation on the structure of this complex is premature until additional measurements are made.[24]

Acknowledgments.—We wish to thank Professor James C. Carter and Br. Francis Swicker for measuring the ^{11}B nmr spectra (on a 80.2-MHz spectrometer constructed under Grant FR-00292 from the National Institutes of Health) and Fred R. Brown for help in measuring the infrared spectra. This work was supported by the Division of Biology and Medicine, Atomic Energy Commission, through Contract AT(30-1)3859.

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[22] D. A. Long and R. T. Bailey, *Spectrochim. Acta*, **19**, 1607 (1963).

[23] H. Siebert and H. H. Eysel, *Z. Naturforsch. B*, **22**, 556 (1967).

[24] NOTE ADDED IN PROOF.—We have recently prepared analytically pure samples of $[Co(Et_2dtc)_3]BF_4$ and $[Mn(Et_2dtc)_3]BF_4$ by the reaction of BF_3 with $[Co(Et_2dtc)_3]$ and $[Mn(Et_2dtc)_3]$.

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Reactions of the 2,3,4-Tricarbahexaborane(7) System. Formation of Tricarbahexaboranylmanganese Carbonyl π Complexes[1]

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The reaction of 2-methyl-, 2,3-dimethyl-, or 2,4-dimethyl-2,3,4-tricarbahexaborane(7) with sodium hydride in diglyme removes the bridge proton and generates the corresponding monoanion. Treatment of the $2,4\text{-}(CH_3)_2C_3B_3H_4^-$ ion with DCl yields the bridge-deuterated neutral carborane. The reaction of $2\text{-}CH_3C_3B_3H_6$ and $2,3\text{-}(CH_3)_2C_3B_3H_5$ with $Mn_2(CO)_{10}$ in the gas phase forms the respective volatile complexes $(\pi\text{-}2\text{-}CH_3C_3B_3H_5)Mn(CO)_3$ and $(\pi\text{-}2,3\text{-}(CH_3)_2C_3B_3H_4)Mn(CO)_3$. The reaction of $Na^+CH_3C_3B_3H_5^-$ with $BrMn(CO)_5$ in diglyme produces a red intermediate characterized as $(\sigma\text{-}CH_3C_3B_3H_5)Mn(CO)_5$, which at 100° loses 2 mol of CO to form $(\pi\text{-}2\text{-}CH_3C_3B_3H_5)Mn(CO)_3$. Evidence concerning the mechanism of formation of the π complexes is discussed.

Since the original discovery of methyl derivatives of 2,3,4-tricarba-*nido*-hexaborane(7),[2-4] at present the only known three-carbon carborane,[4a] several aspects of the chemistry of this cage system, including the preparation of the first transition metal–small carborane complex,[5] have been reported in short communications.[5,6] In this paper we present a more complete account of this work and in addition describe an alternate synthetic route to transition metal π complexes of the tricarbahexaboranes which appears capable of extension to other small carborane–metal complexes.

Results and Discussion

Deprotonation and Bridge Deuteration of Tricarbahexaboranes.—The structure in Figure 1 has been assigned to the $2,3,4\text{-}C_3B_3H_7$ cage system on the basis of boron-11 and proton nmr, infrared, and mass spectroscopic evidence.[2,3] Analogy with other carboranes containing bridge hydrogen atoms (*e.g.*, $2,3\text{-}C_2B_4H_8$ and $1,2\text{-}C_2B_9H_{13}$), which react easily with sodium hydride to remove a bridge proton and produce the corresponding monoanion, suggested that the lone bridge hydrogen in the tricarbahexaborane cage should react similarly. This is in fact the case with the available 2-methyl, 2,3-dimethyl, and 2,4-dimethyl derivatives, all of which are easily deprotonated by excess NaH in dry diglyme or tetrahydrofuran (THF) at room temperature. The resulting methyl- and dimethyltricarbahexaborate(1−) salts are hydrolyzed on contact with water or moist air but are reasonably stable in dry solvents. Sodium 2,4-dimethyltricarbahexaborate(1−) in THF solution reacts readily with deuterium chloride to give the bridge-deuterated neu-

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[1] Abstracted in part from the Ph.D. dissertation of J. W. H., University of Virginia, 1970.

[2] C. L. Bramlett and R. N. Grimes, *J. Amer. Chem. Soc.*, **88**, 4269 (1966).

[3] R. N. Grimes and C. L. Bramlett, *ibid.*, **89**, 2557 (1967).

[4] R. N. Grimes, C. L. Bramlett, and R. L. Vance, *Inorg. Chem.*, **7**, 1066 (1968).

[4a] NOTE ADDED IN PROOF.—Subsequent to the submission of this manuscript, a second three-carbon carborane, *closo*-$C_3B_5H_7$, has been prepared in this laboratory: M. L. Thompson and R. N. Grimes, *J. Amer. Chem. Soc.*, **93**, 6677 (1971).

[5] J. W. Howard and R. N. Grimes, *ibid.*, **91**, 6499 (1969).

[6] D. A. Franz, J. W. Howard, and R. N. Grimes, *ibid.*, **91**, 4010 (1969).

tral carborane. Since the nmr and infrared spectra of the deuterio derivative give no evidence of terminal

$$(CH_3)_2C_3B_3H_5 + NaH \xrightarrow[25°]{THF} Na^+(CH_3)_2C_3B_3H_4^- + H_2$$

$$Na^+(CH_3)_2C_3B_3H_4^- + DCl \longrightarrow (CH_3)_2C_3B_3H_4D + NaCl$$

B–D or C–D bonds, it is apparent that the deprotonation and subsequent deuteration affects only the bridge position. Thus, the ^{11}B nmr spectra of 2,4-$(CH_3)_2C_3B_3H_5$ and 2,4-$(CH_3)_2C_3B_3H_4D$ (Figure 2) differ only in the absence of secondary splitting in the low-field doublet of the deuterated compound. The spectrum of the isotopically normal species clearly displays this splitting, which is attributed to the coupling of the magnetically equivalent borons 5 and 6 with the bridge proton (bridge coupling is also evident in the spectra of the 2,3-dimethyl and 2-methyl derivatives[2] but is less clearly resolved due to the nonequivalence of the basal boron atoms in these molecules).

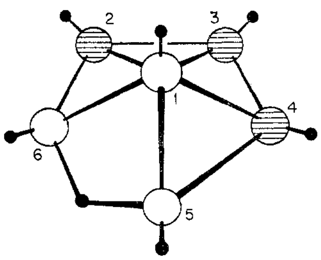

Figure 1.—Structure of the $C_3B_3H_7$ cage system. Shaded circles represent carbon atoms, and open circles, boron.

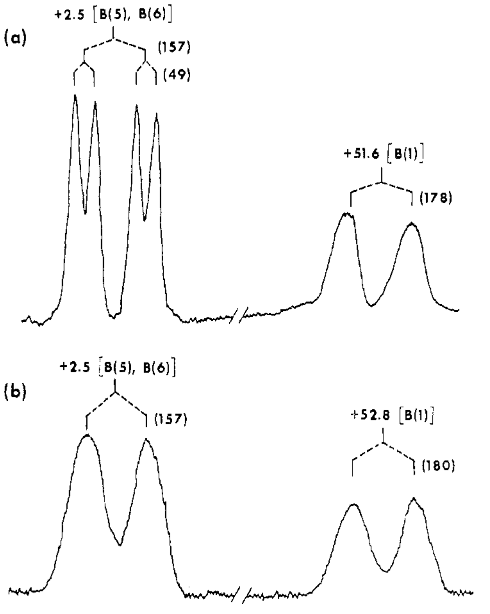

Figure 2.—The 32.1-MHz ^{11}B nmr spectra of (a) 2,4-$(CH_3)_2C_3B_3H_5$ in THF and (b) 2,4-$(CH_3)_2C_3B_3H_4D$ in THF. Chemical shifts are in ppm relative to external $BF_3 \cdot O(C_2H_5)_2$, and coupling constants are in parentheses.

Synthesis of π Complexes from 2-$CH_3C_3B_3H_6$ and 2,3-$(CH_3)_2C_3B_3H_5$.—The tricarbahexaborate anions described above have been of considerable interest to us as potential ligands for π bonding to transition metals. Thus, the basal C_3B_2 ring in the $C_3B_3H_6^-$ derivatives may be regarded as qualitatively analogous to the $C_5H_5^-$ ion and on this basis is presumed to contain six delocalized electrons occupying three bonding molecular orbitals which extend around the ring. Overlap of these filled MO's with d orbitals of appropriate symmetry on a metal ion would be expected to produce stable metallocene-like complexes, as are known for the $C_2B_9H_{11}^{2-}$ (dicarbollide) sandwich compounds and related structures.[7]

As a test of this hypothesis, the preparation of (π-2-$CH_3C_3B_3H_5$)Mn$(CO)_3$ was attempted, taking into consideration that such a complex (1) would have an 18-electron rare gas configuration about the metal atom, (2) would be neutral and thus probably sublimable for ease in characterization, and (3) would be an isoelectronic analog of the known metallocene (π-C_5H_5)Mn$(CO)_3$.[8,9] Accordingly, reactions of the sodium salts of $CH_3C_3B_3H_5^-$ and the isomeric $(CH_3)_2C_3B_3H_4^-$ ions with $Mn_2(CO)_{10}$ in solution were attempted but proved unsuccessful. However, the gas-phase reaction of the neutral carborane 2-$CH_3C_3B_3H_6$ with $Mn_2(CO)_{10}$ at 175–200° generates the desired complex (Figure 3) in 85–90% yield. This material is a thermally stable, somewhat viscous yellow-orange liquid

$$CH_3C_3B_3H_6 + 0.5Mn_2(CO)_{10} \longrightarrow (CH_3C_3B_3H_5)Mn(CO)_3 + 2CO + 0.5H_2$$

at room temperature which has a vapor pressure of ~0.1 mm at 25° and distils easily *in vacuo*. The analogous reaction of 2,3-$(CH_3)_2C_3B_3H_5$ with $Mn_2(CO)_{10}$ yields a product characterized as (π-2,3-$(CH_3)_2C_3B_3H_4$)Mn$(CO)_3$.

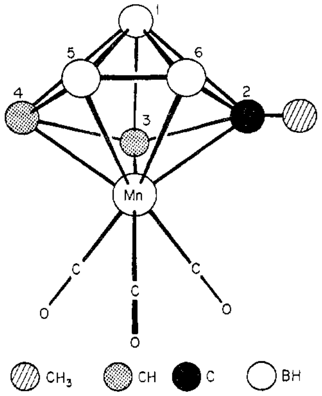

Figure 3.—Proposed structure of (π-2-$CH_3C_3B_3H_5$)Mn$(CO)_3$.

Structural Characterization of (π-2-$CH_3C_3B_3H_5$)Mn$(CO)_3$.—The boron-11 and proton nmr spectra of the complex are shown in Figures 4 and 5, respectively, while Table I lists the significant mass spectroscopic intensities (infrared data are given in the Experimental Section). The presence of three carbonyl groups is established from the mass spectrum and from the two C–O stretching bands at 1956 and 2035 cm^{-1} in the infrared spectrum (the corresponding absorbances in the spectrum of (π-C_5H_5)Mn$(CO)_3$[10] are found at 1939 and 2023 cm^{-1} while those of (π-$CH_3C_5H_4$)Mn-

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[7] The chemistry of carborane–transition metal π complexes has recently been reviewed by M. F. Hawthorne, *Accounts Chem. Res.*, **1**, 281 (1968); L. J. Todd, *Advan. Organometal. Chem.*, **8**, 87 (1970); R. N. Grimes, "Carboranes," Academic Press, New York, N. Y., 1970, pp 207–232.

[8] T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

[9] E. O. Fischer and R. Jira, *Z. Naturforsch. B*, **9**, 618 (1954).

[10] F. A. Cotton, A. D. Liehr, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 175 (1955).

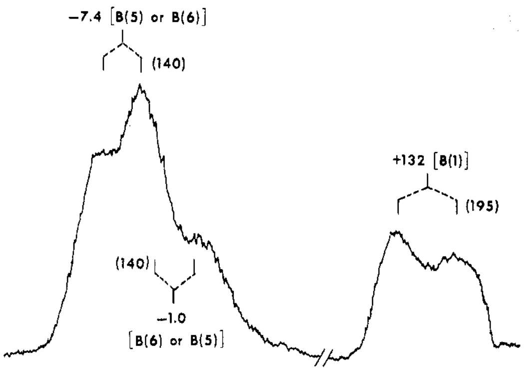

Figure 4.—The 32.1-MHz ^{11}B nmr spectrum of (π-2-$CH_3C_3B_3H_5$)-$Mn(CO)_3$ (neat liquid). Data are presented as in Figure 2.

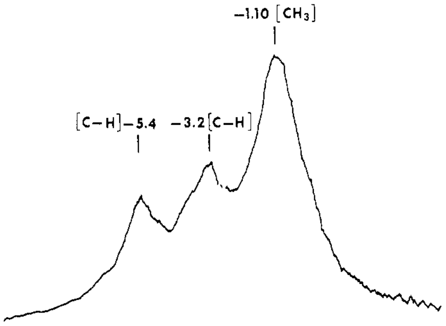

Figure 5.—The 60-MHz ^{1}H nmr spectrum of (π-2-$CH_3C_3B_3H_5$)-$Mn(CO)_3$ (neat liquid). Chemical shifts are in ppm relative to external tetramethylsilane.

TABLE I

PARTIAL MASS SPECTRUM OF (π-2-$CH_3C_3B_3H_5$)$Mn(CO)_3$

m/e	Rel intens	Assignment[a]
229	0.9	($^{13}CH_3C_3B_3H_5$)$Mn(CO)_3^+$
228	12.5	($CH_3C_3B_3H_5$)$Mn(CO)_3^+$
227	9.0	b
226	2.3	b
225	. . .	. . .
200	3.0	($CH_3C_3B_3H_5$)$Mn(CO)_2^+$
199	2.3	b
198	0.7	b
197	. . .	. . .
172	13.3	($CH_3C_3B_3H_5$)$Mn(CO)^+$
171	10.0	b
170	3.1	b
145	4.5	($^{13}CH_3C_3B_3H_5$)Mn^+
144	95.0	($CH_3C_3B_3H_5$)Mn^+
143	73.1	b
142	20.0	b
141	4.7	b
90	58.4	$CH_3C_3B_3H_6^+$
89	100.0	b
88	99.0	b
87	69.2	b
86	36.2	b
85	26.7	b
84	13.4	b
83	11.6	b

[a] Isotopes are ^{12}C, ^{11}B, ^{16}O, ^{55}Mn, and ^{1}H except where otherwise indicated. [b] More than one species assigned, due to statistical distribution of ^{11}B and ^{10}B isotopes.

$(CO)_3$[11] appear at 1940 and 2033 cm^{-1}). The profile in the parent region of the mass spectrum corresponds closely to that calculated for a three-boron species assuming no hydrogen abstraction (since the cleavage of carbonyl groups in the mass spectrometer is extremely facile, hydrogen loss from the parent molecule is negligible). Finally, it is clear from the nmr spectra that the essential cage structure of the original carborane is preserved in the complex. This is also evident from the presence of the $CH_3C_3B_3H_6^+$ fragment in the mass spectrum, identified from the intense peak grouping with a cutoff at m/e 90.

Synthesis of π Complexes from the Tricarbahexaborate Anions.—Since the development of generally applicable routes to the preparation of transition metal–small carborane complexes appeared likely to require solution reactions (in preference to less predictable gas-phase syntheses), attention was returned to the tricarbahexaborate salts. The reaction of $Na^+CH_3C_3B_3H_5^-$ with bromomanganese pentacarbonyl in diglyme solution proceeds rapidly at room temperature without evolution of carbon monoxide, during which the color of the solution changes from yellow to red and sodium bromide is precipitated. Upon refluxing the mixture for several hours, the color changes again to pale yellow and 2 molar equiv of carbon monoxide is released. Fractionation of the volatile materials affords a 20% yield of the yellow complex (π-2-$CH_3C_3B_3H_5$)$Mn(CO)_3$, identical with the compound discussed above. The following scheme summarizes these observations

$$Na^+CH_3C_3B_3H_5^- + BrMn(CO)_5 \xrightarrow[\text{rapid}]{25^\circ} NaBr + \underset{\text{wine red}}{(\sigma\text{-}CH_3C_3B_3H_5)Mn(CO)_5}$$

$$(\sigma\text{-}CH_3C_3B_3H_5)Mn(CO)_5 \xrightarrow[\text{slow}]{100^\circ} 2CO + \underset{\text{yellow}}{(\pi\text{-}CH_3C_3B_3H_5)Mn(CO)_3}$$

The intermediate species which forms initially has been isolated as a nonvolatile red solid whose ir spectrum is consistent with the presence of five CO groups and is assumed to be a σ-bonded carborane–metal complex. This compound is thermally unstable with respect to the loss of two CO groups and concomitant formation of the π-bonded complex. An apparently analogous sequence has been described by Hawthorne, *et al.*,[12,13] for the reaction of the $C_2B_9H_{11}^{2-}$ (dicarbollide) ion with $BrMn(CO)_5$ or $BrRe(CO)_5$. As in the present work, these reactions initially yield an unstable σ-bonded intermediate which on refluxing is converted to the corresponding $(C_2B_9H_{11})Mn(CO)_3^-$ π complex with loss of CO.

The reactions of $BrMn(CO)_5$ with the 2,3- and 2,4-$(CH_3)_2C_3B_3H_4^-$ anions failed to generate isolatable quantities of the corresponding π complexes, which suggests that the formation of σ-bonded intermediates is sterically blocked by the methyl groups in the dimethylated ions. A similar effect is noted in the gas-phase reactions of the methyltricarbahexaboranes with $Mn_2(CO)_{10}$, in which only the monomethylcarborane produces a high yield of the π complex; 2,3-$(CH_3)_2C_3B_3H_5$ generates only a ~4% yield and 2,4-$(CH_3)_2C_3B_3H_5$ gives no identifiable complex at all. A reasonable conclusion is that, in both the gas-phase and solution reactions, π-complex synthesis proceeds *via* initial formation of a metal-to-carbon σ bond and that the process is retarded or blocked by alkyl groups attached to two or more of the cage carbon atoms. As ex-

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(11) L. T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **9**, 86 (1959).

(12) M. F. Hawthorne and T. D. Andrews, *J. Amer. Chem. Soc.*, **87**, 2496 (1965).

(13) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. C. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *ibid.*, **90**, 879 (1968).

pected, the effect seems most pronounced in the 2,4-dimethyl derivative in which both "end" carbons in the cages are alkylated.

The family of transition metal π complexes of the small *nido*-carboranes has recently been extended to additional cage systems and transition metals by the synthesis of *nido*-(π-2,3-$C_2B_4H_6$)Fe$(CO)_3$ and *cyclo*-(π-1,2-$C_2B_3H_7$)Fe$(CO)_3$.[14] Work on these materials and on other related compounds is continuing and will be reported at a later date.

Experimental Section

Materials.—The three 2,3,4-tricarbahexaboranes used in this study, 2-$CH_3C_3B_3H_6$, 2,3-$(CH_3)_2C_3B_3H_5$, and 2,4-$(CH_3)_2C_3B_3H_5$, were obtained from the B_4H_{10}–C_2H_2 gas-phase reaction as described earlier[2-4] and characterized from ir and mass spectra. Deuterium chloride was prepared by the method of Brown and Groot,[15] in which deuterium oxide (Strohler Isotopes, 99.4% deuterium content) is added dropwise to benzoyl chloride at 40°. The product was purified by fractionation through a trap at −128° and checked by infrared spectroscopy. Sodium hydride was obtained as a 61% dispersion in mineral oil (Metal Hydrides, Inc.) and used as received. Diglyme (Ansul) and tetrahydrofuran (Eastman) were vacuum distilled from $LiAlH_4$ directly into the reaction flask immediately before use. Manganese and rhenium carbonyls were obtained from Alfa Inorganics and used as received. Bromomanganese pentacarbonyl was prepared by the method of Abel and Wilkinson.[16] The purity of all reagents was checked by infrared analysis before use.

General Procedure.—All work was conducted using standard high-vacuum techniques. Gas-phase reactions were run in round-bottom Pyrex reactors equipped with break-off seals for removal of volatile products and were sealed after the introduction of reactants. Noncondensable gases (H_2, CO) were collected and measured in a calibrated Toepler pump attached to the vacuum system. When necessary, the relative concentrations of H_2 and CO were determined by mass spectroscopic analysis.

Spectroscopy.—Infrared spectra were obtained on a Beckman IR-8 grating spectrophotometer. Gas infrared spectra were recorded in an 8.2-ml, 9-cm Pyrex cell with NaCl windows, and solution spectra were recorded in 0.1-mm, 9-μl NaCl cavity cells. Proton nmr spectra were recorded on a Hitachi Perkin-Elmer R20 spectrometer at 60 MHz, ^{11}B nmr spectra were obtained on a Varian HA-100 at 32.1 MHz, and mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6 spectrometer.

Chromatography.—Two almost identical preparative-scale gas chromatography systems were used for separating and identifying compounds. Both units were constructed of Pyrex glass and could be evacuated to 10^{-5} Torr. Each chromatographic system consisted of a commercial gas density detector, power supply, and recorder, and all connections were high-vacuum stopcocks or ground-glass joints. Two 9.5-ft × 0.25-in. copper columns were used at different times for chromatographic runs and contained 30% Apiezon L and 30% Kel-F grease, respectively, on Chromosorb W solid support. Nitrogen was used as the carrier gas in both units, and column temperatures above room temperature were maintained by a rheostat-controlled heat lamp. Following separation on the column and passage through the gas density detector, the samples in question were collected in traps cooled to −196°. Relative retention times, which remained essentially constant, are listed in Table II.

TABLE II

RELATIVE GAS CHROMATOGRAPHIC RETENTION TIMES

	Kel-F[a,b]		Apiezon[a,b]	
	25°	40°	50°	75°
2-$CH_3C_3B_3H_6$	2.9	2.7	3.0	3.2
2,3-$(CH_3)_2C_3B_3H_5$	4.9	5.2	4.7	5.3
2,4-$(CH_3)_2C_3B_3H_5$	6.4	7.3	6.2	7.1

[a] 30% on Chromosorb W. [b] B_5H_9 = 1.0.

Reaction of 2-Methyl-2,3,4-tricarbahexaborane(7) with Sodium Hydride.—To an evacuated reactor containing 42.0 mg of a sodium hydride–mineral oil dispersion (61 wt % NaH, 1.07 mmol of active hydride) was added 2.0 ml of dry diglyme by vacuum distillation from $LiAlH_4$ at 80°. After degassing the mixture, 0.725 mmol of 2-$CH_3C_3B_3H_6$ was added and the reactor was warmed to room temperature. Hydrogen evolution began near room temperature and proceeded vigorously for 30 min. After stirring at room temperature for 3 hr followed by heating at 50° for 15 min, the hydrogen evolved (0.675 mmol) was collected and measured.

Reaction of 2,3-Dimethyl-2,3,4-tricarbahexaborane(7) with Sodium Hydride.—Following a procedure identical with that used for the 2-methyl derivative, 2.09 mmol of sodium hydride and 1.48 mmol of 2,3-$(CH_3)_2C_3B_3H_5$ were allowed to react in 2.0 ml of dry tetrahydrofuran (THF). Evolution of H_2 began upon warming the reaction solution to room temperature. The solution was stirred magnetically for 3 hr, after which 1.43 mmol of H_2 was collected and measured. Diglyme was also employed as an alternative solvent for this reaction with no difficulties.

When aliquots of a THF solution of $Na^+(CH_3)_2C_3B_3H_4^-$ were mixed with either 25% aqueous $(CH_3)_4NCl$ or saturated CsCl solutions, extensive decomposition of the carborane anion was indicated by the evolution of hydrogen.

Reaction of 2,4-Dimethyl-2,3,4-tricarbahexaborane(7) with Sodium Hydride.—Using the same procedure employed for the 2-methyl and 2,3-dimethyl derivatives, 1.07 mmol of sodium hydride and 0.83 mmol of 2,4-$(CH_3)_2C_3B_3H_5$ in 2.0 ml of dry THF generated 0.80 mmol of H_2 over a 2-hr period. Again, diglyme proved to be a satisfactory alternative solvent.

Reaction of 2,4-Dimethyl-2,3,4-tricarbahexaborate(1−) with Deuterium Chloride.—Excess deuterium chloride (3 mmol) was added to a filtered solution of $Na^+(CH_3)_2C_3B_3H_4^-$ (0.41 mmol) in 3.0 ml of THF by vacuum distillation. After stirring for 18 hr at room temperature, the reaction mixture was fractionated through traps cooled to −52, −95, and −196°. Unreacted deuterium chloride (2.1 mmol) was recovered in the −196° trap and identified from its infrared spectrum. Chromatography of the material in the −52° trap gave μ-D-2,4-$(CH_3)_2C_3B_3H_4$ (0.1 mmol, 25%), which was identified from its infrared, ^{11}B nmr, and mass spectra. The infrared spectrum of the carborane product is very close to that of 2,4-$(CH_3)_2C_3B_3H_5$[3] but lacks the B–H–B stretching band in the 1800–2000-cm^{-1} region. The mass spectrum exhibits a cutoff at *m/e* 105, corresponding to the $^{12}C_5{}^{11}B_3{}^1H_{10}{}^2D^+$ ion, and the 32.1-MHz ^{11}B nmr spectrum is shown in Figure 2b.

Reaction of 2,3-Dimethyl-2,3,4-tricarbahexaborate(1−) with Dimanganese Decacarbonyl.—A 2.0-ml THF solution containing 195 mg (0.50 mmol) of $Mn_2(CO)_{10}$ was added to a 1.0-ml THF solution of $Na^+(CH_3)_2C_3B_3H_4^-$ (0.923 mmol) in an evacuated reaction flask. After stirring for 2 hr at 45°, the reaction mixture was frozen in liquid nitrogen and all noncondensable material was collected and measured (0.087 mmol). The reaction mixture was stirred at 75° for 2 hr, which yielded only an additional 0.026 mmol of noncondensable material. Refluxing the reaction mixture at 100° with stirring for 48 hr yielded 0.128 mmol of noncondensable gas. The total of noncondensable gas collected from the three separate procedures above amounted to 0.241 mmol and was identified as CO from its mass spectrum. Vacuum fractionation of the reaction mixture through traps cooled to −45 and −196° gave only a fraction in the −196° trap, identified as tetrahydrofuran from its ir spectrum. A nonsublimable green solid coated the bottom of the reaction flask after removal of the THF solvent.

The work-up of the green material remaining in the reaction flask was carried out in a glove box. No characterizable products were found other than $Mn_2(CO)_{10}$, identified from its ir spectrum, and no carborane was recovered.

Reaction of 2-Methyl-2,3,4-tricarbahexaborane(7) with Dimanganese Decacarbonyl.—A mixture of 0.30 mmol of 2-$CH_3C_3B_3H_6$ and 125 mg of $Mn_2(CO)_{10}$ (0.32 mmol) was sealed in a 100-ml flask equipped with a break-off tip and heated at 200° for 15 hr, after which the flask was cooled to −196° and opened to the vacuum line. The noncondensable material was pumped out of the vacuum system through two traps cooled to −196°, and the volatile material in the flask was transferred to a vacuum trap for purification. Vacuum fractionation of this material through traps cooled to 0 and −196° gave a fraction (0.14 mmol) passing 0°, which was chromatographed and identified as 2-$CH_3C_3B_3H_6$ from its infrared and mass spectra. The 0° condensate, a yellow-orange liquid (37.8 mg, 0.166 mmol, 87% yield based on carborane consumed), was characterized as

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[16] E. Q. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959).

(π-2-$CH_3C_3B_3H_5$)$Mn(CO)_3$ as described above. The infrared spectrum in CCl_4 solution *vs.* CCl_4 contains bands at 3060 (w), 3030 (w), 2980 (sh), 2920 (s), 2870 (s), 2810 (sh), 2620 (sh), 2590 (s), 2035 (vs), 1956 (vs), 1440 (s), 1370 (m, b), 1300 (sh), 1200 (m), 1135 (sh), 1105 (s), 1020 (m), 990 (sh), 940 (sh), 920 (m), 880 (m), 860 (m), 700 (w), 660 (sh), and 635 (s) cm^{-1}.

The interior of the reaction flask was coated with a purple metallic-like material, but no $Mn_2(CO)_{10}$ was recovered.

Reaction of 2,3-Dimethyl-2,3,4-tricarbahexaborane(7) with Dimanganese Decacarbonyl.—Following the procedure described for the 2-methyl derivative, 2.37 mmol of 2,3-$(CH_3)_2C_3B_3H_5$ and 390 mg of $Mn_2(CO)_{10}$ (1.0 mmol) were heated at 200° for 40 hr. After opening the reaction flask on the vacuum line the volatile materials were fractionated through traps cooled to −23 and −196°. The material passing −23° was chromatographed to give a component (0.25 mmol) identified from its ir spectrum as 2,3-$(CH_3)_2C_3B_3H_5$. The material trapped at −23° was further purified by several fractionations through a 0° trap to give ~20 mg of a yellow-orange liquid characterized from its mass spectrum as [π-2,3-$(CH_3)_2C_3B_3H_4$]$Mn(CO)_3$. The mass spectrum exhibits a sharp cutoff at *m/e* 242, corresponding to the $^{12}C_8{}^{11}B_3{}^{55}Mn^{16}O_3{}^{1}H_{10}{}^{+}$ parent ion, and contains intense groupings at *m/e* 214, 186, and 158, corresponding to the successive loss of one to three CO groups from the parent molecule. The intensities in the parent region are in close agreement with those calculated for the elemental composition indicated, based on normal isotopic distributions.

Reaction of 2,4-Dimethyl-2,3,4-tricarbahexaborane(7) with Dimanganese Decacarbonyl.—Using the procedure described for the 2-$CH_3C_3B_3H_6$–$Mn_2(CO)_{10}$ reaction, 1.11 mmol of 2,4-$(CH_3)_2C_3B_3H_5$ and 418 mg of $Mn_2(CO)_{10}$ (1.08 mmol) were heated at 200° for 48 hr. The flask was opened into the vacuum line and CO (5.9 mmol) was collected and measured. The remaining volatile material was collected in a vacuum trap and fractionated through traps cooled to −23 and −196°. Unreacted 2,4-$(CH_3)_2C_3B_3H_5$ (0.09 mmol) passed −23° and was identified from its infrared spectrum. A trace of a slightly volatile yellow liquid was trapped at −23° but was not characterized due to insufficient quantity. Unreacted $Mn_2(CO)_{10}$ was recovered from the reaction flask.

A reaction between the same two reactants at 200° for 23.5 hr produced no detectable volatile products other than noncondensables.

Reaction of 2-Methyl-2,3,4-tricarbahexaborane(7) with Dirhenium Decacarbonyl.—A mixture of 0.34 mmol of 2-$CH_3C_3B_3H_6$ and 226 mg of $Re_2(CO)_{10}$ (0.35 mmol) was sealed in a 100-ml flask equipped with a break-off tip and heated at 200° for 24 hr. After removal from the oven the flask was cooled to −196° and opened into the vacuum line. Noncondensable material (CO, 1.45 mmol) was collected and measured. The volatile material was fractionated through traps cooled to −23 and −196°. The fraction passing the −23° trap (0.11 mmol) was identified from its infrared spectrum as 2-$CH_3C_3B_3H_6$, and no material was trapped at −23°. The reaction flask was coated on the inside with a reddish transparent solid which exhibited two C–O stretching bands at 2020 and 1955 cm^{-1} in its infrared spectrum. A trace amount of $Re_2(CO)_{10}$ was recovered from the reaction, but no detectable amount of the expected (π-2-$CH_3C_3B_3H_5$)$Re(CO)_3$ was found.

When the reaction was run at 215° with equimolar amounts of the two starting materials, the products were identical with those described above.

Reaction of 2-Methyl-2,3,4-tricarbahexaborate(1−) with Bromomanganese Pentacarbonyl.—A 3.0-ml diglyme solution containing 0.675 mmol of $Na^+CH_3C_3B_3H_5{}^-$ was added to 277.3 mg (1.01 mmol) of $BrMn(CO)_5$ in a previously evacuated flask equipped with a reflux condenser. After stirring at room temperature for ~1 hr, during which the color of the solution changed from yellow to red without evolution of CO, the mixture was refluxed at 100° for 12 hr, during which 0.95 mmol of CO was generated. Following the reaction, the solvent and volatile material were distilled from the flask to a vacuum line trap. The mixture was fractionated through traps cooled to −12, −45, and −196°. The material passing −45° was purified by gas chromatography and gave a fraction (0.14 mmol) which was identified from its ir spectrum as 2-$CH_3C_3B_3H_6$. The material passing −12° was diglyme. The fraction condensing at −12° was further purified by passage through a trap cooled to 0° to give 23.5 mg (0.11 mmol, 21% yield) of a product identified from its ir and mass spectra as (π-2-$CH_3C_3B_3H_5$)$Mn(CO)_3$, identical with the compound obtained earlier from 2-$CH_3C_3B_3H_6$ and $Mn_2(CO)_{10}$ at 200°. A small amount of $Mn_2(CO)_{10}$ was also recovered from the reaction mixture.

A red nonsublimable solid which remained in the reaction flask was collected; its ir spectrum (Nujol mull) revealed three C–O stretching bands at 2010, 1975, and 1950 cm^{-1} and a green flame test indicated the presence of boron in the sample.

Reaction of 2,3-Dimethyl-2,3,4-tricarbahexaborate(1−) with Bromomanganese Pentacarbonyl.—A 3.0-ml glyme solution containing 0.79 mmol of $Na^+(CH_3)_2C_3B_3H_4{}^-$ was added to 235 mg (0.85 mmol) of $BrMn(CO)_5$ in an evacuated flask equipped with a reflux condenser. The mixture was stirred at room temperature for 18 hr followed by 3 hr at 75°, during which 1.10 mmol of CO was evolved. The volatile material was fractionated through traps cooled to −23, −52, and −196°. The material trapped at −196° was identified as glyme from its ir spectrum, while the fraction trapped at −52° was purified by gas chromatography (0.275 mmol) and was identified as 2,3-$(CH_3)C_3B_3H_5$. The material trapped at −23° was further purified by repeated passage through a 0° trap to give 4.1 mg of a slightly volatile yellow liquid which failed to give an informative mass spectrum. A yellow sublimable solid was recovered from the reaction flask and identified from its ir and mass spectra as $Mn_2(CO)_{10}$.

An analogous reaction between sodium 2,4-dimethyl-2,3,4-tricarbahexaborate and bromomanganese pentacarbonyl also yielded no characterizable materials other than 2,4-$(CH_3)_2C_3B_3H_5$ (0.192 mmol) and $Mn_2(CO)_{10}$.

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