TABLE III

ANALYTICAL RESULTS

Complex	% calcd C	H	N	M	% found C	H	N	M
$Ni(4\text{-}MeT)_2Br_2$ (blue)	23.0	2.40	6.72	14.1	22.7	2.40	6.52	14.1
$Ni(4\text{-}MeT)_2Br_2$ (yellow)				14.1				14.0
$Ni(4\text{-}MeT)_2I_2$	18.8	1.96	5.48	11.5	18.5	2.06	5.49	11.4
$Ni(4\text{-}MeT)_3(NO_3)_2$	30.0	3.15	14.6	12.2	29.9	3.16	14.5	12.1
$Ni(4\text{-}MeT)Br_2$				18.5				18.6
$Cu(4\text{-}MeT)_2Cl_2$	28.9	3.01	8.42	19.1	28.8	3.13	8.29	19.2
$Cu(4\text{-}MeT)_2Br_2$	22.8	2.37	6.64	15.1	22.6	2.40	6.62	14.8
$Cu(4\text{-}MeT)_2(NO_3)_2$	24.9	2.59	14.5	16.5	24.6	2.60	14.5	16.5
$Cu(4\text{-}Me)Cl_2$	20.5	2.17	5.99	27.2	20.7	2.14	6.14	27.0
$Co(4\text{-}MeT)_2(NCS)_2$	32.2	2.68	14.7	15.8	31.9	2.63	14.7	15.6
$Co(4\text{-}MeT)_2Cl_2$	29.3	3.05	8.54	18.0	29.4	3.12	8.69	18.0
$Co(4\text{-}MeT)_2Br_2$	23.0	2.40	6.72	14.1	22.8	2.41	6.66	14.0
$Co(4\text{-}MeT)_2I_2$	18.8	1.96	5.48	11.5	18.6	2.02	5.42	11.6
$Pd(4\text{-}MeT)_2Cl_2$	25.6	2.66	7.45		25.5	2.41	7.24	
$Zn(4\text{-}MeT)_4(ClO_4)_2$	29.0	3.03	8.47	9.90	29.1	3.01	8.39	9.81

complex $Co(4\text{-}MeT)_2(NCS)_2$ has N-bonded thiocyanate ($\nu_{C\equiv N}$ at 2027, 2037 cm^{-1}, δ_{NCS} at 476 cm^{-1}) and has a tetrahedral stereochemistry as confirmed by the intensities and band positions in the electronic spectrum. We have listed the electronic spectra of a number of other cobalt(II) complexes as we appear to have achieved better resolution of the near-infrared band. The isothiocyanate complex has only slight splitting of this band, reflecting the closer approximation of this species to tetrahedral symmetry. We have also prepared tetrahedral $[Zn(4\text{-}MeT)_4](ClO_4)_2$, which is a 1:2 electrolyte in nitromethane ($\Lambda = 187$; 10^{-3} *M* solution), while the infrared spectrum shows no indication of perchlorate coordination. In diamagnetic square-planar $Pd(4\text{-}MeT)_2Cl_2$ the ligand still appears to be N bonded rather than S bonded and we assign bands in the far-infrared spectrum to ν_{Pd-N} and ν_{Pd-Cl}. The far-infrared spectrum indicates a trans structure, there being only one ν_{Pd-Cl} band.

Experimental Section

4-Methylthiazole was supplied by Koch-Light Laboratories. All other materials were AnalaR or the best grade available. Analytical results for the complexes are presented in Table III. The complexes were prepared as follows.

$Cu(4\text{-}MeT)_2Cl_2$.—A 0.99-g sample of ligand (0.01 mol) was added to 0.42 g of $CuCl_2 \cdot 2H_2O$ (0.0025 mol) dissolved in the minimum volume of ethanol. Precipitation of the complex occurred. The product was filtered off and washed with ethanol and ether.

The following complexes were also made by this method; in all cases 0.0025 mol of metal salt and 0.01 mol of ligand were used: **$Cu(4\text{-}MeT)_2Br_2$** (using anhydrous $CuBr_2$), **$Cu(4\text{-}MeT)_2(NO_3)_2$** (from $Cu(NO_3)_2 \cdot 3H_2O$), yellow **$Ni(4\text{-}MeT)_2Br_2$** (from $NiBr_2 \cdot 3H_2O$), and **$Co(4\text{-}Me)T_2Cl_2$** and **$Co(4\text{-}MeT)_2Br_2$** (from $CoCl_2 \cdot 6H_2O$ and anhydrous $CoBr_2$, respectively). Blue **$Ni(4\text{-}MeT)_2Br_2$** was prepared using methanol as the solvent.

The best preparative method for **$Ni(4\text{-}MeT)_3(NO_3)_2$** appears to be that quoted by Hambright, *et al.*[1]

$Ni(4\text{-}MeT)_2I_2$.—This was prepared by dissolving 0.005 mol of NiI_2 in the minimum volume of 50:50 1-butanol–ethanol, slowly adding 0.02 mol of ligand, and refluxing for 1 hr. On standing, crystals formed and were filtered off and washed with ethanol and petroleum ether (bp 30–40°). These were very hygroscopic.

$Co(4\text{-}MeT)_2(NCS)_2$.—A 0.005-mol sample of $Co(NCS)_2$ was dissolved in the minimum volume of acetone and 0.03 mol of ligand was added. The solution was boiled and evaporated to a small bulk, cooled, and filtered. The product was washed with acetone and light petroleum ether. **$Co(4\text{-}MeT)_2I_2$** was obtained by adding 0.02 mol of ligand to 0.005 mol of $CoI_2 \cdot 2H_2O$ in acetone and washing the precipitated product with ethanol and petroleum ether. The complexes **$Co(4\text{-}MeT)_2(NO_3)_2$** and **$[Zn(4\text{-}MeT)_4](ClO_4)_2$** were both prepared by refluxing ethanol–2′,2″-dimethoxypropane solutions of the metal salt hexahydrates (0.005 mol) with excess ligand (0.03 mol) for 30 min and then allowing them to stand. The products were filtered off and washed with ethanol and ether.

Both **$Cu(4\text{-}MeT)Cl_2$** and **$Ni(4\text{-}MeT)Br_2$** were obtained by heating the corresponding 1:2 complex at 140° *in vacuo* to constant weight. Correct weight losses were observed. The complex **$Pd(4\text{-}MeT)_2Cl_2$** was prepared by dissolving 0.005 mol of bis(benzonitrile)palladium(II) chloride in the minimum volume of benzene, adding 0.01 mol of 4-methylthiazole. The precipitated complex was washed with benzene.

Instrumentation was as described in earlier papers.[2,8] The diamagnetic correction for 4-methylthiazole was obtained from the literature.[9]

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[9] E. J. Vincent, R. Phan-Tan-Luu, J. Metzger, and J. M. Surzur, *C. R. Acad. Sci.*, 6345 (1965).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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1:1 Adducts of Tetracyanoethylene with Methylplatinum(II) Complexes

BY H. C. CLARK* AND R. J. PUDDEPHATT

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The unique properties of tetracyanoethylene, TCNE, due to the highly electronegative cyano-group substituents of the olefin have prompted much recent interest in its complexes with transition metals.[1]

We have found that TCNE forms stable 1:1 adducts with *trans*-$PtXCH_3L_2$ (L = tertiary phosphine or arsine, X = halogen). The complexes isolated are given in Table I. They melt sharply with blackening and effervescence in the range 150–190° and are generally insoluble in common organic solvents. The structure (I)

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* To whom correspondence should be addressed.

[1] W. H. Baddley, *Inorg. Chim. Acta Rev.*, 7 (1968).

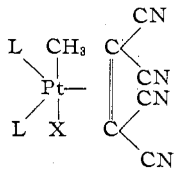
TABLE I
ANALYTICAL DATA AND PHYSICAL PROPERTIES OF COMPLEXES $PtXCH_3L_2 \cdot TCNE$

Compd		Analysis, %						Yield,	
		C		H		N			
X	L	Calcd	Found	Calcd	Found	Calcd	Found	%	Mp, °C
Cl	$P(CH_3)_3$	29.7	30.0	4.0	4.2	10.7	11.2	73	183–185 dec
Cl	$P(CH_3)_2C_6H_5$	42.8	43.3	3.9	4.0	8.6	8.4	93	185 dec
I	$P(CH_3)_2C_6H_5$	37.3	37.3	3.4	3.3	7.6	7.7	85	150–154 dec
Cl	$As(CH_3)_3$	25.4	25.3	3.45	3.6	9.1	9.3	86	174–175 dec
I	$As(CH_3)_3$	22.1	23.3	3.0	2.9	7.9	7.6	91	157–158 dec
Cl	$As(CH_3)_2C_6H_5$	37.4	37.75	3.4	3.5	7.6	7.2	92	188–190 dec

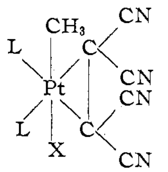
TABLE II
INFRARED (2500–140 CM^{-1}) AND RAMAN (700–70 CM^{-1}) SPECTRA OF $Pt[P(CH_3)_3]_2 \cdot TCNE$ (I) AND $PtXCH_3[Y(CH_3)_3]_2 \cdot TCNE$ (II)

	I		II (X = Cl, Y = P)		II (X = Cl, Y = As)		II (X = I, Y = As)	
Assignment	Ir	R	Ir	R	Ir	R	Ir	R
ν(CN)	2220 s		2230 s		2230 s		2232 s	
	2165 w							
$\delta_a(CH_3Y)$	1420 s		1425 s		1417 s	1414 mw	1417 s	
						1376 vw		
$\delta_s(CH_3Y)$	1299 s		1299 s		1263 s	1271 vw	1270 w	
			1265 ms				1247 s	
ν(C=C)	1191 s		1201 ms		1213 ms	1208 ms	1206 ms	
$\rho(CH_3Y)$	965 sh		959 vs		918 vs	915 w	916 vs	
	949 vs		940 sh		906 s, sh	899 w	898 vs	
			869 ms					
	859 ms		858 sh		842 ms		836 m	
$\nu(YC_3)$	746 s		760 s		635 s	630 ms	622 ms	630 m
	731 sh		731 m					
	682 s	683 m	681 s		601 s	593 s	593 m	598 ms
			677 sh	676 s				
δ(C—C—C)	665 ms	662 ms		644 ms	684 m	676 s	677 m	670 ms
		639 s		605 m		651 m		651 m
$\nu(PtCH_3)$				537 s		558 m		526 s
ν(PtY)	373 ms	370 mw	365 m	358 m			277 m	
			340 sh			260 m	265 sh	262 w
ν(Pt—TCNE)	352 w	353 vs		313 vs		325 vs		318 s
ν(Pt—X)			289 s	289 ms	286 sh	286 sh		
			280 s		280 s			141 s
$\delta(YC_3)$	274 m	277 m			216 mw	219 m	214 m	221 w
Other bands		593 w						
	491 mw	491 w	488 mw				480 mw	
			434 w		348 m	441 w	333 mw	334 w
	235 m		234 w		240 w			
	196 m		211 w		193 mw	192 m	188 w	192 ms
		143 ms				150 ms		
		131 m				118 w		
		96 w		98 s		82 m		91 m

of the complexes may be deduced from the nmr, infrared, and Raman spectra.



Ia



Ib

Only complexes I with X = Cl and L = $P(CH_3)_3$ or $As(CH_3)_3$ were sufficiently soluble in perdeuterioacetone to give satisfactory nmr spectra. The methylphosphine protons in I (X = Cl, L = $P(CH_3)_3$) give a doublet in the nmr spectrum due to coupling with ^{31}P with satellites due to coupling with ^{195}Pt ($I = {}^1/_2$, natural abundance 34%), confirming that the phosphine ligands are mutually cis.[2] The platinum-bound methyl group gives a triplet due to coupling with two identical ^{31}P nuclei, again with satellites due to coupling with ^{195}Pt. These data are only consistent with the structure I for the complexes. Hexafluorobut-2-yne[3,4] and tetrafluoroethylene[4] adducts of *trans*-$PtClCH_3L_2$ as well as the complex $PtHCN[P(C_2H_5)_3]_2 \cdot TCNE$[1] are believed to have similar structures. The tetracyanoethylene complexes are undissociated in solution and hence are more stable than the corresponding hexafluorobut-2-yne or tetrafluoroethylene complexes which decompose to the constituents on dissolution.[4] This greater stability probably reflects the greater ability of TCNE to oxidize the central metal.[5] In this regard, the coupling constant data derived from the nmr spectra are interesting. The coupling constants for I are close to the values ex-

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(2) J. D. Ruddick and B. L. Shaw, *J. Chem. Soc. A*, 2801 (1969).

(3) H. C. Clark and R. J. Puddephatt, *Chem. Commun.*, 92 (1970).

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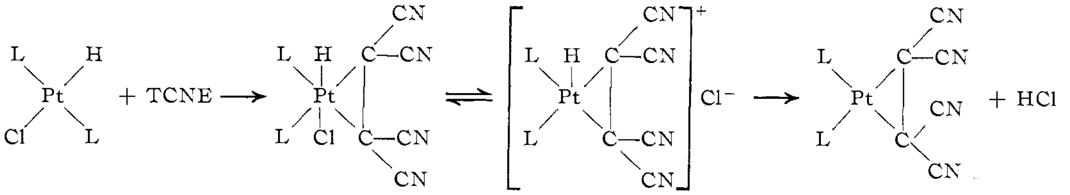
TABLE III

INFRARED (1300–140 CM^{-1}) AND RAMAN (700–70 CM^{-1}) SPECTRA OF *cis*-$Pt(CH_3)_2[Y(CH_3)_3]_2$ (I) AND *trans*-$PtClCH_3[Y(CH_3)_3]_2$ (II)

	I (Y = P)		II (Y = P)		I (Y = As)		II (Y = As)	
Assignment	Ir	R	Ir	R	Ir	R	Ir	R
$\delta_s(CH_3Y)$	1291 mw		1285 s		1273 w		1276 w	
	1281 s		1265 sh		1254 s		1261 ms	
							1255 sh	
$\delta_s(CH_3Pt)$	1204 vw		1234 m		1216 m		1235 ms	
	1185 m				1193 ms			
$\rho(CH_3Y)$	944 vs		950 vs		901 vs		920 sh	
							905 vs	
	866 sh		864 s		825 ms		838 ms	
	853 ms						828 sh	
$\nu(YC_3)$	723 s	726 ms	746 s		605 s	605 s	626 s	622 vs
			730 sh					
	674 ms	681 s	684 ms		592 s	596 vs	600 s	603 vs
$\nu(PtC)$	525 ms	528 vs	570 m	563 vs	542 ms	540 s	566 m	564 m
	513 s	516 s			532 ms	531 m		
$\nu(PtT)$	381 sh	380 w		375 m	273 sh			270 ms
	360 s	356 mw	353 m		267 s	268 m	271 sh	
$\nu(PtCl)$			267 vs	265 s			277 vs	278 sh
$\delta(YC_3)$	282 m	279 mw	279 w, sh	286 m		224 mw		222 m
$\delta(PtC)$	236 w		238 w		232 w			239 sh
$\delta(PtY_2)$	217 sh	219 ms	215 m	214 vs				
Other bands		199 sh	188 w	192 m	193 w	197 sh	189 ms	185 s
		128 m		167 m		185 ms	174 m	124 ms
				133 s		109 m		75 m
						87 ms		

SCHEME I



pected for platinum(IV) complexes,[2,6] while the data for $Pt[P(CH_3)_3]_2\cdot TCNE$ resemble those for platinum(II) complexes of the type *cis*-$PtX_2[P(CH_3)_3]_2$.[7] Quite different behavior would be expected for a trigonal platinum(0) complex.[8] Thus, in the valence bond formalism the complexes may be better described by Ib rather than Ia.

The infrared and Raman spectra of the TCNE complexes are given in Table II, and those of the parent methylplatinum (II) complexes, which are included to aid in the assignment of bands,[4,9] are in Table III. The spectra confirm the presence of methyl–platinum and platinum–halogen bonds in the complexes. Some information about the nature of the platinum–TCNE bond may also be obtained from the spectra. Thus as back-bonding of electrons from d orbitals of platinum into antibonding orbitals of TCNE increases (or as the bonding approaches the limiting case Ib), the C=C and C≡N bonds in TCNE are expected to become weaker while the platinum–TCNE bond should become stronger.[1] For $Pt[P(CH_3)_3]_2\cdot TCNE$ the relevant stretching frequencies are $\nu(CN)$ 2220, 2165 cm^{-1}, $\nu(C{=}C)$ 1191 cm^{-1}, and ν(Pt—TCNE) 353 cm^{-1} while for I (X = Cl, L = $P(CH_3)_3$) the corresponding values are $\nu(CN)$ 2230 cm^{-1}, $\nu(C{=}C)$ 1201 cm^{-1}, and ν(Pt—TCNE) 313 cm^{-1}; these values indicate a greater degree of back-bonding in the former complex, as would be predicted.

The reaction of TCNE with platinum hydrides gives elimination, perhaps by the mechanism shown in Scheme I.

This is a slight modification of the mechanism proposed by Baddley.[1] We consider it more likely since it is the reverse of the mechanism proposed for oxidative additions[10] and is thus favored by the principle of microscopic reversibility. This subsequent elimination reaction does not occur with the methylplatinum compounds, presumably because the methyl–platinum bond is stronger than the platinum–hydrogen bond.

Experimental Section

General methods and details of the far-infrared and Raman spectrometers have been published previously.[4] *trans*-$PtICH_3[As(CH_3)_3]_2$ was prepared by reaction of *trans*-$PtClCH_3[As(CH_3)_3]_2$ with sodium iodide in acetone solution; yield 70%; mp 156–157° (methanol); $\nu(PtC)$ 548 cm^{-1}. Nmr in $CHCl_3$: $\delta(CH_3Pt)$ −0.71 ppm, $^2J(PtH)$ = 77.0 Hz; $\delta(CH_3As)$ −1.63 ppm, $^3J(PtH)$ = 20.6 Hz.

$PtClCH_3[P(CH_3)_3]_2\cdot C_2(CN)_4$ was prepared by addition of $C_2(CN)_4$ (0.020 g, 0.145 mmol) in benzene (2 ml) to a stirred solution of *trans*-$PtClCH_3[P(CH_3)_3]_2$ (0.062 g, 0.160 mmol) in

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[6] H. C. Clark and J. D. Ruddick, *Inorg. Chem.*, **9**, 2556 (1970).

[7] D. A. Duddell, J. G. Evans, P. L. Goggin, R. J. Goodfellow, A. J. Rest, and J. G. Smith, *J. Chem. Soc. A*, 2134 (1969).

[8] H. C. Clark and K. Itoh, unpublished results.

[9] D. A. Long and W. O. George, *Spectrochim. Acta*, **19**, 1717 (1963).

[10] P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, **88**, 3511 (1966).

benzene (2 ml). The precipitate was filtered off, washed thoroughly with benzene and pentane, and dried under vacuum giving the product as pale yellow microcrystals (0.068 g). Nmr in $(CD_3)_2CO$: $\delta(CH_3P)$ −1.95 ppm (doublet + satellites), $^2J + {}^4J$(PH) = 12.2 Hz, ^3J(PtH) = 24 Hz; $\delta(CH_3Pt)$ −0.77 ppm (triplet + satellites), ^3J(PH) = 4.6 Hz, ^2J(PtH) = 60 Hz.

Other complexes were prepared similarly. Analytical data, yields, and melting points are in Table I. Nmr spectrum of $PtClCH_3[As(CH_3)_3]_2 \cdot C_2(CN)_4$ in $(CD_3)_2CO$: (CH_3As) −1.86 ppm, ^3J(PtH) = 17.4 Hz; $\delta(CH_3Pt)$ −0.79 ppm, ^2J(PtH) = 62.0 Hz.

$Pt[P(CH_3)_3]_2 \cdot C_2(CN)_4$ was prepared by the method of Baddley;[1] mp 195–215° dec. Nmr in CH_2Cl_2: $\delta(CH_3P)$ −1.75 ppm, $^2J + {}^4J$(PH) = 10.6 Hz, ^3J(PtH) = 35.4 Hz.

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The Reaction of Pentaborane(9) with Alkali Metal Hydroborates

BY C. G. SAVORY AND M. G. H. WALLBRIDGE*

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Several investigations have shown that both *nido*- and *closo*-borane anions are obtained by the action of a hydridic species on a neutral boron hydride. The anions formed are dependent upon the conditions used, and frequently several products are produced. Thus, diborane(6) and tetraborane(10) react with the hydroborate ion in ethereal solvents at 25 and −45°, respectively, yielding the octahydrotriborate(1−) ion,[1−5] but at higher temperatures (*e.g.*, 100°) the *nido*-$B_{11}H_{14}^-$ and *closo*-$B_{12}H_{12}^{2-}$ ions are the ultimate products.[2,3] In

$$\begin{tikzcd}
 & B_3H_8^- + H_2 \\
B_2H_6 + BH_4^- \arrow[ur, "25^\circ"] \arrow[dr, "100^\circ"'] & \\
 & B_{11}H_{14}^- + B_{12}H_{12}^{2-} + H_2,\ \text{etc.}
\end{tikzcd}$$

general all the boron hydrides from B_2H_6 to $B_{18}H_{22}$ react similarly to yield borane anions[3] although with the more stable higher hydrides proton abstraction (*via* the initial addition of a hydride ion[6]) may occur, as in the case of decaborane(14)[7−9]

$$B_{10}H_{14} + BH_4^- \xrightarrow{25^\circ} B_{10}H_{15}^- \longrightarrow B_{10}H_{13}^- + H_2$$

The products of the reaction of pentaborane(9) with sodium hydroborate are sharply dependent upon the reaction temperature in that at 40° the $B_3H_8^-$ ion is formed and at 60° some $B_{11}H_{14}^-$ ions may be detected, while at 100° the $B_3H_8^-$, $B_{11}H_{14}^-$, and $B_{12}H_{12}^{2-}$ ions occur among the reaction products.[3] Other studies have shown that with the hydride ion and lithium alkyls at −78° the $B_5H_8^-$ ion is probably involved as an intermediate although the final reaction products have yet to be elucidated.[10−12] We have investigated the reaction of pentaborane(9) with lithium (and sodium) hydroborate at low temperatures (*i.e.*, up to 25°) to determine the nature of the initial products in an attempt to define more closely the important intermediates involved in the formation of the higher borane anions.

Experimental Section

Lithium hydroborate and deuterioborate were purified by Soxhlet extractions using dry ethyl ether, sodium hydroborate was recrystallized from diglyme, and pentaborane(9) was distilled *in vacuo*. Monoglyme and diglyme were dried by distillation from lithium aluminum hydride and stored over molecular sieve 4A.

Infrared spectra were recorded using a Perkin-Elmer 457 grating Infracord, and the ^{11}B nmr spectra were recorded using a Varian HA-100 instrument operating at 32.1 MHz. Mass spectra were obtained from an AEI MS9 spectrometer with a source temperature of 50–60° and an ionizing voltage of 70 eV.

Reaction of Pentaborane(9) with Lithium Hydroborate.—Initial experiments were carried out to determine the stoichiometry of the reaction. Thus when pentaborane(9) (0.258 g, 4.0 mol) was condensed onto lithium hydroborate (0.0774 g, 3.52 mmol) in monoglyme (or diglyme) under vacuum and the reaction mixture was allowed to warm slowly from −196° to room temperature, some pentaborane(9) (0.022 g, 0.34 mmol) was recovered from the reaction flask by distillation giving a molar ratio of reactants as $B_5H_9:LiBH_4 = 1.04$. Separate control experiments established that about half of the monoglyme had to be removed to recover all the volatile component, *viz.*, B_5H_9. A typical procedure was as follows. Pentaborane(9) (0.743 g, 11.6 mmol) was distilled onto a solution of lithium hydroborate (0.257 g, 11.6 mmol) in monoglyme (20 ml) at −196° under vacuum. The mixture was warmed to −78° and stirred for 4 hr over which time no hydrogen was evolved. Further stirring over 36 hr at 25° led to the evolution of hydrogen (161 ml, 7.2 mmol) together with small amounts of diborane (0.040 g, 1.4 mmol) and pentaborane(9) (0.073 g, 1.16 mmol). The pentaborane(9) appeared to be liberated during the course of the reaction because none could be recovered in the early stages of the reaction. Although hydrogen was still being evolved after 36 hr, the rate of evolution was extremely slow, and after a further 50 hr only another 4 ml (0.18 mmol) had been recovered. The diborane and pentaborane(9) were separated by vacuum distillation and identified from their ir and mass spectra. Treatment of an aliquot of the residual solution with aqueous tetramethylammonium hydroxide (∼20 ml) yielded a white solid precipitate (0.42 g) which was shown to be $(CH_3)_4NB_9H_{14}$. The solid was analyzed by combustion at 800° in an oxygen stream. *Anal.* Calcd for $C_4H_{26}NB_9$: C, 25.95; H, 14.15; N, 7.54. Found: C, 26.47; H, 15.06; N, 7.16. A further aliquot of the above solution was treated with 1,4-dioxane to precipitate an oil which changed slowly to a solid on shaking. The ^{11}B nmr spectrum of the solid (in diglyme) was consistent with its being predominantly $LiB_9H_{14} \cdot$diox. Concentration of the filtrate precipitated another solid consisting mainly of $LiB_3H_8 \cdot$diox (identified from the ^{11}B nmr spectrum). On redissolving this solid in monoglyme and treating the solution with aqueous tetramethylammonium

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* To whom correspondence should be addressed.

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(2) H. C. Miller, N. E. Miller, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **85**, 3885 (1963).

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