for ammonia exchange of $(1.0 \pm 0.1) \times 10^5$ sec^{-1} at 298°K and a proton coupling constant of $|A/h| = (1.5 \pm 0.2) \times 10^6$ sec^{-1}. The activation parameters of $\Delta H^{\ddagger} = 9.9 \pm 0.5$ kcal/mole and $\Delta S^{\ddagger} = -2 \pm 2$ eu are consistent with previous N^{14} and H^1 studies.[1,2] This proton line broadening study is thus in excellent agreement with independent nitrogen^{14} line broadening[1] and proton contact shift[3] investigations and resolves the previously reported inconsistencies. These data definitely indicate that the proton line broadening for solutions of $Ni(NH_3)_6^{2+}$ in liquid ammonia is sensitive to the exchange of ammonia molecules and not simply proton exchange (see Table I). The activation parameters are consistent with a solvent-assisted exchange process in which both bond making and breaking may be important in the transition state. This ammonia-exchange process may be compared with the exchange of dimethylformamide (DMF) from $Ni(DMF)_6^{2+}$ ($\Delta H^{\ddagger} = 15$ kcal/mole; $\Delta S^{\ddagger} = 8$ eu) in which bond breaking is apparently more important than bond making in the transition state [5]

TABLE I

REPRESENTATIVE PROTON NMR LINE WIDTH DATA FOR $Ni(NH_3)_6(ClO_4)_2$ IN LIQUID AMMONIA AT $P_m = 6.49 \times 10^{-3}$ [a]

$\Delta\nu$, sec^{-1} [b]	$P_m/\pi\Delta\nu = T_{2p} \times 10^4$ sec[c]	$10^3/T$, °K^{-1}
4.3	4.8	4.10
6.1	3.4	4.03
18.9	1.09	3.81
25.5	0.810	3.76
55.5	0.372	3.54
55.8	0.370	3.46
48.1	0.429	3.33
29.1	0.710	3.20
25.8	0.801	3.10

[a] P_m is the fraction of ammonia molecules in the system coordinated to Ni(II). [b] $\Delta\nu$ is the net full width at half-height in reciprocal seconds, after correcting for diamagnetic contribution. [c] $T_{2p} = 1/\pi\Delta\nu$; T_{2p} values tabulated are normalized to $P_m = 1$.

Acknowledgment.—The authors wish to acknowledge the Advanced Research Projects Agency for its generous support through Contract SD-69.

(5) N. A. Matwiyoff, *Inorg. Chem.*, **5**, 788 (1966).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN 53706

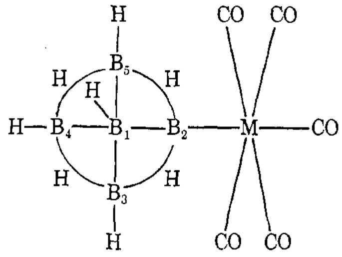
Metal Carbonyl Derivatives of Pentaborane(9)

BY DONALD F. GAINES AND TERRY V. IORNS

Received January 10, 1968

The synthesis of compounds containing group III–transition metal bonds[1] has recently generated considerable interest. Boron hydrides have not generally been thought of as good candidates for the group III moiety because of their electron-deficient nature and inherent lower stability toward heat, moisture, and oxygen. Parshall, however, has prepared salts of $H_3BMn(CO)_5^-$, $H_3BMn(CO)_5P(C_6H_5)_3^-$, $H_3BRe(CO)_5^-$, and $(H_3B)_2Re(CO)_5^-$, which are thought to contain boron–metal dative bonds.[2]

We have for some time been interested in preparing compounds containing σ bonds between transition metals and boron in polyboranes, in order to compare their properties with the properties of compounds having bonds between other P-block elements and transition metals. Pentaborane(9), B_5H_9, was chosen as a representative and reasonably stable polyborane for initial investigations. We found that chloro and bromo derivatives of B_5H_9 react with $NaMn(CO)_5$ and $NaRe(CO)_5$ to produce 2-$[Mn(CO)_5]B_5H_8$ and 2-$[Re(CO)_5]B_5H_8$, respectively. The available spectral data suggest that the transition metal moiety is bonded to the electron-deficient borane moiety by a direct σ bond.



In no case have 1-substituted metal carbonyl derivatives of B_5H_9 been detected, even when 1-BrB_5H_8 or 1-ClB_5H_8 was used in the preparation. At present there is no unequivocal explanation for the isolation of only one of the possible isomers.

The ^{11}B nmr spectra of 2-$[Re(CO)_5]B_5H_8$ and 2-$[Mn(CO)_5]B_5H_8$, Table I, are characteristic of the type generally observed for 2-substituted pentaborane(9) derivatives. For both compounds the B(1)–H chemical shift and coupling constant are in the usual range observed for pentaborane(9) derivatives. In the case of the manganese compound (Figure 1), the B(2)–Mn resonance is shifted 10 ppm downfield from the B(3–5)–H resonance. In the case of the rhenium compound, however, the B(2)–Re resonance is shifted about 1 ppm upfield from the B(3–5)–H resonance and they overlap such that the B–H coupling is obscured (the coupling constant for B(3–5)–H is thus obtained

TABLE I

^{11}B NMR CHEMICAL SHIFTS AND COUPLING CONSTANTS

	B(1)–H		B(2)–M	B(3–5)–H		Area ratio B(1): B(2–5)[c]
	δ[a]	J[b]	δ	δ	J	
2-$[Re(CO)_5]B_5H_8$[d]	49.0	171	11.5	10.6	155	1.0:4.0
2-$[Mn(CO)_5]B_5H_8$[d]	48.6	173	0.2	10.3	151	1.0:3.9

[a] Chemical shifts in ppm from $BF_3 \cdot O(C_2H_5)_2$. Values are ±0.3 ppm. [b] J in cps (±5 cps). [c] Theory 1.0:4.0. [d] The spectra were obtained using solutions in CS_2.

---

(1) For example, see: D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **5**, 1586 (1966); H. Nöth and G. Schmid, *J. Organometal. Chem.* (Amsterdam), **5**, 109 (1966); M. P. Johnson and D. F. Shriver, *J. Am. Chem. Soc.*, **88**, 301 (1966), and references therein.

(2) G. W. Parshall, *ibid.*, **86**, 361 (1964).

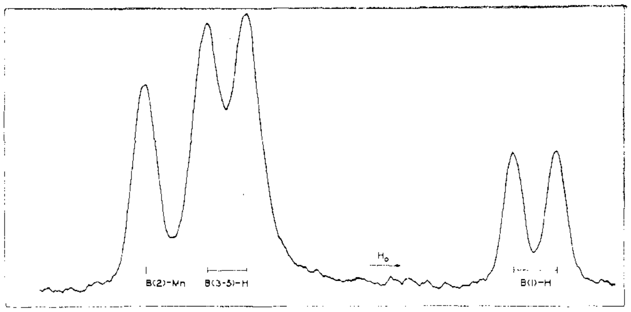


Figure 1.—The ^{11}B nmr spectrum of 2-$[Mn(CO)_5]B_5H_8$ obtained at 32.1 Mc.

from the ^1H nmr spectrum). The upfield direction of the chemical shift of the B(2)–Re resonance from the B(3–5)–H resonance is unusual[3] and has been observed previously only for 2-IB_5H_8.[4] There is no observable *trans* effect on the chemical shift of the B(4)–H resonance in either of the compounds, though in most other 2-substituted pentaboranes(9), the B(4)–H resonance has a pronounced upfield shift. The theory of boron chemical shifts is not well enough developed, however, to allow an explanation of these unusual shifts.

The ^1H nmr spectra of 2-$[Re(CO)_5]B_5H_8$ and 2-$[Mn(CO)_5]B_5H_8$, Table II, are nearly identical and are typical of substituted pentaborane(9) derivatives. The low-field quartet, arising from H–^{11}B(3–5), is broad (Figure 2), suggesting that there is a small chemical shift between the H–^{11}B(3,5) hydrogens adjacent to B(2) and the H–^{11}B(4) hydrogen *trans* to B(2). The H–^{10}B resonances are not resolved in these spectra though their probable positions are indicated in Figure 2. The ratio of terminal to bridge hydrogens was determined by dividing the spectra at the point indicated by the long vertical line in Figure 2, integrating the two parts, and then determining the ratio of the low-field area to the high-field area. This ratio was then compared to the calculated area ratio based on the assignments in Figure 2 and on the assumption that four terminal and four bridge hydrogens were present as required in a 2-substituted pentaborane(9) derivative. The area ratios observed for the manganese and rhenium compounds were 0.88 and 0.90, respectively, in good agreement with the calculated value of 0.89.

Table II

^1H Nmr Chemical Shifts and Coupling Constants

	H–^{11}B(1)		H–^{11}B(3–5)		H bridge
	δ^a	J^b	δ	J	δ
2-$[Re(CO)_5]B_5H_8$[c]	−0.88	176	−2.6	155	2.1
2-$[Mn(CO)_5]B_5H_8$[c]	−0.67	170	−2.5	150	2.1

[a] Chemical shifts in ppm from TMS obtained at 60 and 100 Mc. Values are ±0.1 ppm. [b] *J* values in cps (±5 cps). [c] The spectra were obtained using solutions in CS_2.

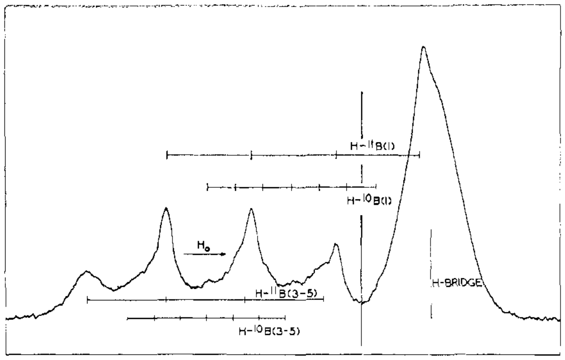


Figure 2.—The ^1H nmr spectrum of 2-$[Mn(CO)_5]B_5H_8$ obtained at 100 Mc.

The infrared absorptions of 2-$[Re(CO)_5]B_5H_8$ and 2-$[Mn(CO)_5]B_5H_8$ are tabulated in Table III. The spectra are much more similar in the region between 1900 and 500 cm^{-1} than for the 2-halopentaboranes(9), probably as a result of the lack of bands arising from the B–Mn(Re) interaction. The carbonyl stretching region was recorded under higher resolution conditions, and a tentative assignment is included in the table based on the assignments that have been made for other compounds having the general formulas $RMn(CO)_5$ and $RRe(CO)_5$.[5,6]

Table III

Infrared Data (cm^{-1}) for 2-$[Mn(CO)_5]B_5H_8$ and 2-$[Re(CO)_5]B_5H_8$

2-$[Re(CO)_5]B_5H_8$	2-$[Mn(CO)_5]B_5H_8$	Assignments[a]
2580[b] s	2600[b] s	
2117 m	2100 m	$A_1^{(2)}$
2109 w		A' ($A_1^{(2)}$)
2041 m	2030 m	B_1
2003 s	2000 s	E
1998 m, sh	1996 m, sh	$A_1^{(1)}$
1958 w	1970 w	A_1' (E)
1380 m	1380 m	
970 w, br	970 w	
880 m	880 m	
850 w, br	810 w	
650 w	750 w	
600 m	650 s	
575 m		

[a] Tentative, based on ref 5 and 6. The notation is that used in ref 6. [b] Frequencies are ±10 cm^{-1} except in the CO stretching region where they are ±2 cm^{-1}.

The thermal stability of 2-$[Re(CO)_5]B_5H_8$ and 2-$[Mn(CO)_5]B_5H_8$ is not great. The rhenium compound appears to be stable at room temperature for several hours. The manganese compound, however, upon melting develops a yellow color which becomes more pronounced when the sample is warmed to room temperature for several hours. On the other hand, more than half of a sample of the manganese compound was recovered after 12 days at room temperature. In the decomposition some $Mn_2(CO)_{10}$ is formed. Hydrogen chloride does not appear to have a measurable effect on the room-temperature decomposition of the

---

(3) T. Onak, G. B. Dunks, I. W. Searcy, and J. Spielman, *Inorg. Chem.*, **6**, 1465 (1967).

(4) A. B. Burg, *J. Am. Chem. Soc.*, **90**, 1407 (1968).

(5) J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, **4**, 389 (1965).

(6) F. A. Cotton, A. Musco, and G. Yagupsky, *ibid.*, **6**, 1357 (1967).

manganese compound. Bromine reacts with the manganese compound to produce HBr and traces of $BrMn(CO)_5$, $Br_2Mn_2(CO)_8$, and 2-BrB_5H_8, the only tractable products. Both the rhenium and manganese compounds survive short exposure to the atmosphere.

Experimental Section

All experiments were carried out in a nitrogen atmosphere or in a high-vacuum system. Ether solvents were dried over $LiAlH_4$. The ^1H nmr spectra were obtained at 60 and 100 Mc using Varian A-60A and HA-100 spectrometers. The ^{11}B nmr spectra were obtained at 32.1 Mc using the HA-100 spectrometer. Infrared spectra were obtained in carbon disulfide and cyclohexane solutions using a Beckman IR-10 spectrometer. The carbonyl stretching regions were examined more closely using cyclohexane solutions in a Perkin-Elmer 421 spectrometer.

2-[$Re(CO)_5$]B_5H_8.—Sodium pentacarbonylrhenate(-1) was prepared by stirring overnight a mixture of 5 ml of 1% sodium amalgam with 0.837 g (1.28 mmol) of $Re_2(CO)_{10}$ dissolved in about 10 ml of tetrahydrofuran (THF). The resulting solution was decanted from the excess amalgam and the THF evaporated under vacuum. Diethyl ether was then distilled onto the salt, and after warming to room temperature, the ether was evaporated and the salt heated to about 50° for 0.5 hr under high vacuum in order to remove as much of the THF as possible. About 30 ml of ether and 0.455 g (4.66 mmol) of 2-ClB_5H_8[7] were then condensed onto the reddish orange salt. The reaction flask was warmed to ambient temperature and stirred for 2 hr, during which a brown precipitate was formed. The reaction products were separated by fractional condensation. In the fractionation, 0.150 g (1.54 mmol) of 2-ClB_5H_8 was recovered along with 0.265 g (0.68 mmol) of 2-[$Re(CO)_5$]B_5H_8, a yield of 27%, which was purified by repeated condensations at $-16°$. The melting range of 2-[$Re(CO)_5$]B_5H_8 is 10–11°. A significant, though unmeasured, amount of $HRe(CO)_5$ (identified by its volatility and infrared spectrum)[8] was produced in the reaction.

The analysis of 2-[$Re(CO)_5$]B_5H_8 for hydrogen and carbon monoxide was accomplished by allowing a weighed sample of the material to distil slowly through a Vycor tube heated with two Meeker burners.[9] The liberated CO and H_2 were continuously removed by an automatic Toepler pump. The quantity of the CO–H_2 mixture was determined volumetrically. The mixture was then oxidized to CO_2 and H_2O by circulation over CuO at 300–320° until no materials volatile at $-196°$ remained. The H_2O was separated from the CO_2 by fractional condensation of the H_2O at $-78°$. The CO_2 was determined volumetrically, and the H_2O was obtained by difference. *Anal.* Calcd for 2-[$Re(CO)_5$]B_5H_8: CO, 36.0; H, 2.08. Found: CO, 36.6; H, 2.05.

2-[$Mn(CO)_5$]B_5H_8.—Sodium pentacarbonylmanganate(-1) was prepared by stirring an ether solution of 1.03 g (2.64 mmol) of $Mn_2(CO)_{10}$ with excess 1% sodium amalgam. Then 0.620 g (6.35 mmol) of 2-ClB_5H_8 was condensed onto the $NaMn(CO)_5$ solution at $-196°$. The reaction flask was warmed to room temperature and stirred for 1 hr, during which the solution turned deep red and a brown precipitate formed. The product, 2-[$Mn(CO)_5$]B_5H_8, was separated by high-vacuum distillation through a U tube cooled to $-8°$ and by condensation in a U tube at $-22°$. The melting range of carefully purified samples of 2-[$Mn(CO)_5$]B_5H_8 is -11 to $-10°$. The yield was 0.93 g (3.6 mmol), or 69%.

A number of attempts to obtain CO and H analyses using the same procedure as for the 2-[$Re(CO)_5$]B_5H_8 gave variable results for no apparent reasons. The characterization is therefore based entirely on the infrared and nmr data. The similarities observed in these data leave little doubt that the compound is correctly formulated as 2-[$Mn(CO)_5$]B_5H_8.

Acknowledgments.—We wish to thank John A. Martens for experimental assistance and Professor P. M. Triechel for helpful discussions. This work was supported by a grant from the National Science Foundation.

---

[7] D. F. Gaines and J. A. Martens, *Inorg. Chem.*, **7**, 704 (1968).

[8] W. Beck, W. Hieber, and G. Braun, *Z. Anorg. Allgem. Chem.*, **308**, 23 (1961).

[9] The apparatus and procedure used was similar to that described by A. B. Burg and R. Kratzer, *Inorg. Chem.*, **1**, 725 (1962).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CALIFORNIA STATE COLLEGE AT LOS ANGELES,
LOS ANGELES, CALIFORNIA 90032

Boron-11 Decoupling Studies on the Proton Nuclear Magnetic Resonance of $C_2B_4H_8$

BY THOMAS ONAK

Received February 8, 1968

The proton nmr of $C_2B_4H_8$ has been recorded and consists of a single peak (τ 3.68), a 1:1:1:1 quartet (τ 6.56), another 1:1:1:1 quartet (τ 10.13), and a broad peak (τ 12.6) which have been assigned to the H–C, $H_{terminal}$–$B_{4,5,6}$, $H_{terminal}$–B_1, and H_{bridge} hydrogen nuclei, respectively.[1] The assignment of the high-field quartet to H_t–B_1, however, was based more on analogy[2] than on direct evidence. On this assumption it was necessary, from area considerations, to assign the low-field quartet to two overlapping resonances, H_t–$B_{4,6}$ and the chemically unique H_t–B_5. Without direct evidence available there still remained the ambiguity of the H_t–B_1 and H_t–B_5 assignments. With this in mind the present study was undertaken.

The structure of $C_2B_4H_8$ has been verified by X-ray studies[3] and it is clear that each of the basal boron atoms (4,6 and 5) of the pentagonal-pyramidal framework has, in addition to a terminal hydrogen, an attached bridge hydrogen(s) whereas the apex boron has an attached terminal hydrogen only. With boron-11 decoupling experiments carried out at 19.2 Mc it is possible to irradiate selectively the high- and low-field proton nmr quartets. When the high-field quartet is collapsed, the rest of the spectrum remains unchanged. In striking contrast, collapse of the low-field quartet is accompanied by a markedly sharpened bridge hydrogen region. Such observations are consistent only with the original H_t–B_1 (no bridge hydrogens) assignment to the high-field quartet.

Acknowledgment.—This work was supported in part by a grant from the Office of Naval Research.

[1] T. Onak, R. P. Drake, and G. B. Dunks, *Inorg. Chem.*, **3**, 1686 (1964).

[2] B. Figgis and R. L. Williams, *Spectrochim. Acta*, 331 (1959); see also references mentioned on pp 312 and 313 of the work of T. Onak, *Advan. Organometal. Chem.* (Amsterdam), **3**, 263 (1966).

[3] W. E. Streib, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85**, 2331 (1963); *Inorg. Chem.*, **3**, 1666 (1964).