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Studies of Metallaborane Complexes. Synthesis and Selected Reactions of 2,2,2-$(CO)_3$-2-MnB_5H_{10}

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Reaction of B_5H_9 with $HMn(CO)_5$ (or H_2 and $Mn_2(CO)_{10}$) at elevated temperatures produces 2,2,2-$(CO)_3$-2-MnB_5H_{10}, in which the $(CO)_3Mn$ moiety is bound by two M–H–B bridge hydrogen bonds to the basal borons of a pentagonal-pyramidal cluster and by another bond to the apical boron. Spectroscopic studies indicate the molecule has C_s symmetry. Reaction of this with Br_2 produces the apically substituted derivative 1-Br-2,2,2-$(CO)_3$-2-MnB_5H_9, while the anion 2,2,2-$(CO)_3$-2-$MnB_5H_9^-$ is prepared by removal of a bridging hydrogen, as H^+, from a position on the mirror plane between basal boron atoms.

Introduction

In recent years many new metallaboranes have been prepared, and several reviews illustrate the many types of metal–boron bonding modes that exist.[1-9] Known manganaboranes include $LMn(CO)_4BH_3^-$ (L = CO and $P(C_6H_5)_3$),[10] $(CO)_4MnB_3H_7X$ (X = H, halogen),[11a,b] $(CO)_3MnB_3H_8$,[11] 2-$[Mn(CO)_5]B_5H_8$,[12] $(CO)_3MnB_8H_{13}$,[13] $(CO)_3MnB_9H_{12}L$ (L = ether,[14] H^-,[14] or $-O(CH_2)_4N(C_2H_5)_3$[15]), and $HMn_3(CO)_{10}(BH_3)_2$.[16] In addition, $Mn(CO)_5BH_4$[17] and $Li^+(B_5H_5)Mn(CO)_3^{-2}$ have been reported but not fully characterized. Less attention has been paid to the chemistry of metallaboranes.

Investigations of the trace products in the reaction of $Mn(CO)_5Br$ with KB_9H_{14} lead to the discovery of a new stable manganaborane,[18] subsequently identified as 2,2,2-$(CO)_3$-2-MnB_5H_{10}, which is a formal structural analogue of hexaborane(10), B_6H_{10}.[19] We report here our investigations of rational synthetic routes to 2,2,2-$(CO)_3$-2-MnB_5H_{10}, its spectral characterization, and its reactions to form the derivatives 1-Br-2,2,2-$(CO)_3$-2-MnB_5H_9 and 2,2,2-$(CO)_3$-2-$MnB_5H_9^-$ anion.

Experimental Section

Air-sensitive compounds were handled by using inert-atmosphere or high-vacuum techniques.[20] Pentane, isopentane, benzene, diethyl ether, and tetrahydrofuran were dried over $LiAlH_4$. CH_2Cl_2 was dried over 3-Å molecular sieves. Reaction solvents were vacuum distilled before use. The deuterated solvents used in NMR studies were treated in the same manner as their protonic counterparts, except for diethyl-d_{10} ether, which was treated with diborane.

Reactants $Mn_2(CO)_{10}$,[21] $HMn(CO)_5$,[22] $Mn(CO)_5Br$,[23] B_2H_6,[24] KB_9H_{14},[25] and 2-$[Mn(CO)_5]B_5H_8$[26] were prepared by standard methods. B_5H_9 was from laboratory stock. $B_{10}H_{14}$, from laboratory stock, was sublimed before use. All other chemicals were reagent grade and were used as received.

The ultraviolet irradiation was accomplished by using a 450-W photochemical immersion lamp (No. 6515-34, medium pressure, Hanovia).

Low-resolution (±10 cm^{-1}) infrared spectra were obtained on a Perkin-Elmer Model 700 infrared spectrophotometer using cells with NaCl windows. Low-temperature infrared spectra were obtained by coating a thin film of the compound on a 1 mm thick IRTRAN2 (ZnS) window in vacuo at −196 °C. The ultraviolet and visible spectra were recorded on a Cary 14 UV spectrophotometer. Mass spectra were obtained by using an AEI MS 902 spectrometer. The NMR spectra were obtained on a Bruker WH-270 spectrometer, operating at 270.071 MHz (^1H) and 86.653 MHz (^{11}B), controlled by a Nicolet Instruments B-NC 12 computer. Selective ^{11}B decoupling of ^1H spectra was accomplished with a Bruker Type B-FS 100 frequency synthesizer, a Bruker B-BM1 broad-band modulator, and a B-LV 80 selective power amplifier.

Table I. Infrared Frequencies of $(CO)_3MnB_5H_{10}$ and Its Derivatives in cm^{-1} [a]

$(CO)_3MnB_5H_{10}$ (gas phase)	2615 w, 2565 w, 2090 ms, 1995 s, 1500 vvw, 1390 vvw, 1370 vvw, 1080 vvw, 1025 vvw, 880 vvw, 790 vvw
$(CO)_3MnB_5H_{10}$ (thin film, −196 °C)	2595 s, 2540 s, 2065 s, ~1970 vs, br, 1900 vw, 1790 vw, br, 1770 vw, br, 1740 vw, br, 1595 vw, 1495 s, 1400 s, 1380 s, 1360 m, sh, 1310 w, 1200 vw, 1115 vw, 1075 s, 1020 s, 970 vw, 950 w, 905 m, 875 s, 860 w, sh, 795 s, sh, 785 s, 740 w, 715 m
$(CO)_3MnB_5H_9Br$ (KBr mull)	2610 m, 2580 m, 2100 s, 1950 vs, br, 1490 mw, 1440 w, 1340 w, 1320 vw, 1070 mw, 1015 mw, 900 m, 880 m, 830 w, 820 vw, 790 w, 775 vw, 715 w, 650 m
$[(n\text{-}C_4H_9)_4N]$-$[(CO)_3MnB_5H_9]$ (CH_2Cl_2 soln)	2930 vs, 2910 vs, sh, 2860 s, 2500 vs, 1990 vs, 1920 vs, br, 1900 vs, br, 1460 m, 1390 w, 1350 vw, 1160 mw, 1120 w, 1075 mw, 1030 w, 990 w, 820 vw

[a] ±10 cm^{-1}.

Synthesis of 2,2,2-$(CO)_3$-2-MnB_5H_{10}. A. Pyrolysis of $Mn_2(CO)_{10}$, B_5H_9, and H_2. A 300-mL cylindrical flask was equipped with a side arm consisting of a 19/38 standard taper joint and a constriction for sealing the reaction mixture and a tube containing a break-tip for subsequent removal of volatile compounds after reaction. The flask was loaded with 2.25 g (5.78 mmol) of $Mn_2(CO)_{10}$, evacuated, and then cooled with liquid nitrogen, and 11.6 mmol of B_5H_9 was added by condensation. Finally, the flask was charged with 376 torr (6.1 mmol) of H_2, sealed at the constriction, warmed to room temperature, and then heated in an oven at 140 °C for 136 h. The flask was reattached to the vacuum line and cooled in liquid nitrogen, and the breaktip was broken. The amount of noncondensable gas amounted to 7.1 mmol, an increase of 1.0 mmol. The volatile contents of the flask were then distilled into traps cooled to −63 and −196 °C in series. The −196 °C trap contained a mixture of B_5H_9 and $HMn(CO)_5$. The −63 °C trap contained the 2,2,2-$(CO)_3$-2-MnB_5H_{10}, which was further purified by passage through a −30 °C trap. The product is a yellow liquid having a melting range of −2.5 to −2.3 °C and a vapor pressure of less than 1 torr at ambient temperature. It is relatively stable in air, decomposing slowly over a period of weeks. It is not appreciably soluble in water but is very soluble in nonpolar solvents, including stopcock greases. Infrared, ^1H NMR, and ^{11}B NMR spectra of 2,2,2-$(CO)_3$-2-MnB_5H_{10} and its derivatives are tabulated in Tables I, II, and III, respectively. The $Mn_2(CO)_{10}$ recovered from the reaction flask and the −30 °C trap amounted to 1.74 g; thus 0.51 g (1.31 mmol) of $Mn_2(CO)_{10}$ was consumed. The product, which passed through the −30 °C trap, amounted to 0.050 g (0.24 mmol), a 9.3% yield based on $Mn_2(CO)_{10}$ consumed according to reaction 1. At temperatures much above 140 °C $B_{10}H_{14}$ is coproduced (see synthesis B).

B. Hot–Cold Pyrolysis of $HMn(CO)_5$ and B_5H_9. A reactor consisting of a 34 cm long cylindrical Pyrex tube of 3.5-cm o.d. equipped with a Kontes 4-mm O-ring stopcock was loaded with 1.13 g (5.77 mmol) of $HMn(CO)_5$ and 23 mmol of B_5H_9. The reactor was clamped in a vertical position, and the upper portion of the tube was heated to 220 °C for 3.5 h while the bottom was maintained at ambient temperature. The reactor was cooled to −196 °C, and 2.6

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Table II. ^{11}B NMR Spectra (86.653 MHz)

compd	solvent	B(3,6)[a]	B(4,5)	B(1)
2,2,2-$(CO)_3$-2-MnB_5H_{10}	C_6D_6	+31.84 b {140, 870} [2]	+11.27 (156) {156, 44 t} [2]	−53.70 (142) [1]
2,2,2-$(CO)_3$-2-MnB_5H_{10}	CD_2Cl_2	+32.37 b {137, 72} [2]	+11.63 (161) {155, 48 t}	−53.45 (146) [1]
1-Br-2,2,2-$(CO)_3$-2-MnB_5H_9	C_6D_6	+32.06 b {70 m} [2]	+11.05 (161) {161, estd 41 t} [2]	−39.56 s [1]
Na[2,2,2-$(CO)_3$-2-MnB_5H_9]	$(C_2D_5)_2O$	+32.00 b {59 d} [2]	+17.57 b [2]	−43.85 (122) [1]
[$(n\text{-}C_4H_9)_4N$][2,2,2-$(CO)_3$-2-MnB_5H_9]	CD_2Cl_2	+31.12 b [2]	+20.92 b [2]	−41.32 (119) [1]

[a] Values are chemical shifts in ppm with positive values downfield from $BF_3 \cdot O(C_2H_5)_2 = 0$: *J. Organomet. Chem.*, **131**, C43 (1977); values in parentheses are coupling constants in Hz; values in braces are coupling constants in Hz available only from the line-narrowed or selectively decoupled data; values in brackets are relative areas; b = broad, d = apparent "doublet", m = multiplet, s = singlet, t = triplet.

Table III. ^{1}H NMR Spectra (270 MHz)

compd	solvent	H(3,6)[a]	H(4,5)	H(1)	H(BHB)	H(MHB)
2,2,2-$(CO)_3$-2-MnB_5H_{10}	C_6D_6	+5.11 (148) [2]	+3.92 (159) [2]	−1.11 (144) [1]	−1.24 b [3]	−12.25 (84) [2]
2,2,2-$(CO)_3$-2-MnB_5H_{10}	CD_2Cl_2	+5.21 (140) [2]	+4.08 (155) [2]	−1.43 (145) [1]	−0.37 b [2] −0.67 b [1]	−11.67 (77) [2]
1-Br-2,2,2-$(CO)_3$-2-MnB_5H_9	C_6D_6	+5.52 (137) [2]	+4.27 (162) [2]	...	−0.39 (24) [2] −0.89 b [1]	−12.01 (74) [2]
Na[2,2,2-$(CO)_3$-2-MnB_5H_9]	$(C_2D_5)_2O$	+5.42 (169) [2]	+4.00 (estd 170) [2]	−2.08 (130) [1]	−3.00 b [2]	−12.06 (47) [2]
[$(n\text{-}C_4H_9)_4N$]-[2,2,2-$(CO)_3$-2-MnB_5H_9]	CD_2Cl_2	*b*	*b*	*b*	−2.74 b [2]	−11.64 b [2]

[a] Values are chemical shifts in ppm with positive values downfield from $(CH_3)_4Si$; values in parentheses are coupling constants, real or, in the case of H(BHB) or H(MHB), apparent, in Hz; values in brackets are relative areas; H(1, 3–6) resonances are quartets; H(MHB) are apparent doublets or broad singlets; b = broad singlet. [b] Obscured by $(n\text{-}C_4H_9)_4N^+$ and CH_2Cl_2 resonances.

mmol of noncondensable gases was measured. The volatile contents of the reactor were separated as above to yield 2,2,2-$(CO)_3$-2-MnB_5H_{10} contaminated with $B_{10}H_{14}$ and $Mn_2(CO)_{10}$. The $B_{10}H_{14}$ contamination presented a problem in that its volatility is virtually identical with that of the $(CO)_3MnB_5H_{10}$. The product was therefore purified by preparative thin-layer chromatography on silica gel. The eluting solvent was 5% dichloromethane in isopentane. The yellow band contained low yields of the product, which was extracted from the silica gel with CH_2Cl_2 and further purified on the vacuum line.

C. Photolysis of $Mn_2(CO)_{10}$, B_5H_9, and H_2. A quartz reaction flask of approximately 225-mL volume was loaded with 2.02 g (5.18 mmol) of $Mn_2(CO)_{10}$, evacuated, and cooled to −196 °C, and 11.0 mmol of B_5H_9 and ca. 20 mL of isopentane were condensed in. The flask was then charged with 470 torr (5.7 mmol) of H_2, sealed, allowed to thaw, and irradiated at ca. 20 °C with the Hanovia lamp for 25 h. The flask was then cooled to −196 °C and opened to the vacuum line, and the volatile contents were separated as above. The modest yield of $(CO)_3MnB_5H_{10}$ was not measured.

Synthesis of 1-Br-2,2,2-$(CO)_3$-2-MnB_5H_9. A solution of 0.1018 g (0.501 mmol) of $(CO)_3MnB_5H_{10}$ in ca 1 mL of dichloromethane in a 50-mL reaction flask (containing a magnetic stir bar) was cooled to −196 °C, the flask was evacuated, and 0.05 mL (0.52 mmol) of bromine was condensed onto the solution. The flask was then quickly warmed to −78 °C and then to ambient temperature over 4 h while the solution was stirred. The orange solution was cooled to −196 °C, and 0.7 mmol of noncondensable gases was measured. The volatile flask contents were distilled into traps cooled to −63, −125, and −196 °C in series. The −196 °C trap contained HBr, and the −125 °C trap contained dichloromethane. The −63 °C trap contained a light yellow solid, presumably $Mn_2(CO)_{10}$, and trace amounts of $(CO)_3MnB_5H_{10}$. The residual solids in the reaction flask were dissolved in dichloromethane and preabsorbed onto Florisil. The preabsorbed Florisil was placed on the top of a Florisil liquid-chromatography column. Elution with heptane removed starting material. Dichloromethane–heptane (1:3) eluted an orange band, which upon evaporation left an orange solid, which was sublimed at room temperature onto a 0° °C cold finger to yield 0.0382 g (0.136 mmol or 27%) of 1-Br-2,2,2-$(CO)_3$-2-MnB_5H_9, which is relatively air stable, decomposing slowly over a matter of months. It has a melting range of 112–115 °C with no apparent decomposition and is soluble in dichloromethane, alkanes, and benzene.

Synthesis of Na[2,2,2-$(CO)_3$-2-MnB_5H_9]. A 50-mL round-bottom reaction flask containing a magnetic stirring bar and equipped with a 4-mm O-ring stopcock and a side arm attached to a 12-mm o.d. type C frit which in turn was attached to a 5-mm o.d. Pyrex NMR tube and was loaded in a nitrogen-filled glovebag with 0.5 g (1.2 mmol as 57%) of NaH in oil dispersion. The NaH was washed three times with anhydrous diethyl ether. After the washings were decanted, the flask was evacuated for several hours, filled with dry nitrogen, and cooled in liquid nitrogen, and a solution of 0.1355 g (0.667 mmol) of $(CO)_3MnB_5H_{10}$ in 2 mL of diethyl-d_{10} ether was syringed onto the frozen portion of the flask, away from contact with the sodium hydride. The flask was reevacuated, and the orange solution was allowed to thaw in contact with the sodium hydride while being stirred. After 20 min of stirring at room temperature, the dark red solution was refrozen, and 0.27 mmol of noncondensable gas was measured. The solution was then filtered through the frit into the NMR tube, cooled to −78 °C, and sealed for subsequent NMR analysis.

Synthesis of [$(n\text{-}C_4H_9)_4N$][2,2,2-$(CO)_3$-2-MnB_5H_9]. A solution of 0.1360 g (0.670 mmol) of $(CO)_3MnB_5H_{10}$ in 2 mL of diethyl ether was reacted with 0.06 g (1.3 mmol or 57%) of sodium hydride in oil dispersion in the same manner as previously described. The filtered solution was then added to a 50-mL round-bottom flask with a stir bar, a 24/40 standard taper joint, and a side arm connected to a 22-mm o.d. type C frit which in turn was connected to a 30-mL round-bottom flask equipped with a stir bar and a 4-mm O-ring stopcock. In the first chamber was 0.2172 g (0.674 mmol) of $(n\text{-}C_4H_9)_4NBr$, which mixed with the Na[$(CO)_3MNB_5H_9$] solution and metathesized. The solution was then filtered through the frit into the second chamber, and the diethyl ether was removed. Dichloromethane-d_2 was condensed into the second chamber, and the resulting solution of the metathesis product was analyzed by NMR.

Ultraviolet Spectra. Solutions of $(CO)_5MnB_5H_{10}$ pentane gave a maximum at 340 nm (ε 1965) and an inflection point at 234 nm (ε 15 260). Solutions of $(CO)_3MnB_5H_9Br$ in pentane gave maxima at 345 nm (ε 1507) and 293 nm (ε 3316) and an inflection point at 245 nm (ε 5994). Solutions of [$(n\text{-}C_4H_9)_4N$][$(CO)_3MnB_5H_9$] in dichloromethane gave an inflection point at 345 nm and a maximum at 309 nm. A possible absorption occurs near the solvent cutoff (235 nm).

Mass Spectra. The 70-eV mass spectra of $(CO)_3MnB_5H_{10}$ and $(CO)_3MnB_5H_9Br$ follow the pattern established for metal carbonyl metallaboranes.[14] Exact parent peak mass determinations established molecular weights: calculated for $(^{12}C^{16}O)_3{}^{55}Mn^{11}B_5{}^{1}H_{10}$ 204.0476, found 204.0482; calculated for $(^{12}C^{16}O)_3{}^{55}Mn^{11}B_5{}^{1}H_9{}^{79}Br$ 281.9581, found 281.9592.

Results and Discussion

Preparation of 2,2,2-$(CO)_3$-2-MnB_5H_{10}. Initially, $(CO)_3MnB_5H_{10}$ was found as a trace product in the reaction of $Mn(CO)_5Br$ with KB_9H_{14} in refluxing tetrahydrofuran.[27] Subsequently modest yields of the product were obtained in the reaction of $HMn(CO)_5$ and B_5H_9 in a hot–cold reactor operating at 220/22 °C. The route used most successfully in this study, however, was the pyrolysis of $Mn_2(CO)_{10}$, B_5H_9, and H_2 at 130–150 °C. Modest yields could be obtained in the photolysis of $Mn_2(CO)_{10}$ and B_5H_9 in isopentane in an

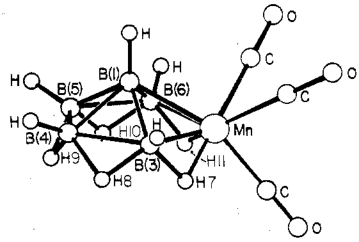


Figure 1. Proposed structure of 2,2,2-$(CO)_3$-2-MnB_5H_{10}. Terminal hydrogens are numbered the same as the boron to which they are attached.

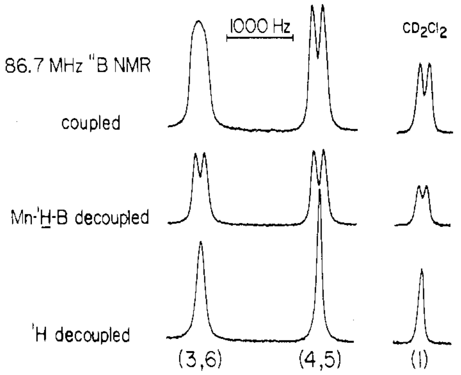


Figure 2. ^{11}B NMR spectra of 2,2,2-$(CO)_3$-2-MnB_5H_{10} in CD_2Cl_2 solution. Boron assignments are below each resonance.

atmosphere of hydrogen. A minor amount of $(CO)_3MnB_5H_{10}$ has been obtained recently in the pyrolysis of 2-[$Mn(CO)_5$]B_5H_8 in hydrogen at 130 °C. The proposed reactions are

$$Mn_2(CO)_{10} + H_2 + 2B_5H_9 \xrightarrow{130/150\ ^\circ C} 2(CO)_3MnB_5H_{10} + 4CO \quad (1)$$

$$HMn(CO)_5 + B_5H_9 \xrightarrow[\text{hot-cold}]{220/22\ ^\circ C} (CO)_3MnB_5H_{10} + 2CO \quad (2)$$

$$Mn_2(CO)_{10} + H_2 + 2B_5H_9 \xrightarrow[i\text{-}C_5H_{12}]{h\nu} 2(CO)_3MnB_5H_{10} + 4CO \quad (3)$$

$$2\text{-}[Mn(CO)_5]B_5H_8 + H_2 \xrightarrow{130\ ^\circ C} (CO)_3MnB_5H_{10} + 2CO \quad (4)$$

The NMR spectra of $(CO)_3MnB_5H_{10}$ are consistent with a structure based on a pentagonal pyramid in which one of the basal positions is occupied by the manganese (position 2) and the remaining positions are occupied by boron atoms (positions 1, 3–6) as shown in Figure 1. The result is a molecule with C_s-*m* symmetry, with a carbonyl group, manganese, B(1), H(1), and H(9) on the mirror plane.

The ^{11}B NMR spectrum of $(CO)_3MnB_5H_{10}$ (Figure 2), showing three types of boron in a ratio of 2:2:1, is tabulated in Table II. All these resonances become sharp singlets upon broad-band ^1H decoupling. Upon ^1H decoupling at a frequency corresponding to M–H–B bridge resonances (vide infra), the unresolved low-field resonance becomes a doublet with a coupling constant of 132 Hz. Figure 3 shows the results obtained when the normal spectrum is line narrowed. The low-field resonance resolves into a doublet of doublets with coupling constants of 140 and 70 Hz, attributed to $B(3,6)H_t$ and $B(3,6)H_{\mu\text{-}M}$, respectively. The midfield doublet (at +11.27 ppm) resolves into a doublet of triplets with coupling constants of 156 and 44 Hz, respectively. The major doublet is attributed to $B(4,5)H_t$ and the minor "triplet" to nearly equivalent coupling to the two adjacent bridging hydrogen atoms.

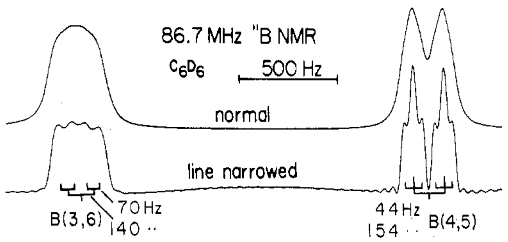


Figure 3. Expanded and line-narrowed ^{11}B NMR spectra (low-field resonances) of 2,2,2-$(CO)_3$-2-MnB_5H_{10} in C_6D_6 solution. The small couplings arise from adjacent bridge hydrogens; the large couplings, from terminal hydrogens.

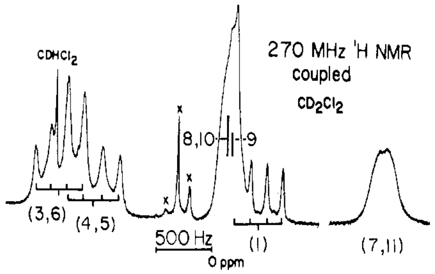


Figure 4. ^1H NMR spectrum of 2,2,2-$(CO)_3$-2-MnB_5H_{10} in CD_2Cl_2 solution. Assignments based on selective decoupling experiments are indicated in parentheses.

The ^1H NMR spectra (Figure 4 show three quartets typical of hydrogens terminally bound to ^{11}B ($I = {}^3/_2$) in relative area ratios of 2:2:1, corresponding to the three different types of boron. The broad resonance at δ –0.45 of relative area 3 is typical of B–H–B bridge hydrogens. A broad resonance at δ –11.7 of relative area 2 is typical of hydrogens bridging between a transition metal and a boron atom.[28] Residual coupling can be observed in this resonance of 77–84 Hz which seems to match the coupling observed in other M–H–B resonances of M–B_3H_8 complexes[11] and M–B_5H_{10} complexes.[29,30]

Selectively decoupling the different ^{11}B resonances allows individual boron–hydrogen assignments within the ^1H NMR spectrum. For example, upon decoupling B(4,5), the quartet at δ +4.07 becomes a singlet and the broad resonance of area 3 at δ –0.45 resolves into two peaks of areas 2:1 at δ –0.37 and –0.66, respectively, corresponding to the two types of B–H–B hydrogens.

The ^{11}B NMR spectrum of $(CO)_3MnB_5H_9Br$ strongly resembles that of $(CO)_3MnB_5H_{10}$. Instead of a high-field doublet at –53.70 ppm, however, the brominated derivative has a singlet at –39.56 ppm. The bromine is thus in an apical position on the mirror symmetry plane of the molecule. Upon ^1H decoupling at a frequency corresponding to M–H–B bridge resonances (vide infra), the lowest field resonance at +32.06 ppm becomes a doublet with a coupling constant of 137 Hz.

The ^1H NMR spectrum of $(CO)_3MnB_5H_9Br$ closely resembles the ^1H NMR spectrum of the parent. The bridge hydrogen resonances are unobscured, however, and two resonances, one half the height of the other, are observed. The larger bridge hydrogen resonance, assigned to H(8,10), contains two maxima with a separation of 34 Hz.

The ^{11}B NMR spectrum of Na[$(CO)_3MnB_5H_9$] in $(C_2D_5)_2O$ has three resonances in the ratio 2:2:1; however, there are several differences from the parent. In the fully coupled spectrum, the only resolved coupling is in the high-field resonance at –43.85 ppm with a coupling constant of 122 Hz, compared to the equivalent resonance of the parent at –53.70 ppm with a coupling constant of 142 Hz. The tetrabutylammonium salt in CD_2Cl_2 has the equivalent resonance at

Table IV. NMR Spectra of Related Metallaboranes

^{11}B NMR	B(3,6)	B(4,5)	B(1)
2,2,2-$(CO)_3$-2-MnB_5H_{10}[a]	+32.3 (140, 70)[i]	+11.6 (154, 44 (t))	−53.4 (147)
2,2,2-$(CO)_3$-2-FeB_5H_9[b]	+46.1 (150)	+8.6 (150)	−47.2 (140)
2-(η^5-C_5H_5)-2-FeB_5H_{10}[c]	+44.4 (145)	+8.2 (146)	−53.0 (140)
2,2′-*commo*-$Be(B_5H_{10})_2$[d]	−8.1 (127, 98)	+5.3 (159)	−54.6 (139)
B_6H_{10}[e]	+13.5 (171)		−55.2 (180)
2-CB_5H_9[f]	+15.4 (158, 36)	−4.7 (159)	−51.8 (155)

^1H NMR	H(3,6)	H(4,5)	H(1)	H(BHB)	H(MHB)
2,2,2-$(CO)_3$-2-MnB_5H_{10}[a]	+5.2 (145)	+4.1 (154)	−1.5 (145)	−0.4, −0.7	−11.7
2,2,2-$(CO)_3$-2-FeB_5H_9[b]	+6.40	+4.19	−1.19	+0.10	−16.82
2,2,2-$(CO)_3$-2-$FeB_5H_8^-$[b]	*h*	*h*	*h*	*h*	−16.0
2-(η^5-C_5H_5)-2-FeB_5H_{10}[c]	+6.96 (147)	+3.86 (153)	−0.55 (141)	−1.70, −2.33	−15.99
2,2′-*commo*-$Be(B_5H_{10})_2$[d]	+2.52 (130)	+3.53 (152)	−0.03 (140)	−1.28, −2.47	+2.36
B_6H_{10}[g]	+4.16		−1.27	−1.10	

[a] This work. [b] Reference 34. [c] Reference 29. [d] Reference 30b. [e] J. L. Walsh, measurement done at University of Wisconsin on a Bruker WH-270 at 86.653 MHz. [f] G. B. Dunks and M. F. Hawthorne, *Inorg. Chem.*, **8**, 2667 (1969). [g] V. T. Brice, H. D. Johnson II, and S. G. Shore, *J. Am. Chem. Soc.*, **95**, 6629 (1973). [h] Unreported. [i] Shifts are measured in ppm; positive values downfield, from reference, $BF_3 \cdot O(C_2H_5)_2$ for ^{11}B and $(CH_3)_4Si$ for ^1H; values in parentheses are measured in Hz.

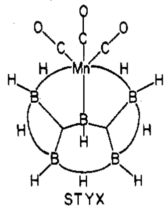
−41.32 ppm with a coupling constant constant of 119 Hz. The two lowest field broad resonances of the sodium salt are at +32.00 and +17.57 ppm. The equivalent broad resonances of the tetrabutylammonium salt are at +31.12 and +20.92 ppm. In comparison, the equivalent resonances of the parent in CD_2Cl_2 are at +32.37 and +11.63 ppm, and the +11.63-ppm resonance is a clear doublet with a coupling constant of 161 Hz. Upon ^1H decoupling at a frequency corresponding to M–H–B resonances, the +32.00-ppm resonance of the sodium salt develops two maxima with a separation of 59 Hz while the resonance at +17.57 ppm remains unaltered.

In the ^1H NMR spectrum of $Na[(CO)_3MnB_5H_9]$ in $(C_2D_5)_2O$, the two lowest field quartet resonances depart from ideality, which has been attributed[11b] to additional proton coupling to ^{10}B (20% abundance, $I = 3$, $J_{^1H-^{10}B} \approx 0.33J_{^1H-^{11}B}$) as well as line-shape dependence on nuclear quadrupole effects.[31,32] Upon selective decoupling of the different ^{11}B resonances, assignments have been established for the various resonances in the ^1H spectrum. The areas of the B–H–B and M–H–B hydrogens appear equal, and as there are no differences between spectra taken at −60 °C and spectra at ambient temperatures and distinct resonances can be seen for all types of hydrogens, a static structure of the anion is proposed. As the B–H–B resonance is sharp when either basal boron is decoupled, only one type of B–H–B is present, and it is proposed that the proton that is removed from the parent molecule is the one that lies between B(4) and B(5) on the molecular mirror plane.

Bonding. The bonding in these compounds can be considered from different viewpoints: the effective atomic number (EAN) rule, polyhedral skeletal electron-pair theory (Wade's rules),[19] or Lipscomb's *styx* representations.[33] The compound can be formally considered as a $(CO)_3Mn^0$ moiety with a $B_5H_{10}^0$ ligand or a $(CO)_3Mn^+$ moiety with a $B_5H_{10}^-$ ligand. The former assignment requires that the Mn, having seven electrons, acquire eleven more. Three carbonyls provide six electrons, and the borane ligand provides five.

The polyhedral skeletal electron-pair theory counts the electrons of the molecule as follows: five $B-H_t$ groups contribute ten electrons to the polyhedron (two electrons per B–H), five bridge hydrogens contribute five electrons, and the $Mn(CO)_3$ moiety contributes one electron, for a total of sixteen electrons or eight pairs. There are six vertices (one manganese and five borons); therefore the number of skeletal electron pairs is 2 in excess of the number of vertices, resulting in a nido cage. A nido six-membered cage in borane chemistry is a pentagonal pyramid. The compound is skeletally isoelectronic to hexaborane(10), B_6H_{10}.

Application of the Lipscomb topological theory indicates the most likely *styx* representation for B_6H_{10} to be 4220; by analogy, $(CO)_3MnB_5H_{10}$ would be 5210.



STYX
5210

Comparison to Other Metallaboranes. There are a few other 2-metallahexaboranes of general formula MB_5H_{8+x} in which a heteroatom replaces a boron in a basal position of a pentagonal pyramid. Most of these compounds are listed in Table IV, along with a comparison of their ^{11}B and ^1H NMR chemical shifts. For the sake of comparison, B_6H_{10} and CB_5H_9 are included in the ^{11}B listing, and B_6H_{10} is listed in the ^1H listing. It is interesting to note the effect of substituting a transition metal for a boron upon the chemical shift of the borons and the hydrogens adjacent to the metal. Surprisingly, the substitution has little effect upon the chemical shift of the apical boron. If the substituent is not a transition metal, the chemical shift of B(3,6) increases to higher field with the more electropositive substituent, while the hydrogens bridging between these borons and the substituent shift to lower field. In the carborane, the reverse trend occurs. In transition metallaboranes, the B(3,6) resonance is located 20–30 ppm further downfield than the basal boron resonance in B_6H_{10}. Similarly, the M–H–B bridge hydrogens resonate at least 10 ppm to a higher field than the bridge hydrogens in B_6H_{10}.

The 2,2,2-$(CO)_3$-2-MnB_5H_{10} molecule is usually stable to oxidation and hydrolysis. Its stability is due perhaps to the fact that the open face of the pentagonal pyramid has each boron–boron or boron–manganese edge bridged with a hydrogen, rendering nucleophilic attack on the metallaborane cage difficult. The manganadecaboranes[14,15] are also quite stable, perhaps as a result of similar shielding of the metallaborane cage's open face by bridge hydrogens. The only other manganaborane with similar stability is $HMn_3(CO)_{10}(BH_3)_2$,[16] in which the boron atoms are well protected by $Mn(CO)_3$ and $Mn(CO)_4$ groups.

Mechanism of Formation. Although a detailed mechanism is unknown for the production of $(CO)_3MnB_5H_{10}$, evidence seems to indicate three factors. First, $HMn(CO)_5$ appears to be a necessary reactant. Second, the borane reactant preferably should already have all five boron atoms. Third, borane growth reactions that require more than two reacting molecules to form the final product are improbable.

The evidence for the first factor is that each synthesis attempt has had $HMn(CO)_5$ present either as a reagent or as a byproduct.[35] Thus a first step in the reactions involving $Mn_2(CO)_{10}$ is postulated to be

$$Mn_2(CO)_{10} + H_2 \rightleftharpoons 2HMn(CO)_5{}^{36} \qquad (5)$$

A pyrolysis reaction involving B_5H_9 and $Mn_2(CO)_{10}$, but no initial hydrogen, produced only a trace of $(CO)_3MnB_5H_{10}$; however, hydrogen was coproduced and could react with the $Mn_2(CO)_{10}$ to make $HMn(CO)_5$ which in turn could then react with B_5H_9. A pyrolysis reaction of B_2H_6 and $Mn_2(CO)_{10}$ also produced B_5H_9, $HMn(CO)_5$, H_2, and a trace of $(CO)_3MnB_5H_{10}$.[35]

In support of the second factor, the previously mentioned pyrolysis of B_2H_6 and $Mn_2(CO)_{10}$ produced only a trace of $(CO)_3MnB_5H_{10}$. The third factor is supported by the evidence of the second factor along with the investigations by Chen and Gaines of pyrolyses of $(CO)_4MnB_3H_8$ with B_5H_9 or $B_{10}H_{14}$ producing traces of $(CO)_3MnB_5H_{10}$.[37]

A possible intermediate might be 2-$[Mn(CO)_5]B_5H_8$, which could obtain H_2 from the reaction atmosphere to produce the final product:

$$HMn(CO)_5 + B_5H_9 \rightleftharpoons 2\text{-}[Mn(CO)_5]B_5H_8 + H_2 \qquad (6)$$

$$2\text{-}[Mn(CO)_5]B_5H_8 + H_2 \rightarrow (CO)_3MnB_5H_{10} + 2CO \qquad (7)$$

In support of this mechanism, pyrolysis of 2-$[Mn(CO)_5]B_5H_8$ and H_2 did produce $(CO)_3MnB_5H_{10}$ as well as B_5H_9 and $HMn(CO)_5$,[35] suggesting a possible reversible reaction in eq 6 as well as evidence for eq 7.

Reactions of 2,2,2-$(CO)_3$-2-MnB_5H_{10}. Bromine reacts with $(CO)_3MnB_5H_{10}$ to replace the hydrogen attached to the apical boron, according to reaction 8. The molecular symmetry of

$$2,2,2\text{-}(CO)_3\text{-}2\text{-}MnB_5H_{10} + Br_2 \xrightarrow[CH_2Cl_2]{-78\text{ to }-22\text{ °C}} 1\text{-Br-}2,2,2\text{-}(CO)_3\text{-}2\text{-}MnB_5H_9 + HBr \qquad (8)$$

the parent is preserved, and the NMR spectra of the parent and the brominated derivative are remarkably similar.

This reaction is unique in that hexaborane(10), by comparison, brominates in a basal position,[38] and the only other brominated derivative of a metallahexaborane is $B_5H_{10}BeBr$ in which the bromine is attached to the beryllium.[30b] The only 1-substituted hexaboranes are synthesized by boron insertion reactions using $H_2BCl{\cdot}O(C_2H_5)_2$ and $(CH_3)_3M^{IV}{-}B_5H_7^-$ anions (M^{IV} = Si, Ge).[39]

The reaction of 6,6,6-$(CO)_3$-6-$MnB_9H_{13}^-$ with iodine in tetrahydrofuran under some conditions produces 2-I-6,6,6-$(CO)_3$-6-$MnB_9H_{12}^-$.[27b] The electrophilic reactivity of the apical boron in $(CO)_3MnB_5H_{10}$ may be related to the fact that it is σ bonded to the adjacent manganese with no intervening bridging hydrogen.

Sodium hydride reacts with $(CO)_3MnB_5H_{10}$, to remove a bridging hydrogen between B(4) and B(5) as H^+.

$$2,2,2\text{-}(CO)_3\text{-}2\text{-}MnB_5H_{10} + NaH \xrightarrow[(C_2H_5)_2O]{-196\text{ to }-22\text{ °C}} Na[2,2,2\text{-}(CO)_3\text{-}2\text{-}MnB_5H_9] + H_2 \qquad (9)$$

The anion is relatively stable, about one-third decaying in diethyl ether at room temperature in 1 week to regenerate the parent. Upon contact with proton donors, such as Florisil or traces of water in eluting solvents, the parent is regenerated. A diethyl ether solution of the anion also partially regenerated the parent in the presence of diborane. This deprotonation reaction is different from other reported bridge hydrogen abstractions from metallapenta- and -hexaboranes. For example, an X-ray crystal study of $[(n\text{-}C_4H_9)_4N][(CO)_3FeB_5H_8]$ shows that a bridge hydrogen is removed between B(3) and B(4).[34] On the other hand, the anion and its parent are fluxional in solution, and, in addition, reaction with $[P(C_6H_5)_3]_3CuCl$ results in insertion of a bridging diphosphinocopper between B(4) and B(5).[40] When 2-$(\eta^5\text{-}C_5H_5)CoB_4H_8$ is deprotonated, a hydrogen bridging between a cobalt atom and a boron atom is removed.

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Registry No. 2,2,2-$(CO)_3$-2-MnB_5H_{10}, 71230-48-3; 1-Br-2,2,2-$(CO)_3$-2-MnB_5H_9, 71230-47-2; Na[2,2,2-$(CO)_3$-2-MnB_5H_9], 71230-46-1; $[(n\text{-}C_4H_9)_4N]$[2,2,2-$(CO)_3$-2-MnB_5H_9], 71230-45-0; B_5H_9, 19624-22-7; $Mn_2(CO)_{10}$, 10170-69-1; $HMn(CO)_5$, 16972-33-1.

Supplementary Material Available: Tabulated mass spectra and graphic mass and NMR spectra of 2,2,2-$(CO)_3$-2-MnB_5H_{10} and 1-Br-2,2,2-$(CO)_3$-2-MnB_5H_9 (6 pages). Ordering information is given on any current masthead page.

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Chlorine(I) Derivatives of Fluorinated Carboxylic Acids. Synthesis and Properties of CF_3CO_2Cl, $C_2F_5CO_2Cl$, $C_3F_7CO_2Cl$, $ClCF_2CO_2Cl$, HCF_2CO_2Cl, and $CF_2(CF_2CO_2Cl)_2$

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The syntheses of the chlorine(I) derivatives of six fluorinated carboxylic acids are described. Low-temperature reaction of the sodium salts of the acids with ClF is the preferred method of preparation. The new compounds CF_3CO_2Cl, $C_2F_5CO_2Cl$, $C_3F_7CO_2Cl$, HCF_2CO_2Cl, and $ClCF_2CO_2Cl$ have been characterized by IR, NMR, and Raman spectroscopy as well as by their decomposition products. $CF_2(CF_2CO_2Cl)_2$ could not be completely characterized due to its low volatility and explosiveness above −10 °C. All the compounds are thermally unstable at 22 °C and are explosive, especially in the gas phase at pressures greater than 20–50 torr. Reactions of CF_3CO_2Cl and $C_3F_7CO_2Cl$ with SO_2 and CO are also discussed.

Introduction

Halogen(I) derivatives of strong oxy acids and acid alcohols (hypohalites) provide a variety of reactive reagents for synthetic chemistry.[3,4] The majority of these compounds are chlorine derivatives, with the bromine(I) and iodine(I) analogues, in general, having much lower thermal stabilities. In nearly every case where the chlorine(I) compound is known, the fluoro derivative is also known. Historically, the fluoro derivatives preceded the chlorine compounds in most instances. The fluorine derivatives are not strictly analogous to the halogen(I) derivatives because the concept of a formal +1 oxidation state for fluorine has no validity. As a qualitative indicator, however, the existence of the fluoro derivative implies the chlorine(I) compound can be prepared and vice versa.

Methods for the synthesis of chlorine(I) derivatives have normally involved reactions of ClF with the acids or cesium salts of the acids.

$$HOA + ClF \rightarrow HF + ClOA$$

$$CsOA + ClF \rightarrow CsF + ClOA$$

Mercury and potassium salts have been utilized in some cases and $ClOSO_2F$ has been shown to be an effective replacement of ClF in several reactions. The use of metal salts has allowed the preparation of some chlorine(I) compounds where the parent acid or alcohol is not known, as is the case for several fluorocarbon derivatives of the type R_fOCl. In some cases for R_fOCl, the isolated metal salt is not used and the apparent addition of the elements of ClF across the carbon–oxygen double bond in ketones (or OSF_4) is accomplished by carrying out the reaction in the presence of KF or CsF.

As part of ongoing effort in the synthesis and properties of compounds containing halogen–oxygen single bonds, we decided to explore the synthesis of the chlorine(I) derivatives of fluorinated carboxylic acids. The fluoro derivatives of CF_3CO_2H, $C_2F_5CO_2H$, and $C_3F_7CO_2H$, while explosive and not well studied, were known.[5-7] This implied that the chlorine(I) compounds could be obtained. In addition, indirect evidence for the existence of $CF_3C(O)OX$ (X = I, Br) was available via the Hunsdiecker reaction applied to the synthesis of perfluoroalkyl iodides and bromides.[8] In this paper, the syntheses of CF_3CO_2Cl, $C_2F_5CO_2Cl$, $C_3F_7CO_2Cl$, HCF_2CO_2Cl, and $ClCF_2CO_2Cl$ by reaction of the corresponding acids or their sodium salts with ClF are described.[9] Evidence is also presented for the existence of $CF_2(CF_2CO_2Cl)_2$. The compounds have been characterized by NMR, IR, and Raman spectroscopy and by their thermal decomposition. Reactions of CF_3CO_2Cl and $C_3F_7CO_2Cl$ with CO and SO_2 are also discussed. During the course of this work an independent synthesis of CF_3CO_2Cl and $ClCF_2CO_2Cl$, different from that described here, was reported.[10]

Experimental Section

General Procedures. Volatile compounds were handled in a glass and stainless steel vacuum system equipped with glass–Teflon or stainless steel valves. Pressures were measured with a Wallace and Tiernan differential pressure gage, Series 1500. All reactions were carried out in 4HS75 Hoke cylinders or ~10-mL Kel-F tubes fitted with stainless steel valves. Separation of volatile products was by trap-to-trap distillation and GLC with columns packed with 40% Halocarbon 11-21 polymer oil on Chromosorb P.

Infrared spectra were recorded on Perkin-Elmer Model 180 or 337 spectrophotometers using a 10-cm glass cell fitted with AgCl windows. Raman spectra were recorded at low temperatures by using a Spex 14018 double monochromator with photon counting detection. A low-temperature cell similar to that described by Brown et al. was employed.[11] Excitation was by the ~600-nm line of a CW dye laser pumped by an argon ion laser. NMR spectra were recorded at ca. −40 °C with a Varian XL-100-15 spectrometer using ~15 mol % solutions in $CFCl_3$. Chemical shifts are reported as ϕ^* values (δ relative to internal $CFCl_3$ not at infinite dilution).

Reagents. Fluorine, chlorine, CF_3COOH, $CClF_2COOH$, CF_2HCOOH, C_2F_5COOH, C_3F_7COOH, CO, SO_2, and NaOH were obtained from commercial sources. Sodium salts of the acids were prepared by reactions between acids and NaOH and then drying under vacuum. ClF was prepared by a reaction between equimolar amounts of fluorine and chlorine (90 mmol) in a 150 mL Monel vessel (5000 psi) at 250 °C for 12 h. (**Caution**! Contained explosions are observed under these conditions as the temperature approaches ~100 °C.) ClF for reaction was removed at −112 °C from the storage vessel to eliminate contamination by any ClF_3 present.

Preparation of Hypochlorites. Method A. The initial method of synthesis was via reaction of the acids with ClF. In a typical reaction, 3.0 mmol of the acid was condensed into a Kel-F reactor and allowed to liquefy in the bottom of the reaction tube. The reactor was then cooled to −195 °C and 3.3 mmol of ClF was condensed in the upper walls of the reactor. The vessel was then placed in ~500 mL of a $CFCl_3$ slush at −112 °C containing solid CO_2. Over a period of about 6 h, the reaction temperature increased slowly to −78 °C. After a total reaction time of 14–18 h, the reactor was cooled to −112 °C and pumped on. This removed unreacted ClF and CO_2 and R_fCl from decomposition of the hypochlorite.

The remaining mixture of R_fCO_2Cl and HF was then transferred slowly through a short connection onto ~25 g of NaF in a 75-mL stainless steel cylinder at −195 °C. This was most readily accomplished by allowing the reactor to warm from −195 °C in an empty Dewar. The vessel was then warmed to −70 °C and allowed to stand for a few minutes with gentle shaking. The hypochlorite was then collected

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