^{11}B nmr spectra indicated that bromination had taken place on boron of the carborane cage rather than carbon of the π-cyclopentadienyl ring. The C_5H_5 proton resonance for III was a single peak at τ 5.53 (benzene solvent).

The 32-Mcps ^{11}B nmr spectrum of III could not be clearly interpreted owing to extensive overlap of the resonances. A reasonable structure for III could possibly have bromine substituted at the 8 and 10 boron positions of the $B_7C_2H_9$ cage. Single-crystal X-ray diffraction studies are in progress.

Nitration

Compound I was nitrated very easily by stirring a solution of I in methylene chloride over concentrated nitric acid. The infrared spectrum of the semisolid crude product contained strong bands around 1600 and 1300 cm^{-1} which are characteristic of a nitro group. The material was *extremely* shock sensitive and therefore no further work on isolation of a pure product was done.

Experimental Section

Preparation of (π-C_5H_5)Co(π-1,6-$B_7C_2H_8$-8-$COCH_3$).—Aluminum chloride, 0.67 g (5 mmol), and acetyl chloride, 0.4 g (5 mmol), were dissolved in 25 ml of dry dichloromethane and placed in a 100-ml, three-necked flask equipped with an addition funnel, a magnetic stirrer, and a condenser with a nitrogen inlet. The flask and contents were cooled to 0° and flushed with dry nitrogen. To the cooled mixture was added a solution of 1 g (4.3 mmol) of $(C_5H_5)Co(B_7C_2H_9)$ (I) in 25 ml of dichloromethane. The mixture was stirred for 45 min at 0°, then warmed to room temperature, and finally refluxed for 3 hr.

The reaction solution was then poured into ice water and the layers were separated. The water layer was extracted once with CH_2Cl_2. The combined dichloromethane extract was dried over magnesium sulfate, filtered, and evaporated to dryness. The product may be recrystallized from ether–hexane or chromatographed with a silica gel column. The red acetyl derivative was eluted with 1:1 C_6H_{14}–CH_2Cl_2 whereas unreacted starting material came off the column first with 9:1 C_6H_{14}–CH_2Cl_2; total yield, 6.8 g (72%); mp 162°. *Anal.* Calcd for $(C_5H_5)Co(B_7C_2H_8COCH_3)$: C, 39.32; H, 5.87; B, 27.55; Co, 21.44. Found: C, 39.41; H, 5.88; B, 27.42; Co, 21.33. A 2,4-dinitrophenylhydrazone derivative was easily prepared and recrystallized as small orange plates from ethanol. The compound explodes with violence at 183°.

Bromination of $(C_5H_5)Co(B_7C_2H_9)$.—$(C_5H_5)Co(B_7C_2H_9)$ (I), 0.5 g (2.2 mmol), was dissolved in 50 ml of carbon tetrachloride along with 3 ml (8.8 g, 55 mmol) of bromine. The mixture was stirred in a round-bottomed flask at room temperature for 20 hr. Some orange solid crystallized from solution. The reaction mixture was poured into water and the excess bromine was removed by extraction with aqueous sodium sulfite. Some additional methylene chloride was added and the organic layer was washed several times with water. The carbon tetrachloride extract was separated, dried over magnesium sulfate, filtered, and evaporated to dryness. The crude product was chromatographed from a silica gel column. Complete elution was accomplished with hexane–methylene chloride (1:1). After concentration of the column extracts, 0.55 g of orange solid was filtered from the hexane. Two recrystallizations from ether–hexane afforded orange crystals which melted at 129–130° (the orange melt slowly turns yellow at 130–140°). *Anal.* Calcd for $(C_5H_5)Co(B_7C_2H_7Br_2)$: C, 21.53; H, 3.09; B, 19.38; Co, 15.09; Br, 40.92. Found: C, 21.21; H, 3.09; B, 19.83; Co, 16.13; Br, 42.71. (A mass spectrum of the sample indicated that a small amount of a tribromo derivative was also formed.)

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Polyhedral Manganese Carbonyl Derivatives of the $B_6C_2H_8^{2-}$ Ligand

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It has been found that 1,3-$B_7C_2H_{11}^{2-}$ reacts with some group VIII transition metal salts to give π complexes containing the dicarbazapide ligand $B_7C_2H_9^{2-}$.[1] It therefore seemed of interest to examine the behavior of $Na_2B_7C_2H_{11}$ with transition metal carbonyl derivatives. The formation of stable complexes in the reaction of the dicarbollide ion with group VII pentacarbonyl halides has already been demonstrated;[2] hence the reactions of $Na_2B_7C_2H_9R_1R_2$ (R_1 and R_2 are substituents at carbon) with group VII carbonyls were selected as an area of study.

Reactions with Manganese Carbonyls.—In all of the reactions involving $Na_2B_7C_2H_9R_1R_2$, a suspension of the salt was prepared in diethyl ether. It has been shown[1] that under the reaction conditions employed, 2 mol of hydrogen is evolved and the $B_7C_2H_{11}^{2-}$ ion is formed.

$$B_7C_2H_{13} + 2NaH \longrightarrow Na_2B_7C_2H_{11} + 2H_2$$

When molar equivalents of manganese pentacarbonyl bromide and $Na_2B_7C_2H_{11}$ were heated in tetrahydrofuran at the reflux temperature, the mixture turned from yellow to deep amber, gas was evolved, and sodium bromide precipitated out. When the reaction was carried out at room temperature, the products were identical with those formed in refluxing tetrahydrofuran, indicating the instability of any assumed intermediate containing five carbonyl groups. Infrared spectra of the tetramethylammonium salt of the isolated product anion contained a B–H stretch at 2490 cm^{-1} and carbonyl stretching bands at 1992 and 1910 cm^{-1} (Table IV). The elemental analysis, formula weight, and equivalent weight (Table I) satisfied, much to our suprise, the general formula $B_6C_2H_8Mn(CO)_3^-$ for the anion. Table II presents the 32-Mcps ^{11}B nmr spectrum of the proposed compound $(CH_3)_4N[B_6C_2H_8Mn(CO)_3]$, which consists of four discrete doublets. If the low-field doublet is assumed to be of relative inten-

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(2) (a) M. F. Hawthorne and T. D. Andrews, *ibid.*, **87**, 2496 (1965); (b) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *ibid.*, **90**, 879 (1968).

Table I

Elemental Analyses, Formula Weights, Equivalent Weights and Yields of the Salts of $B_6C_2H_6R_1R_2Mn(CO)_3^-$

Compound		% B	% C	% H	% Mn	% Cs	% N	Formula wt[a]	Equiv wt	Yield, %
$CsB_6C_2H_8Mn(CO)_3$	Calcd	17.54	16.27	2.17	14.88	36.03	...	366	309.7[c]	44[d]
	Found	17.91	16.22	2.13	14.54	34.85	...	369[b]	312	
$(C_5H_5N)_2BH_2B_6C_2H_8Mn(CO)_3$	Calcd	18.64	44.40	4.94	13.52	...	6.91	...	...	17.8[e]
	Found	19.90	43.87	5.17	12.73	...	6.99	...	...	
$(CH_3)_4NB_6C_2H_6(CH_3)_2Mn(CO)_3$	Calcd	19.86	37.2	7.36	16.86	...	4.3		...	25.4
	Found	18.81	35.69	7.14	15.89	...	4.4			
$(CH_3)_4NB_6C_2H_7(C_6H_5)Mn(CO)_3$	Calcd	16.80	46.70	6.22	14.22	...	3.63		395	35.5
	Found	16.38	46.13	6.31	14.28	...	3.74		386	

[a] Osmometric. [b] Tetraethylammonium salt in acetone. [c] Tetramethylammonium salt. [d] A combination of cesium and tetraethylammonium salts. [e] Room-temperature preparation.

Table II

The 32-Mcps ^{11}B Nmr Chemical Shifts and Relative Intensities for $B_6C_2H_6R_1R_2Mn(CO)_3^-$ Ions[a]

R_1	R_2	Chem shift, ppm ($BF_3 \cdot O(C_2H_5)_2 = 0$)	Rel intens
H	H	−20.49, +6.57, +11.57, +18.75	1:2:2:1
H	C_6H_5	−16.75, +1.8, +6.8, +11.6	1:2:2:1
CH_3	CH_3	−12.45, −2.31, +3.23, +7.00	1:2:2:1

[a] Determined in acetone solution.

Table III

The ^1H Nmr Data for the Compounds $(CH_3)_4N[B_6C_2H_6R_1R_2Mn(CO)_3]$[a]

R_1	R_2	Resonance, ppm (rel area)	Assignment
H	H	Broad singlet −5.70 (1.0)	Carborane C–H
		Sharp singlet −3.73 (5.9)	Methyl protons of the cation
CH_3	CH_3	Sharp singlet −3.38 (2.1)	Methyl protons of the cation
		Broad singlet −2.46 (1.0)	Carborane methyl protons
H	C_6H_5	Broad doublet −7.40 (5.0)	Carborane phenyl protons
		Broad singlet −4.87 (1.0)	Carborane C–H
		Sharp singlet −3.10 (12.0)	Methyl protons of the cation

[a] Determined in deuterioacetone solution.

sity 1, a 1:2:2:1 pattern of doublets is obtained. A ^{11}B nmr spectrum of the bis(pyridine)boronium salt exhibited a high-field multiplet of relative intensity 6 in addition to the low-field doublet or area 1 confirming the fact that the product is a monoanion.

The reactions of $Na_2B_7C_2H_{10}(C_6H_5)$ and $Na_2B_7H_9(CH_3)_2$ with manganese pentacarbonyl bromide in tetrahydrofuran at the reflux temperature yielded products which analyzed satisfactorily for $(CH_3)_4N[B_6C_2H_7(C_6H_5)Mn(CO)_3]$ and $(CH_3)_4N[B_6C_2H_6(CH_3)_2Mn(CO)_3]$. The ^1H nmr spectra (Table III) of the unsubstituted and C,C′-dimethyl-substituted complexes exhibited single resonances at $\delta - 5.7$ and -2.46, respectively, ascribed to equivalent carborane hydrogen atoms and equivalent methyl groups attached to two equivalent C atoms in each ligand. The ^{11}B nmr spectra of tetramethylammonium salts of the dimethyl and monophenyl ligand complexes were similar to that of the unsubstituted compound with considerable differences in chemical shifts (Table II).

A structure for the $B_6C_2H_8Mn(CO)_3^-$ ion which satisfies the above characterization data is shown in Figure 1. The geometry is that of a tricapped trigonal prism having a plane of symmetry through the $Mn(CO)_3$ moiety. This structure accounts for the unique boron atom (apical) observed in the ^{11}B nmr spectrum as a low-field doublet and the equivalence of the carbon atoms demonstrated by ^1H nmr data.

The reaction between $Na_2B_7C_2H_9(CH_3)_2$ and $Mn(CO)_5Cl$ also resulted in the formation of the C,C′-substituted $(CH_3)_2B_6C_2H_6Mn(CO)_3^-$ ion which was identified spectroscopically. Similarly, the reaction of $Na_2B_7C_2H_{11}$ with $Mn_2(CO)_{10}$ yielded $(CH_3)_4N[B_6C_2H_8Mn(CO)_3]$ after isolation of products. Further work is in progress to determine the fate of the boron atom removed from the starting material, $B_7C_2H_{11}^{2-}$.

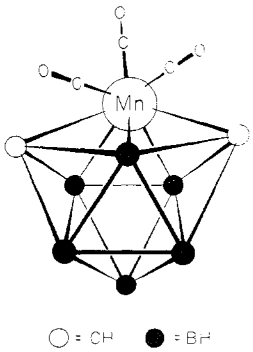

Figure 1.—Proposed structure of the $B_6C_2H_8Mn(CO)_3^-$ ion with H atoms removed.

Experimental Section

Physical Measurements.—Infrared spectra were determined using a Beckman IR-5 infrared spectrophotometer and a Perkin-Elmer Model 137 sodium chloride spectrophotometer. Table IV reports the infrared data obtained. Proton nmr spectra were obtained by means of a Varian A-60 spectrometer and ^{11}B nmr spectra were obtained with a Varian HA-100 spectrometer at 32.2 Mcps. Molecular weights were determined with a Mechrolab Model 301A osmometer. Titrations were carried out using a Leeds and Northrup Model 7664 pH meter with a Thomas Combination electrode, Model 4858-L60. Analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Materials.—The preparation of the disodium dicarba-*nido*-undecahydrononaborate(−2) salts and their carbon-substituted derivatives as suspensions in ether has been described previously.[1] Manganese pentacarbonyl halides were prepared by the method

TABLE IV

INFRARED SPECTRAL DATA (cm^{-1}) (NUJOL MULLS)

$(CH_3)_4N[B_6C_2H_8Mn(CO)_3]$

2490 s, 1970 s, 1930 s, 1890 s, 1365 m, 1128 m, 1085 w, 1065 m, 948 s, 895 w, 847 w, 828 m, 773 m, 743 m, 670 s, (1992 s, 1910 s)[a]

$(CH_3)_4N[B_6C_2H_6(CH_3)_2Mn(CO)_3]$

2480 s, 1974 s, 1865 s, 1365 s, 1283 w, 1272 w, 1120 w, 970 m, 945 s, 830 m, 775 w, 723 m (2076 s, 1978 s)[a]

$(CH_3)_4N[B_6C_2H_7(C_6H_5)Mn(CO)_3]$

2503 s, 1980 s, 1875 s, 1590 m, 1380 s, 1283 w, 1180 w, 1125 w, 1102 w, 1080 m, 950 s, 913 w, 848 w, 768 s, 737 m, 702 s, 677 m, 663 m (2000 s, 1925 s)[a]

[a] In tetrahydrofuran solution.

of Abel and Wilkinson.[3] Bis(pyridine)boronium iodide was prepared as reported by Ryschkewitsch.[4] Sodium hydride was obtained from Metal Hydrides, Inc., as a dispersion in mineral oil. Manganese and rhenium carbonyls were obtained from Strem Chemicals Co. All tetrahydrofuran and diethyl ether was freshly distilled from lithium aluminum hydride and collected under nitrogen. All manganese compounds were purified in an atmosphere of nitrogen.

Preparation of Salts of $B_6C_2H_8Mn(CO)_3^-$. (a) **The Reaction of $Na_2B_7C_2H_{11}$ with $Mn(CO)_5Br$.**—A solution of $Mn(CO)_5Br$ (2.72 g, 9.9 mmol) in 100 ml of tetrahydrofuran was added to an ethereal suspension of $Na_2B_7C_2H_{11}$ (10 mmol). The amber reaction mixture was heated vigorously for 6 hr, cooled, and filtered. Solvent was evaporated from the filtrate *in vacuo*. An ethereal solution of a major portion of the residue was shaken with a saturated aqueous solution of tetraethylammonium chloride, pentane was added, and the resulting precipitate was filtered and dried under vacuum. The dry salt was chromatographed on silica gel, eluting with dichloromethane. Recrystallization from dichloromethane–hexane yielded 1.53 g (40.7%) of amber $(C_2H_5)_4N[B_6C_2H_8Mn(CO)_3]$. A minor portion of the crude sodium salt was chromatographed on silica gel, eluting with dichloromethane–acetone. An aqueous solution of the residue was shaken with an excess of cesium chloride and the resulting precipitate was recrystallized from aqueous acetone and from ether–hexane yielding 0.14 g (3.7%) of $Cs[B_6C_2H_8Mn(CO)_3]$. The bis(pyridine)boronium salt was similarly prepared.

(b) **The Reaction of $Na_2B_7C_2H_{11}$ with $Mn_2(CO)_{10}$.**—A solution of $Mn_2(CO)_{10}$ (5.17 g, 13.1 mmol) in 100 ml of tetrahydrofuran was added to an ethereal suspension of $Na_2B_7C_2H_{11}$ (13 mmol) and the mixture was stirred for 26 hr at ether reflux. The brown reaction mixture was stripped to a tar from which residual $Mn_2(CO)_{10}$ (1.4 g) was extracted with hexane. The residue from the extraction was chromatographed on a polyamide column, eluting with 5% acetone–ether. Addition of aqueous tetramethylammonium chloride to an aqueous solution of the eluted material, filtration, and recrystallization from dichloromethane–ether yielded 0.23 g (7.8% calculated from $Mn_2(CO)_{10}$ consumed) of $(CH_3)_4N[B_6C_2H_8Mn(CO)_3]$.

Preparation of Salts of $B_6C_2H_6(CH_3)_2Mn(CO)_3^-$. (a) **By the Reaction of $Na_2B_7C_2H_9(CH_3)_2$ with $Mn(CO)_5Br$.**—A tetrahydrofuran solution of $Mn(CO)_5Br$ (2.05 g, 7.4 mmol) was added to an ethereal suspension of $Na_2B_7C_2H_9(CH_3)_2$ (7.1 mmol) and the mixture was heated under reflux for 6.5 hr. Solvent was removed *in vacuo*. An ethereal solution of the residue was shaken with an aqueous solution of $(C_2H_5)_4NCl$, pentane was added, and the mixture was filtered. Chromatography on silica gel, eluting with dichloromethane, followed by recrystallization from dichloromethane–ether yielded orange needles of $(C_2H_5)_4N[B_6C_2H_6(CH_3)_2Mn(CO)_3]$ (0.73 g, 25.4%). The product was converted to a tetramethylammonium salt by ion exchange and reprecipitation with the appropriate cation.

(b) **By the Reaction of $Na_2B_7C_2H_9(CH_3)_2$ with $Mn(CO)_5Cl$.**—Three grams of $Mn(CO)_5Cl$ (15 mmol) in 100 ml of tetrahydrofuran was added to an ethereal suspension of $Na_2B_7C_2H_9(CH_3)_2$ (15 mmol). The mixture was heated at reflux for 40 hr, cooled, and filtered. The residue from the filtrate was treated with an aqueous solution of tetramethylammonium chloride. The mixture was filtered and the precipitate was chromatographed on silica gel using an upflow technique. A brown-orange band was eluted with 8% acetone–92% dichloromethane, solvent was evaporated from the eluent, and the residual orange material was recrystallized from dichloromethane–ether to give 0.12 g (2.4%) of $(CH_3)_4N[B_6C_2H_6(CH_3)_2Mn(CO)_3]$.

Preparation of $(CH_3)_4N[B_6C_2H_7(C_6H_5)Mn(CO)_3]$.—A tetrahydrofuran solution of $Mn(CO)_5Br$ (2.70 g, 9.82 mmol) was added to an ethereal suspension of $Na_2B_7C_2H_{10}(C_6H_5)$ (9.6 mmol). The resulting mixture was heated under reflux for 15 hr, cooled, and filtered. Solvent was evaporated from the filtrate and the residue was chromatographed on silica gel by an upflow technique. An amber material was eluted with dichloromethane and was converted to a tetramethylammonium salt by aqueous precipitation. Recrystallization from dichloromethane–ether–hexane yielded 1.32 g of $(CH_3)_4N[B_6C_2H_7(C_6H_5)Mn(CO)_3]$ (35.5%).

Equivalent Weight Determination.—A solution consisting of approximately 0.25 mmol of the tetramethylammonium salts of the B_6 manganese carbonyl derivatives in 50% aqueous acetone was run through an acid ion-exchange column (0.5 × 10 in. Dowex 50W-X12, 50–100 mesh). The materials were eluted with 30 ml of 50% aqueous acetone and then with distilled water. The eluents were titrated with standard sodium hydroxide solution. The titrations were typical of strong acids, with the exception of the dimethyl derivative, which appeared to decompose.

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Ionization Potentials of Some Sulfur Compounds

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Although there are many experimental observations which tend to support the idea that divalent sulfur atoms can act as electron acceptors when bonded to, for example, aromatic systems and carbanions[1] and that sulfur-chain compounds and radicals such as $CH_3S_x\cdot$ ($x > 1$) are stabilized by resonance interaction with adjacent sulfur atoms,[2,3] little quantitative information about the extent of delocalization of the formally non-

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