typical experiment, a 126-mg (1.00-mmol) quantity of $K^+H_3BC(O)OC_2H_5^-$ was dissolved in 20 ml of absolute ethanol in a 50-ml round-bottomed flask. The flask was attached to the vacuum line, evacuated, and cooled to −196°. A 1.10-mmol quantity of HCl was condensed into the flask and the apparatus was allowed to warm to room temperature. A 1.23-mmol mixture of hydrogen and carbon monoxide was measured by a Toepler pump system indicating the ethyl ester was formed in 95% yield. Distillation of the volatile components through a −23° trap led to the separation of the dimeric ethyl ester (II).

Acknowledgment.—The author gratefully acknowledges the partial support of this work by Petroleum Reserch Fund Grant No. 1077-G3 administered by the American Chemical Society.

Contribution from the John Harrison Laboratory of
Chemistry and Laboratory for Research on the
Structure of Matter, University of Pennsylvania,
Philadelphia, Pennsylvania 19104

Ammonia Proton Relaxation Studies for Solutions of $Ni(NH_3)_6(ClO_4)_2$ in Liquid Ammonia

By W. L. Rice and B. B. Wayland

Received December 27, 1967

Nickel(II) hexaammine in liquid ammonia has recently been investigated by both N^{14} and H^1 nuclear magnetic resonance.[1-3] Analysis of the proton line broadening has previously been reported to yield a pseudo-first-order rate constant for ammonia exchange of $k = (1.9 \pm 0.1) \times 10^5$ sec^{-1} at 298°K and a proton coupling constant of $|A/h| = (3 \pm 1) \times 10^6$ sec^{-1}.[2] Nitrogen-14 line broadening[1] and proton contact shift studies[3] for this system gave values of $k = (1.0 \pm 0.1) \times 10^5$ sec^{-1} at 298°K and $A/h = (-1.5 \pm 0.1) \times 10^6$ sec^{-1}, respectively. In an attempt to resolve these inconsistencies, the temperature dependence of the proton nmr line width for solutions of $Ni(NH_3)_6^{2+}$ in liquid ammonia has been redetermined and extended to higher temperatures.

Experimental Section

Preparation of Complexes.—The hydrated perchlorate complex $Ni(H_2O)_6(ClO_4)_2$ was dehydrated by stirring in contact with 2,2-dimethoxypropane for approximately 3 hr. Anhydrous ammonia (Matheson) was then bubbled through the solution and the resulting precipitate was filtered and dried under vacuum. Representative analysis: Calcd for $Ni(NH_3)_6(ClO_4)_2$: H, 5.05; N, 27.25; Ni, 16.31. Found: H, 5.17; N, 27.27; Ni, 16.05.

Solutions.—Solutions of the nickel(II) ammine complex in liquid ammonia were prepared by weighing into a thick-walled nmr tube the dried amine complex along with NH_4ClO_4 used to prevent amide precipitation. The nmr tube was placed on the vacuum system, and ammonia was quantitatively distilled into the nmr tube using a standard technique.

Apparatus.—The nmr spectra were determined on a Varian A-60-A spectrometer. The thick-wall nmr tubes were obtained from Ace Glass Co. and NMR Specialties Inc. The thick-walled nmr tubes were altered for temperature studies from 50 to 90°. The major problem of solution boiling was overcome by sealing the tubes as close as possible to the ammonia solution allowing sufficient volume to accommodate the expansion of the solution when heated.

Results and Discussion

The temperature dependence of the proton line widths has been analyzed using the equations developed by Swift and Connick[4] from solution of the Bloch equations including chemical exchange. The general line width relationship is

$$\frac{1}{T_{2\text{p}}} = \frac{P_\text{m}}{\tau_\text{m}}\left[\frac{\left(\dfrac{1}{T_{2\text{m}}}\right)^2 + \dfrac{1}{T_{2\text{m}}\tau_\text{m}} + \Delta\omega_\text{m}{}^2}{\left(\dfrac{1}{T_{2\text{m}}} + \dfrac{1}{\tau_\text{m}}\right)^2 + \Delta\omega_\text{m}{}^2}\right]$$

where P_m is the fraction of ligand complexed, τ_m is the mean lifetime of ligand in the first coordination sphere, $\Delta\omega$ is the contact shift in radians per second, $1/T_{2\text{m}}$ is the transverse relaxation rate for the nucleus in the coordinated ligand, and $1/T_{2\text{p}}$ is the observed transverse nuclear relaxation rate. In the low-temperature region ($10^3/T = 3.8$–4.1°K^{-1}), where $\Delta\omega_\text{m}{}^2 \gg (1/T_{2\text{m}})^2$, $(1/\tau_\text{m})$, the limiting relationship $T_{2\text{p}} = \tau_\text{m}/P_\text{m}$ is obtained. At temperatures above $10^3/T = 3.7$°K^{-1} two or more relaxation mechanisms contribute to the observed relaxation times. The contributing mechanisms have been resolved by curve fitting and are given by the limiting straight lines in Figure 1. The experimental data points and the theoretical curve calculated from the general line width relationship appear in Figure 1.

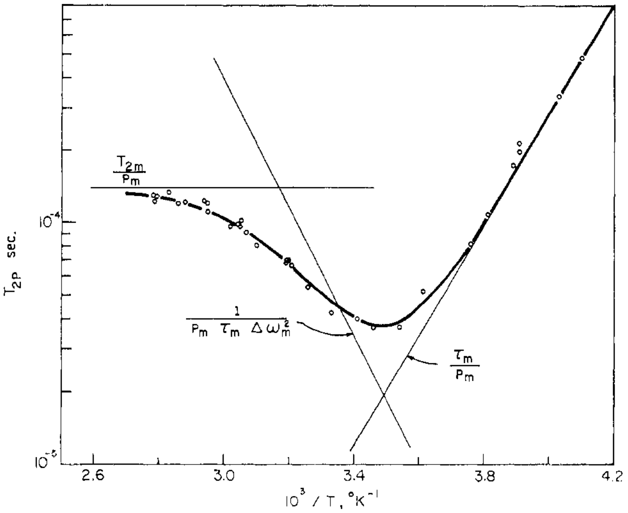


Figure 1.—Plot of proton $T_{2\text{p}}$ *vs.* $10^3/T$ for solutions of $Ni(NH_3)_6^{2+}$ in liquid ammonia. The data points represent three independent concentrations normalized to $P_\text{m} = 1$. The solutions contain NH_4ClO_4 in order to inhibit amide formation. $T_{2\text{p}} = 1/\pi\Delta\nu$ where $\Delta\nu$ (sec^{-1}) is the full line width at half-height: O, data points; —, calculated curve.

The curve-fitting process results in a rate constant

---

[1] H. H. Glaeser, G. A. Lo, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **4**, 206 (1965).

[2] T. J. Swift and H. H. Lo, *J. Am. Chem. Soc.*, **88**, 2994 (1966).

[3] B. B. Wayland and W. L. Rice, *Inorg. Chem.*, **6**, 2270 (1967).

[4] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

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

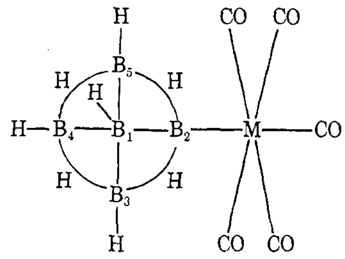
Metal Carbonyl Derivatives of Pentaborane(9)

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).