Chemistry, Structure, and Molecular Dynamics of the Tetrahydroboratotetracarbonylmolybdate(1−) Anion, $Mo(CO)_4BH_4^-$

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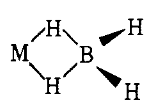
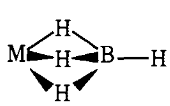
Abstract: The compound $[(Ph_3P)_2N][Mo(CO)_4BH_4]$ can be prepared in 25% yield by the reaction of $[(Ph_3P)_2N][Mo(CO)_5I]$ and $[(Ph_3P)_2N][BH_4]$ in anhydrous tetrahydrofuran. Mechanistic studies show that iodide ion acts as a catalyst in the synthesis. X-ray diffraction studies reveal that the compound crystallizes in the space group $P\bar{1}$ (a = 17.828 (8) Å, b = 9.714 (4) Å, c = 12.371 (5) Å, α = 101.77 (1)°, β = 115.36 (1)°, γ = 94.40 (1)°, V = 1886.9 Å^3, ρ_{obsd} = 1.33 g cm^{-3}, ρ_{calcd} = 1.34 g cm^{-3} for Z = 2). Data were collected with Zr-filtered Mo Kα radiation to a 2θ limit of 45°. Standard Patterson, Fourier, and least-squares techniques resulted in final agreement factors: R = 8.3%, R_w = 8.1% for 3208 reflections with $I > 3\sigma$. The tetrahydroborate ligand is attached to the metal via two Mo-H-B bridge bonds with Mo-H_b = 2.02 (8) Å. The coordination about the central molybdenum atom is approximately octahedral, but two notable distortions occur in the equatorial plane: C(eq)-Mo-C(eq) = 84.5 (5)° and H_b-Mo-H_b = 59 (4)°. The geometry about the boron is virtually tetrahedral, with Mo-B = 2.41 (2) Å. The ligational analogy between η^3-allyl and BH_4^- is further strengthened by the results of this study. Boron-decoupled ^1H NMR spectra reveal that bridge-terminal hydrogen interchange occurs within the tetrahydroborate ligand with $\Delta G_c^{\ddagger}$ = 10.0 ± 0.2 kcal/mol. As revealed by ^{13}C NMR studies, this rearrangement process is *not* coupled to axial-equatorial CO exchange about the molybdenum coordination polyhedron; $\Delta G^{\ddagger} \geq$ 18.6 kcal/mol for this process. This result places significant restrictions on operational BH_4^- rearrangement mechanisms. These are discussed in the light of a permutational analysis of differentiable rearrangement modes in covalent metal tetrahydroborates.

The tetrahydroborate ion, BH_4^-, one of the more useful reagents in organic synthesis,[4] has also been employed extensively in inorganic and organometallic chemistry as a hydridic reagent and as a ligand. In synthesis, BH_4^- has been used to reduce metal carbonyls to form cluster compounds containing bridging hydride ligands.[5] Metal tetrahydroborates have also been used as catalysts[6,7a] and as reagents in metal hydride syntheses.[8] A variety of metal complexes incorporating BH_4^- as a ligand[7] exhibit interesting fluxional behavior[7a,9] as well as varying BH_4^- bonding modes,[7] i.e., bidentate (A) and tridentate (B).



A



B

We wish to describe here the synthesis of the new metal carbonyl tetrahydroborate, $Mo(CO)_4BH_4^-$ (I). This complex is the first reported example of a stable transition metal BH_4^- complex in which the formal oxidation state of the metal is zero, and also the first in which the only other ligand type in the complex is carbonyl.[7,10,11] Since these features provide an unusual opportunity to investigate certain important aspects of tetrahydroborate chemistry, bonding, and structural dynamics, we have undertaken a thorough study of the properties of this complex. We report here, besides chemical observations on the mechanism of $Mo(CO)_4BH_4^-$ formation, the molecular structure as determined by x-ray diffraction and an ^1H and ^{13}C NMR study of fluxional behavior.

Experimental Section

All operations were carried out in a prepurified nitrogen atmosphere using Schlenk techniques. Solvents were dried, deaerated, and stored under nitrogen over Linde 3A molecular sieves, with the exception of tetrahydrofuran (THF), which was distilled from calcium hydride or lithium aluminum hydride. Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer and calibrated against polystyrene. Solution spectra were recorded in THF using CaF_2 cells with a 0.5-mm spacer, and solid spectra were recorded using KBr disks. Room temperature ^1H NMR spectra were recorded on Varian A-60D and T-60 spectrometers in acetone-d_6. Variable temperature, boron-decoupled ^1H NMR studies were performed in tetrahydrofuran-d_8 with a Perkin-Elmer R20-B spectrometer having an R-209PA heteronuclear double resonance power amplifier, a Schomandl ND30M frequency synthesizer, and a Calrad Model 65-287 rf power meter. Temperatures were calibrated with a Wilmad NMR probe thermometer. Variable temperature ^{13}C NMR studies employed a Varian CFT-20 Fourier transform spectrometer with 16K memory and single sideband filter. With small amounts (ca. 1:100) of the relaxation reagent $Cr(acac)_3$ added, typical pulse delay times were maintained in excess of 1.5 s. Conductivities were measured on a YSI-31 conductivity bridge using acetonitrile as the solvent. Analyses were performed by the Schwarzkopf Microanalytic Laboratory, Woodside, N.Y., and PCR Inc., Gainesville, Fla. Melting points were determined in sealed capillaries and are uncorrected. Metal carbonyls were purchased from Pressure Chemical Co. and used without further purification. The BH_3·THF was purchased from Aldrich Chemical Co., Inc. [PPN][Cl] was prepared using the literature method.[12]

Preparation of [PPN][I]. [PPN][Cl][12] (38.0 g, 66.2 mmol) was dissolved in a minimum amount of a 50% acetone/50% ethanol solution, and to this was added NaI (11.4 g, 76.1 mmol) dissolved in a minimum amount of 50% acetone/50% ethanol. The mixture was allowed to stand and the sodium chloride filtered off. The filtrate was poured into 2 L of deionized water to precipitate [PPN][I]. The product was separated by filtration, washed, dried, and slurried with a small amount of diethyl ether for several days. The product was again filtered and dried to give [PPN][I] (36.0 g, 54.1 mmol) (82%), mp 244–246 °C.

Preparation of [PPN][BH_4]. $NaBH_4$ (4.0 g, 106 mmol) was dissolved in 120 mL of absolute ethanol and added to [PPN][Cl] (10.3 g, 17.9 mmol) dissolved in 40 mL of absolute ethanol. A small amount of gas evolution was observed at this time. After filtration to remove sodium chloride the solution was poured into 1 L of ice water and the resulting [PPN][BH_4] precipitate removed by filtration, washed, slurried with ether overnight, refiltered, and dried to give [PPN][BH_4] (8.0 g, 14.5 mmol) (81%). The infrared spectrum (Nujol mull) exhibits B-H stretching transitions at 2280 (ms, sh), 2220 (vs), and 2130 cm^{-1} (m).

Preparation of [PPN][$Mo(CO)_5I$]. Using a modification of the procedure of King,[13] $Mo(CO)_6$ (2.02 g, 7.66 mmol) and [PPN][I]

(5.12 g, 7.60 mmol) were added to 100 mL of THF and the solution refluxed for 2–3 h to produce a clear, bright yellow solution. The solvent was removed with a water aspirator to leave the yellow-green powder [PPN][$Mo(CO)_5I$] in virtually quantitative yield. Solution IR of the carbonyl region: 2050 (w), 1921 (vs), 1852 cm^{-1} (s).

Preparation of [PPN][$Mo(CO)_4BH_4$] (I). [PPN][$Mo(CO)_5I$] (1.10 g, 1.22 mmol) was refluxed in 50 mL of THF with a molar excess of [PPN][BH_4] (0.83 g, 1.50 mmol). IR spectra at intermediate times showed the presence of $Mo(CO)_5I^-$, $HMo_2(CO)_{10}^-$,[14] and $Mo(CO)_4BH_4^-$. After 16 h, the solution was a clear orange-yellow with an orange solid on the sides of the reaction vessel. The settled solution was transferred away from the solids via syringe and the solvent evaporated in vacuo to leave an orange tar which was redissolved in diethyl ether to give a clear, bright yellow solution and an insoluble brown tar. The solution was filtered, the volume reduced in vacuo, and the flask placed in the freezer overnight to form 0.23 g of yellow-orange crystals of [PPN][$Mo(CO)_4BH_4$] (I) (25%): mp 100–107 °C; solution IR of the 2500–1800-cm^{-1} region 2395 (sh), 2376 (m), 2340 (sh), 2282 (w), 2018 (m), 1925 (w, sh, br), 1897 (vs), 1877 (s), 1835 cm^{-1} (s); IR (KBr) of the 2600–1000-cm^{-1} region excluding PPN^+ absorptions 2390 (sh), 2375 (m), 2330 (sh), 2280 (w), 2020 (m), 1975 (m, sh, br), 1900 (vs), 1878 (s), 1810 (s), 1395 (m, br), 1145 cm^{-1} (m); conductivity [$c \times 10^3$ (M) (ohm^{-1}), Λ_e (cm^2 $equiv^{-1}$ ohm^{-1})] 5.90, 110.2; 2.95, 116.9; 1.47, 122.4; 0.74, 125.7; 0.37, 132.4; 0.18, 136.1 ($\Lambda_0 = 137$, $A = 400$) (values indicative of a 1:1 electrolyte). The compound is soluble in THF and acetonitrile, slightly soluble in diethyl ether, and insoluble in nonpolar organic solvents, and reacts with acetone. Solutions and the solid are extremely air sensitive, but the crystals are stable indefinitely under nitrogen. Anal. Calcd for $C_{40}H_{34}BMoNO_4P_2$: C, 63.10; H, 4.50; B, 1.42; Mo, 12.60; N, 1.84; P, 8.14. Found: C, 62.57; H, 4.70; B, 1.56; Mo, 11.55; N, 2.28; P, 8.04.

Reaction of $Mo(CO)_6$, BH_4^- and I^- (Catalytic). This and the following reactions pertain to our analysis of the mode of formation of $[Mo(CO)_4BH_4]^-$ (see Discussion section).

$NaBH_4$ (0.44 g, 11.6 mmol) and [Bu_4N][I] (0.10 g, 0.28 mmol) were added to $Mo(CO)_6$ (1.51 g, 5.72 mmol) dissolved in 60 mL of THF. The solution was refluxed and solution IR spectra were of the carbonyl region recorded periodically. Over a period of 80 h, the relative percentages of $HMo_2(CO)_{10}^-$ and $Mo(CO)_4BH_4^-$ changed from ca. 70/30 at 3 h to 10/90 at 80 h. At no time were any other carbonyl region absorptions noted except those of $Mo(CO)_6$.

Reaction of $HMo_2(CO)_{10}^-$ and I^- (Molar). [Et_4N][$HMo_2(CO)_{10}$] (0.35 g, 0.58 mmol), prepared using published methods,[14] was added to NaI (0.09 g, 0.59 mmol) dissolved in 25 mL of THF. After refluxing for 24 h, the solution IR showed only $Mo(CO)_5I^-$, but the flask also contained a large amount of a brown-purple precipitate which, when dissolved in acetone, gave an extremely air-sensitive dark red solution.

Reaction of $HMo_2(CO)_{10}^-$, BH_4^-, and I^- (Catalytic). [Et_4N][$HMo_2(CO)_{10}$] (0.27 g, 0.45 mmol) was dissolved in 60 mL of THF and to the solution was added [PPN][BH_4] (0.30 g, 0.54 mmol) and [PPN][I] (0.03 g, 0.047 mmol). The mixture was then refluxed and the carbonyl region IR monitored for 48 h. After 3 h, the solution contained $HMo_2(CO)_{10}^-$ (II) and a small amount of $Mo(CO)_5I^-$. After 24 h, all of II had reacted producing small amounts of $Mo(CO)_5I^-$, only a trace of I, and large amounts of a red, air-sensitive precipitate.

Reaction of $HMo_2(CO)_{10}^-$, I^-, and BH_3·THF (Molar). To [PPN][$HMo_2(CO)_{10}$] (0.45 g, 0.45 mmol) dissolved in 50 mL of THF was added [PPN][I] (0.30 g, 0.45 mmol) and BH_3·THF (2 mL, 1 M, 2 mmol). The solution was refluxed for 16 h, at which time the IR showed I and $Mo(CO)_5I^-$.

Reaction of $HMo_2(CO)_{10}$, I^-, and BH_3·THF (Excess). [Et_4N][$HMo_2(CO)_{10}$] (0.42 g, 0.70 mmol), [PPN][I] (0.48 g, 0.72 mmol), and BH_3·THF (6 mL, 1 M, 6 mmol) were dissolved in 50 mL of THF and the solution refluxed for 16 h. [PPN][Cl] (0.60 g, 1.04 mmol) was added and the solution stirred briefly. After being allowed to settle, the solution was transferred via syringe to another flask, and the solvent removed with a water aspirator to leave a yellow tar. The tar was extracted with 45 mL of diethyl ether to give a pale yellow solution which was filtered and placed in the freezer overnight to produce light yellow crystals of [PPN][$Mo(CO)_4B_3H_8$]:[10] solution IR of the carbonyl region 2026 (w), 1908 (vs), 1881 (m), 1849 cm^{-1} (s); preliminary crystal data $V = 1980$ Å^3, $\rho_{obsd} = 1.36$ (1) g cm^{-3} (flotation in carbon tetrachloride/cyclohexane), $\rho_{calcd} = 1.32$ g cm^{-3} for $Z = 2$. Anal. Calcd for $C_{40}H_{38}B_3MoNO_4P_2$: C, 61.04; H, 4.87; N, 1.78. Found: C, 58.84; H, 4.81; N, 1.70.

Table I. Crystal Data for [PPN][$Mo(CO)_4BH_4$]

$a = 17.828$ (9) Å	Triclinic unit cell
$b = 9.714$ (4) Å	Space group $P\bar{1}$
$c = 12.471$ (5) Å	$Z = 2$
$\alpha = 101.77$ (1)°	Mol wt 761.4
$\beta = 115.36$ (1)°	
$\gamma = 94.40$ (1)°	$\mu = 4.40$ cm^{-1} for Mo Kα x-rays
$V = 1886.9$ Å^3	Crystal size 0.15 × 0.25 × 0.62 mm
$\rho_{calcd} = 1.34$ g cm^{-3}	Variation in transmission coefficient[b] 0.93–1.05
$\rho_{obsd} = 1.33$ (1) g cm^{-3} [a]	

[a] Obtained by flotation in carbon tetrachloride/cyclohexane. [b] Normalized to an average of unity.

Preparation of [PPN][$Mo(^{13}CO)_n(CO)_{4-n}BH_4$]. No exchange was observed by infrared spectroscopy when a solution of [PPN]-[$Mo(CO)_4BH_4$] in THF was stirred for 48 h under a ^{13}CO atmosphere. Therefore a catalytic carbon monoxide exchange procedure was employed. In a three-necked flask equipped with a gas inlet, stopper, and a serum cap over one joint, 1.0 g (3.8 mmol) of $Mo(CO)_6$ was dissolved, under nitrogen, in 40 mL of 4:1 cyclohexane–THF. A small amount (ca. 5 mg) of 10% Pd on charcoal was added to the reaction vessel, and then 80 mL of the atmosphere over the reaction mixture was removed through the serum cap via gas-tight syringe and 80 mL of 90% ^{13}CO injected in its place. The reaction mixture was then stirred vigorously, and the progress of the enrichment was monitored by infrared spectroscopy. After equilibrium was reached (ca. 6 h), another 80 mL of atmosphere was removed and replaced by ^{13}CO, and the reaction monitored as before. This procedure was repeated until the desired percent enrichment was achieved (ca. 15%). Next, the Pd(C) was allowed to settle and the supernatant was carefully transferred via syringe into another reaction vessel, diluted with 75 mL of THF, and used in the reaction scheme outlined above to prepare 15% ^{13}CO enriched [PPN][$Mo(CO)_4BH_4$].

Crystallographic Section. [PPN][$Mo(CO)_4BH_4$] crystallizes from diethyl ether as bright yellow parallelepipeds with well-formed faces. A specimen of dimensions 0.15 × 0.25 × 0.62 mm was mounted in a capillary tube along its long axis in an atmosphere of helium. Precession photographs indicated a triclinic crystal system. The unit cell parameters, obtained by measuring the setting angles of 27 reflections on a Nonius CAD-3 automated diffractometer, are given together with other relevant crystal data in Table I.

One hemisphere of data was collected[15] by the $\theta/2\theta$ scan technique with Zr filtered Mo Kα radiation up to a 2θ limit of 45°. A scan speed of 10°/min was used, with the scan range defined as $\Delta\theta = 1.2 + 0.15 \tan\theta$. Each reflection was scanned between two and six times depending on its intensity. Background counts were taken at the beginning and end of each scan. Zirconium foil attenuators were automatically inserted to prevent the counting rate from exceeding 2500 counts/s. A takeoff angle of 4° was used and the upper and lower level discriminators of the pulse height analyzer were set to obtain a 90% window centered on the Mo Kα peak. As a check on the stability of the diffractometer and the crystal, the ($\bar{7}$00), (040), and (00$\bar{6}$) reflections were measured at 50 reflection intervals during data collection. No significant variation in the monitor intensities was noted.

The standard deviation of each intensity reading was estimated using the expression[16]

$$\sigma(I) = [(\text{peak} + \text{background counts}) + (0.04)^2\,(\text{net intensity})^2]^{1/2}$$

Out of the total of 7110 reflections collected,[15] there were 3208 independent reflections with intensities greater than 3σ; these were retained for the subsequent structure analysis. The intensities were further corrected for Lorentz, polarization, and absorption effects.

The coordinates of the molybdenum and phosphorus atoms were obtained from a Patterson map, and the other nonhydrogen atoms were readily located from two difference Fourier maps.[17] After several cycles of least-squares refinement, in which the phenyl carbon atoms were assigned isotropic temperature factors and all other atoms were assigned anisotropic temperature factors, a difference Fourier revealed the tetrahydroborate hydrogen atoms. Calculated phenyl hydrogen positions, generated from consideration of the planar phenyl geometry, were entered but not refined. The parameters were then blocked into two matrices: one with the scale factor, anion coordinates, and thermal parameters; the other with the cation coordinates and thermal parameters. Several cycles of least squares resulted in final agreement factors of $R = 8.3\%$, $R_w = 8.1\%$.[18]

Results and Discussion

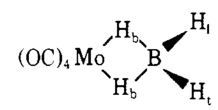
Synthesis and Properties. $[PPN][Mo(CO)_4BH_4]$ can be prepared in reasonable yield via a straightforward metathesis reaction (eq 1).

$$[PPN][Mo(CO)_5I] + [PPN][BH_4] \xrightarrow{THF} [PPN][Mo(CO)_4BH_4] + [PPN][I] + CO \quad (1)$$

I

The product is an air-sensitive, yellow-orange crystalline material.

Infrared spectra of I are identical in the solid state and in solution. The transitions associated with the tetrahydroborate functionality are in agreement with spectroscopic criteria[7a,19] for a bidentate ligation geometry, C. In tetrahydrofuran solution, the symmetric and antisymmetric (A_1 and B_1 under C_{2v}



C

symmetry) B–H_t stretching absorptions are observed at 2376 (m) and 2395 cm^{-1} (m); in a KBr disk the A_1 bridge expansion mode is observed at 1395 cm^{-1} (m), and the BH_2 deformation mode (B_2) at 1145 cm^{-1} (m). These values are in good agreement with those for other highly covalent bidentate transition metal tetrahydroborates.[7a] Because of the strong carbonyl stretching absorption in the 2000–1800-cm^{-1} region, it is not possible to assign the A_1 and B_2 νB–H_b transitions with certainty. A shoulder at 1925 cm^{-1} may be one of the transitions.[66] The four-band carbonyl stretching pattern is in good agreement with C_{2v} local symmetry about molybdenum:[20] 2020 (m), 1900 (vs), 1878 (s), and 1810 cm^{-1} (s).

The mechanism by which I arises was investigated because the BH_4^--induced incorporation of borane fragments into a metal carbonyl had been observed only once before[21] (usually a metal or metal hydride cluster is formed[5]) and because compounds such as I are attractive percursors for metal cluster synthesis. Furthermore, it was of interest to explore the role of I^- in reaction 1 since

$$Mo(CO)_6 + BH_4 \xrightarrow{THF} HMo_2(CO)_{10}^{-1} \quad (2)$$

II

represents an efficient synthesis of the hydride-bridged complex II,[14] and I is only detected in trace quantities. Several observations concerning eq 2 vis-à-vis eq 1 are noteworthy. First, infrared spectra reveal that II is produced during the course of reaction 1, but is consumed as the reaction nears completion. Second, when reaction 1 is carried out in diethyl ether instead of THF, considerable quantities of II are produced and the yield of I falls. Third, when catalytic amounts of I^- are added in reaction 2, the major product is I. A plausible scheme to explain these observations is shown in eq 3–7.

$$Mo(CO)_6 + Y \xrightarrow{slow} Mo(CO)_5Y + CO \quad (3)$$

$$Mo(CO)_5Y + BH_4^- \overset{fast}{\rightleftharpoons} Mo(CO)_5BH_4^- + Y \quad (4)$$

$$Mo(CO)_5BH_4^- \xrightarrow{slow} Mo(CO)_4BH_4^- \text{ (I)} + CO \quad (5)$$

$$Mo(CO)_5BH_4^- \overset{fast}{\rightleftharpoons} HMo(CO)_5^- + [BH_3] \quad (6)$$

$$HMo(CO)_5^- + Mo(CO)_5Y \overset{fast}{\rightleftharpoons} HMo_2(CO)_{10}^- \text{ (II)} + Y \quad (7)$$

$$Y = \text{THF or } I^-$$

Reaction 3 is well known for the formation of $Mo(CO)_5THF$[22] or $Mo(CO)_5I^-$.[13] When $Y = I^-$, reaction 4 is a halide displacement by BH_4^- for which there is ample precedent.[7] Presumably the pentacarbonyl tetrahydroborate is short lived (it could not be detected spectroscopically) and either decarbonylates to produce I (eq 5) or enters into reaction 6. The loss of CO in step 5 is essentially irreversible as evidenced by the ^{13}CO exchange experiments (see Experimental Section) and drives the reaction to completion. As written, reactions 3, 4, and 5 would only require catalytic amounts of I^- to produce I; this was verified experimentally (see Experimental Section for details). The equilibria represented by eq 6 and 7 serve to explain the buildup and subsequent decay of II as the overall reaction for formation of I goes to completion. The presence of I^- and THF should favor consumption of II and formation of I. The cleavage of M–H–M units by soft Lewis bases such as $(C_6H_5)_3P$ and CH_3CN has been observed before,[23a,b] and Hayter has postulated equilibrium 7 to explain why, when equimolar mixtures of $HM_2(CO)_{10}^-$ (M = Cr, Mo, W) are refluxed, statistical mixtures of the mixed metal compounds are produced.[14] When I^- is absent, cleavage at room temperature by THF is not as facile and the predominant product is II. The optimum role of THF in this scheme is to complex BH_3 and to retain it for equilibrium 6. With solvents such as diethyl ether, which are weaker Lewis bases, the volatile BH_3 is lost (as B_2H_6) and the equilibrium is driven toward II.

Support for the form of equilibria 6 and 7 was derived from several additional chemical experiments (see Experimental Section). It can be shown that II is readily cleaved by I^- (eq 8).

$$HMo_2(CO)_{10}^- + I^- \text{ (molar)} \rightarrow Mo(CO)_5I^- + [HMo(CO)_5^-] \quad (8)$$

The iodide ion would be expected to cleave the dimer to form equal amounts of $HMo(CO)_5^-$ and $Mo(CO)_5I^-$. Although the iodide complex is observed, the $HMo(CO)_5^-$ is apparently so unstable that in the absence of BH_3, it decomposes to cluster complexes of higher molecular weight. This assumption is supported by the fact that previous attempts to synthesize $HMo(CO)_5^-$ using methods identical with those for $HCr(CO)_5^-$ and $HW(CO)_5^-$ produced only H.[23c,d] It was next shown that BH_3 is essential to produce I from II. Reaction 9 reveals that BH_4^- will not serve for this purpose (see Experimental Section).

$$HMo_2(CO)_{10}^- + BH_4^- + I^- \text{ (catalytic)} \rightarrow MoCO)_5I^- \text{ (trace)} + \text{I (trace)} + ? \quad (9)$$

However, when a source of BH_3 is introduced in stoichiometric quantities, the equilibria of eq 6 and 7 are set up and I is produced from II.

$$HMo_2(CO)_{10}^- + I^- + BH_3{\cdot}THF \text{ (molar)} \rightarrow Mo(CO)_4BH_4^- + Mo(CO)_5I^- \quad (10)$$

Interestingly, when a large excess of $BH_3{\cdot}THF$ is used, the air-stable $Mo(CO)_4B_3H_8^-$ [10] complex is produced.

$$HMo_2(CO)_{10}^- + I^- + BH_3{\cdot}THF \text{ (excess)} \rightarrow Mo(CO)_4B_3H_8^- \quad (11)$$

Although unexpected, this result is understandable since the

Table II. Final Atomic Parameters for [PPN][$Mo(CO)_4BH_4$][a]

Atom	x	y	z	Atom	x	y	z
Mo	0.21374 (6)	0.39312 (10)	0.07375 (9)	C(29)	−0.0059 (8)	0.5104 (13)	−0.7133 (12)
P(1)	0.18621 (15)	0.86684 (30)	−0.38790 (20)	C(30)	−0.0344 (10)	0.6021 (17)	−0.6472 (16)
P(2)	0.36220 (15)	0.86982 (30)	−0.34455 (20)	C(31)	0.0275 (9)	0.7106 (14)	−0.5393 (13)
N	0.2772 (4)	0.8304 (8)	−0.3425 (7)	C(32)	0.1766 (6)	1.0311 (9)	−0.4371 (9)
B	0.2665 (11)	0.4707 (19)	−0.0574 (17)	C(33)	0.1434 (7)	1.0214 (11)	−0.5614 (10)
H(1)	0.300 (4)	0.512 (7)	0.047 (8)	C(34)	0.1457 (8)	1.1542 (14)	−0.5926 (12)
H(2)	0.206 (6)	0.368 (10)	−0.093 (8)	C(35)	0.1807 (7)	1.2749 (13)	−0.5077 (12)
H(3)	0.301 (6)	0.402 (10)	−0.077 (9)	C(36)	0.2130 (8)	1.2841 (13)	−0.3860 (11)
H(4)	0.252 (4)	0.557 (9)	−0.117 (7)	C(37)	0.2124 (6)	1.1577 (11)	−0.3503 (9)
C(10)	0.1213 (8)	0.2660 (12)	0.0694 (10)	C(38)	0.4132 (6)	0.7147 (9)	−0.3332 (8)
O(11)	0.0682 (6)	0.1934 (10)	0.0714 (9)	C(39)	0.3854 (6)	0.6081 (10)	−0.3000 (9)
C(12)	0.2578 (6)	0.4312 (10)	0.2487 (10)	C(40)	0.4280 (8)	0.4919 (12)	−0.2817 (11)
O(13)	0.2857 (5)	0.4532 (8)	0.3554 (7)	C(41)	0.4953 (8)	0.4858 (13)	−0.3060 (12)
C(14)	0.1447 (8)	0.5490 (13)	0.0737 (11)	C(42)	0.5224 (8)	0.5929 (13)	−0.3413 (11)
O(15)	0.1052 (6)	0.6342 (10)	0.0793 (9)	C(43)	0.4828 (7)	0.7109 (12)	−0.3588 (10)
C(16)	0.2789 (7)	0.2275 (11)	0.0749 (10)	C(44)	0.4323 (6)	1.0173 (9)	−0.2163 (8)
O(17)	0.3142 (5)	0.1369 (8)	0.0744 (8)	C(45)	0.4100 (6)	1.0744 (10)	−0.1270 (9)
C(20)	0.1577 (5)	0.8881 (9)	−0.2664 (8)	C(46)	0.4623 (7)	1.1925 (12)	−0.0328 (11)
C(21)	0.1961 (6)	0.8203 (10)	−0.1772 (10)	C(47)	0.5372 (7)	1.2497 (12)	−0.0274 (11)
C(22)	0.1727 (7)	0.8263 (11)	−0.0806 (10)	C(48)	0.5612 (7)	1.1884 (12)	−0.1088 (11)
C(23)	0.1117 (7)	0.9017 (12)	−0.0811 (11)	C(49)	0.5086 (7)	1.0698 (12)	−0.2077 (10)
C(24)	0.0750 (7)	0.9707 (11)	−0.1646 (10)	C(50)	0.3527 (6)	0.9198 (10)	−0.4811 (8)
C(25)	0.0965 (7)	0.9677 (11)	−0.2615 (10)	C(51)	0.3328 (6)	0.8132 (11)	−0.5860 (10)
C(26)	0.1097 (6)	0.7254 (9)	−0.5133 (8)	C(52)	0.3159 (8)	0.8618 (15)	−0.6950 (12)
C(27)	0.1351 (6)	0.6374 (9)	−0.5864 (9)	C(53)	0.3189 (8)	0.9864 (15)	−0.6946 (12)
C(28)	0.0766 (8)	0.5312 (12)	−0.6890 (11)	C(54)	0.3385 (8)	1.0915 (13)	−0.5980 (12)
				C(55)	0.3566 (6)	1.0614 (11)	−0.4818 (10)

Thermal Parameters

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$[b]
Mo	48.0 (5)	142.7 (14)	116.2 (11)	27.1 (12)	81.0 (11)	59.2 (18)
P(1)	30 (1)	115 (4)	71 (3)	20 (3)	42 (3)	50 (5)
P(2)	28 (1)	114 (4)	70 (3)	20 (3)	39 (3)	52 (5)
N	20 (3)	138 (11)	95 (8)	31 (10)	42 (9)	93 (16)
B	87 (10)	193 (26)	171 (23)	102 (29)	158 (26)	144 (41)
C(10)	65 (7)	181 (19)	106 (13)	74 (19)	64 (16)	2 (25)
O(11)	80 (5)	260 (16)	257 (15)	−84 (15)	201 (16)	−37 (24)
C(12)	38 (5)	150 (16)	102 (12)	48 (14)	46 (14)	42 (24)
O(13)	64 (4)	234 (14)	120 (9)	68 (12)	75 (11)	53 (19)
C(14)	72 (7)	222 (21)	150 (15)	80 (20)	137 (18)	188 (30)
O(15)	120 (7)	297 (18)	281 (15)	272 (18)	246 (18)	362 (28)
C(16)	66 (6)	130 (16)	104 (12)	14 (16)	93 (15)	56 (23)
O(17)	91 (5)	161 (12)	228 (13)	101 (13)	198 (14)	150 (21)

H(1)	3.7 (18)	C(26)	3.7 (2)	C(36)	6.4 (3)	C(46)	6.0 (2)
H(2)	6.6 (23)	C(27)	4.7 (2)	C(37)	4.8 (2)	C(47)	6.1 (2)
H(3)	6.6 (26)	C(28)	6.3 (3)	C(38)	4.6 (2)	C(48)	6.4 (3)
H(4)	5.1 (20)	C(29)	7.0 (3)	C(39)	6.6 (3)	C(49)	6.1 (2)
C(20)	3.5 (2)	C(30)	9.9 (4)	C(40)	6.9 (3)	C(50)	3.7 (2)
C(21)	4.9 (2)	C(31)	8.0 (3)	C(41)	7.0 (3)	C(51)	5.3 (2)
C(22)	5.6 (2)	C(32)	4.1 (2)	C(42)	5.7 (2)	C(52)	7.8 (3)
C(23)	5.9 (2)	C(33)	5.5 (2)	C(43)	3.7 (2)	C(53)	7.4 (3)
C(24)	5.4 (2)	C(34)	7.1 (3)	C(44)	3.7 (2)	C(54)	6.8 (2)
C(25)	5.5 (2)	C(35)	6.3 (3)	C(45)	4.5 (2)	C(55)	5.4 (2)

[a] Numbering scheme for the PPN cation: C(20)–C(25) = phenyl(1), C(26)–C(31) = phenyl(2), etc. with phenyl(1)–phenyl(3) attached to P(1) and phenyl(4)–phenyl(6) attached to P(2). [b] For the expression $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

$B_3H_8^-$ ligand is believed to have a greater degree of bidentate efficacy than the BH_4^- group.[10]

Molecular Structure of [PPN][$Mo(CO)_4BH_4$]. The final atomic parameters of [PPN][$Mo(CO)_4BH_4$] are given in Table II. Bond lengths and angles for the anion and cation are collected in Tables III and IV, respectively. Structure factor tables are available.[24] The geometry of the anion is shown in Figures 1 and 2. The coordination about the central molybdenum atom is approximately octahedral, but two notable distortions occur in the equatorial plane: $\angle C(eq)-Mo-C(eq) = 84.5\ (5)°$ and $\angle H_b-Mo-H_b = 59\ (4)°$. The tetrahydroborate ligand is coordinated to the molybdenum atom via two metal-hydrogen-boron bridges; this bidentate attachment is often observed for covalent metal tetrahydroborates,[7] although for Zr, Hf, U, and a few other elements triple bridge attachment is also observed.[7] Bond angles and distances within the BH_4 group are normal; the average B–H distance of 1.15 (10) Å is comparable to the neutron-diffraction determined B–H distances of 1.26 (2) Å in KBH_4,[25a] 1.25 (2) Å in $Hf(BH_4)_4$ (average of B–H_b and B–H_t in this tridentate structure),[25b] 1.24 (4) Å in $U(BH_4)_4$ (average of B–H_b and B–H_t in the isolated tridentate BH_4^- unit),[25c] and 1.192 (16) (B–H_t), 1.255 (9), 1.208 (13) Å (B–H_b) in $(CH_3C_5H_4)_2Hf(BH_4)_2$.[25d] Although they show considerable variation, the H–B–H angles in I are approximately tetrahedral.

The geometry of the PPN^+ cation is similar to that found

Table III. Bond Lengths and Angles for the $Mo(CO)_4(BH_4)^-$ Anion

	Bond Lengths		
Mo-B	2.413 (20)	C(10)-O(11)	1.145 (18)
Mo-H(1) (b)	2.04 (8)	C(12)-O(13)	1.168 (13)
Mo-H(2) (b)	1.99 (9)	C(14)-O(15)	1.136 (18)
Mo···H(3) (t)	2.92 (11)	C(16)-O(17)	1.120 (15)
Mo···H(4) (t)	3.30 (12)		
Mo-C(10) (eq)	1.954 (14)		
Mo···O(11) (eq)	3.099 (11)	B-H(1) (b)	1.14 (9)
Mo-C(12) (eq)	1.917 (11)	B-H(2) (b)	1.26 (11)
Mo···O(13) (eq)	3.085 (8)	B-H(3) (t)	1.01 (11)
Mo-C(14) (ax)	2.021 (14)	B-H(4) (t)	1.20 (9)
Mo···O(15) (ax)	3.155 (11)		
Mo-C(16) (ax)	2.051 (12)		
Mo···O(17) (ax)	3.171 (9)		
	Bond Angles		
H(1)-Mo-H(2)	59 (4)	O(13)-Mo-O(15)	88.8 (2)
C(10)-Mo-C(12)	84.5 (5)	O(13)-Mo-O(17)	89.4 (2)
C(10)-Mo-C(14)	86.8 (6)	O(15)-Mo-O(17)	175.6 (3)
C(10)-Mo-C(16)	89.9 (5)	H(1)-B-H(2)	112 (6)
C(12)-Mo-C(14)	89.6 (5)	H(1)-B-H(3)	105 (7)
C(12)-Mo-C(16)	89.6 (4)	H(1)-B-H(4)	118 (5)
C(14)-Mo-C(16)	176.7 (6)	H(2)-B-H(3)	90 (8)
O(11)-Mo-O(13)	83.8 (3)	H(2)-B-H(4)	115 (6)
O(11)-Mo-O(15)	85.6 (3)	H(3)-B-H(4)	113 (7)
O(11)-Mo-O(17)	90.2 (3)	Mo-H(1)-B	96 (5)
O(11)-Mo-O(17)	90.2 (3)	Mo-H(1)-B	96 (5)
		Mo-H(2)-B	93 (5)

in the majority of PPN^+ structure determinations. Although there are two known cases of a linear P-N-P framework,[26] the majority exhibit angles similar to the 141.1 (5)° angle found in this work.

The interaction between the $Mo(CO)_4$ fragment and the BH_4^- ligand is the most interesting feature of this structure. The average $Mo-H_b$ distance, 2.02 (8) Å, is within two standard deviations of the range of numerous observed M-H-M (M = Mo, W) M-H distances, 1.85-1.89 (1) Å.[27] The observed Mo-B distance, 2.41 (2) Å, is identical with the average Mo-B distance found in $B_{10}H_{10}COMoCO(CO)_3{}^{2-}$ [28] and slightly shorter than the sum of the estimated covalent radii, 2.44-2.49 Å.[29] The $Mo-H_b$ and Mo-B bond distances, therefore, suggest significant direct Mo-B interaction as well as $Mo-H_b$ bonding. Although the longer than usual $Mo-H_b$ distance may not be significant, at least the observed trend toward greater M-H distances for bridging hydrogen atoms seems correct (Mo-H terminal bonds have been estimated to be ca. 1.77 Å).[31]

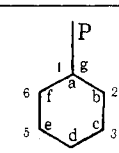
The H_b-Mo-H_b angle is a result of the small "bite size" of the BH_4^- ligand. The 59 (4)° value can be compared with other bidentate metal tetrahydroborates, where H_b-M-H_b angles range from 60 to 76°.[7a,32] The H_b-M-H_b angle in $Cr(CO)_4B_3H_8^-$ is 101 (4)°,[33] which is considerably closer to the ideal octahedral value of 90° than is found in $Mo(CO)_4BH_4^-$. Indeed, the thermal instability of $Mo(CO)_4BH_4^-$ in comparison to $Mo(CO)_4B_3H_8^-$ may reflect this contracted bite angle and accompanying poorer ligand-metal orbital overlap.[10]

Within the $Mo(CO)_4$ fragment the average Mo-C(eq) distance of 1.94 (1) Å is 0.1 Å shorter than the average Mo-C(ax) distance, 2.04 (1) Å, as is expected when equatorial carbonyl ligands are trans to a σ bonding ligand such as M, H, or BH_4.[34] Most angles within the fragment are consistent with the octahedral coordination, but the C(eq)-Mo-C(eq) angle of 84.5 (5)° is unexpectedly small. Normally, we would expect a deviation in the direction of a larger angle because of steric factors. We can offer no explanation for the significantly small C(eq)-Mo-C(eq) angle at this time, although it is interesting to note that the deviation serves to keep the $H_b-Mo-C(eq)$ angles close to 180°.

Molecular Dynamics. NMR Studies. In general, the ^1H NMR spectra of covalent metal tetrahydroborates exhibit a single BH_4 resonance at room temperature.[7] This situation obtains regardless of whether the ground state metal tetrahydroborate coordination geometry is bidentate or tridentate, and is due to exceedingly rapid intramolecular interchange of bridge and terminal hydrogen atoms.[7a] At present, only limited kinetic data are available for the dynamic process in tridentate tetrahydroborates, viz., paramagnetic $(C_5H_5)_3UBH_4$ ($\Delta G^\ddagger \approx 5.0 \pm 0.6$ kcal/mol)[9b] and $M(BH_4)_4$, M = Zr, Hf, in the solid state ($\Delta G^\ddagger \approx 8.4$ kcal/mol).[35] Likewise, in the bidentate series, only the highly covalent complex $(C_5H_5)_2VBH_4$ has so far proven amenable to barrier height determination ($\Delta G_c^\ddagger \approx 7.6 \pm 0.3$ kcal/mol),[9a] though several complexes of the type $L_2M(H_2)BH_4$, L = a bulky phosphine, M = Rh, Ir, were noted to have what appears to be comparable or even greater energetic barriers to hydrogen interchange[36] (no quantitative rate data were reported). It is not at present clear what effect the ground state BH_4^- ligation geometry, the metal, and the nature of the other ligands in the complex have

Table IV. Bond Lengths and Angles for the PPN Cation[a]

N-P(1)	1.565 (8)	P(2)-C(38)	1.816 (10)
N-P(2)	1.545 (9)	P(2)-C(44)	1.805 (9)
P(1)-C(20)	1.797 (10)	P(2)-C(50)	1.805 (10)
P(1)-C(26)	1.792 (10)		
P(1)-C(32)	1.815 (9)	P(1)-N-P(2)	141.8 (6)



	Phenyl(1)	Phenyl(2)	Phenyl(3)	Phenyl(4)	Phenyl(5)	Phenyl(6)
1-2	1.342 (14)	1.396 (16)	1.381 (15)	1.326 (14)	1.366 (15)	1.382 (14)
2-3	1.426 (17)	1.396 (16)	1.421 (18)	1.409 (16)	1.385 (16)	1.396 (18)
3-4	1.352 (18)	1.356 (22)	1.306 (19)	1.357 (22)	1.373 (19)	1.303 (21)
4-5	1.312 (16)	1.364 (23)	1.352 (18)	1.340 (19)	1.316 (18)	1.305 (19)
5-6	1.412 (17)	1.454 (23)	1.388 (17)	1.396 (18)	1.413 (17)	1.440 (17)
6-1	1.390 (16)	1.346 (21)	1.356 (14)	1.407 (18)	1.366 (18)	1.373 (15)
a	121.5 (10)	120.2 (10)	118.3 (7)	121.1 (10)	120.1 (9)	121.6 (9)
b	119.7 (10)	120.8 (11)	115.2 (10)	120.8 (11)	119.7 (11)	118.6 (11)
c	117.7 (10)	119.8 (12)	121.2 (12)	119.1 (12)	120.2 (12)	119.0 (12)
d	123.0 (12)	120.4 (14)	123.4 (13)	119.8 (13)	119.9 (12)	124.9 (13)
e	121.0 (12)	118.3 (16)	117.8 (11)	123.0 (14)	121.3 (13)	119.7 (12)
f	117.0 (10)	119.6 (14)	119.7 (10)	116.1 (11)	118.6 (11)	116.0 (10)
g	117.1 (8)	119.1 (9)	122.5 (9)	120.0 (9)	120.4 (8)	118.8 (8)

[a] See footnote *a* of Table II for PPN numbering scheme.

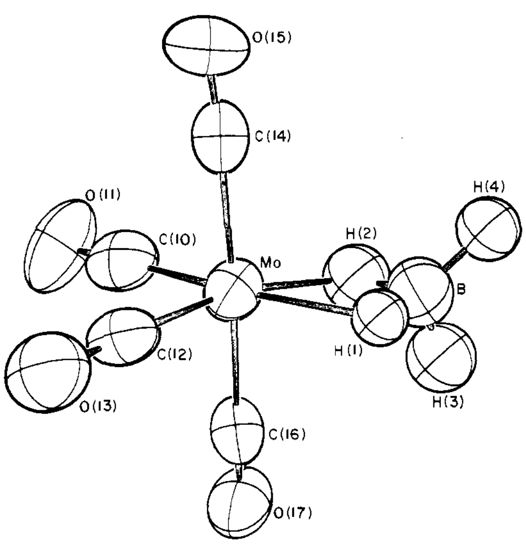
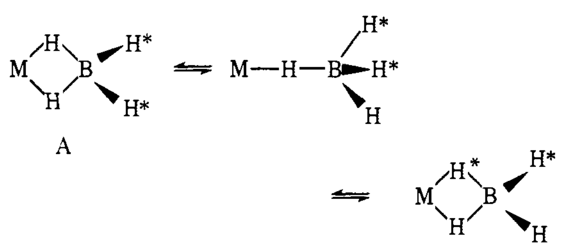


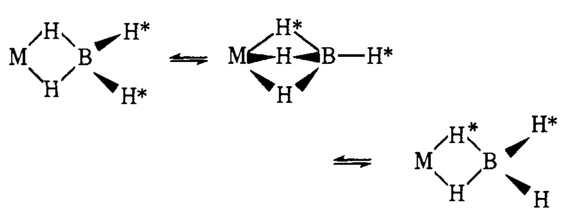
Figure 1. The molecular structure of the $[Mo(CO)_4BH_4]^-$ anion.

on tetrahydroborate molecular dynamics. Even less is known about the mechanism(s). To provide further information on these questions, dynamic NMR studies of $Mo(CO)_4BH_4^-$ were undertaken.

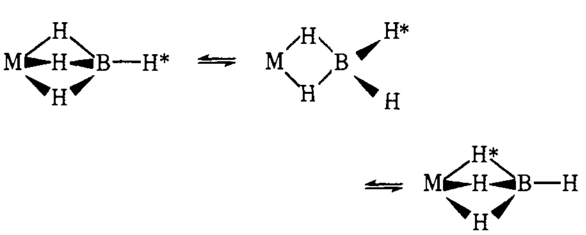
The processes depicted in eq 12–14 have been suggested



(12)



(13)



(14)

(none have been identified) as possible pathways for bridge-terminal hydrogen permutation in bidentate and tridentate tetrahydroborate complexes.[7a,37,38] These involve rapid oscillation between structures with different formal metal coordination numbers. As written these reactions are not strictly concerted[39] in that bond breaking and bond making are not simultaneous events along the reaction coordinate. It is also possible to devise a concerted fluxional process for metal tetrahydroborates with bidentate (or tridentate[40]) ground state geometries by twisting the ligand about one of the B–H_b bonds (darkened) as illustrated in eq 15.[7a] The parameters θ and r could presumably have some variability since the transition state is not necessarily a "relaxed" tridentate structure. Though the above reactions may appear superficially to be different in character, it is necessary to determine rigorously if there are modes of tetrahydroborate nuclear permutation (the dynamic

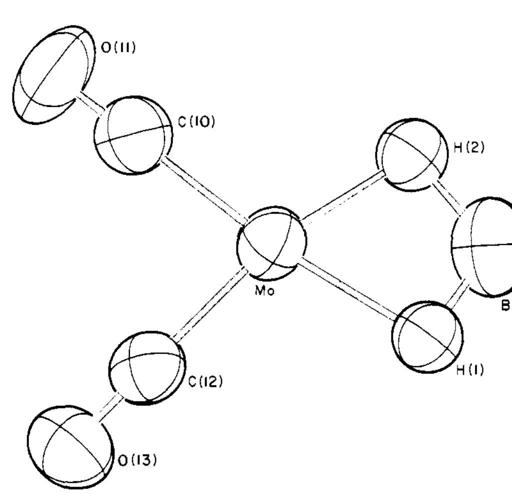
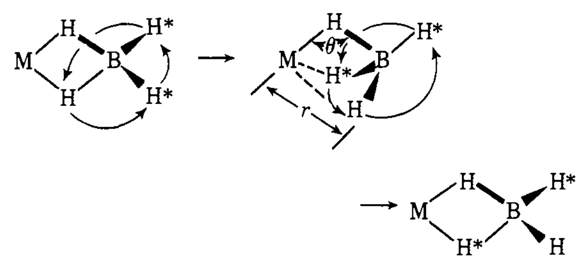
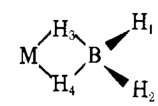


Figure 2. A view of the equatorial plane of $[Mo(CO)_4BH_4]^-$.



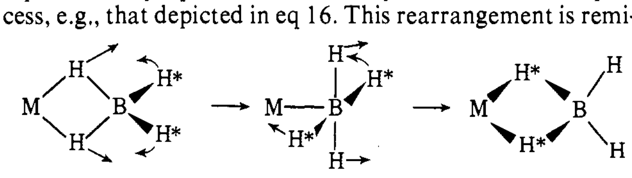
(15)

NMR observable) which will actually be differentiable in an NMR experiment, and then to see if these can be identified with plausible (e.g., 12–15) reaction mechanisms. The first step is to analytically partition the enumerated set of nuclear permutations into equivalency classes.[7a,42] The result relevant to $Mo(CO)_4BH_4^-$ is shown below. Besides the identity operation,



reaction A	reaction B
(13)(2)(4)	(13)(24)

two reactions (and their equivalents)[43] are, in theory, differentiable by NMR. These permutations differ in whether one bridge and one terminal hydrogen or both bridge and both terminal hydrogens are interchanged each time the reaction coordinate is traversed. This interesting multiplicity in pathways has not been previously recognized for tetrahydroborates.[44,45] It can be seen that the rearrangements depicted in eq 12, 13, and 15 can all be identified with a single permutation: the one bridge H atom for one terminal H atom interchange process, i.e., reaction A. Differentiable reaction B, which involves synchronous permutation of both bridge hydrogen atoms with both terminal hydrogen atoms during each traversal of the reaction coordinate, is mechanistically not represented by eq 12, 13, or 15 but by a different kind of process, e.g., that depicted in eq 16. This rearrangement is remi-



(16)

niscent of the Berry pseudorotation.[44] It should be noted that reaction 16 involves major changes in the coordination environment about the metal, and an intermediate or transition state with C_{4v} local symmetry at boron. Though there is some precedent for five-coordinate boron (e.g., BH_5),[46] metal-boron bonds,[47] and substantial M–B interaction in metal tetrahy-

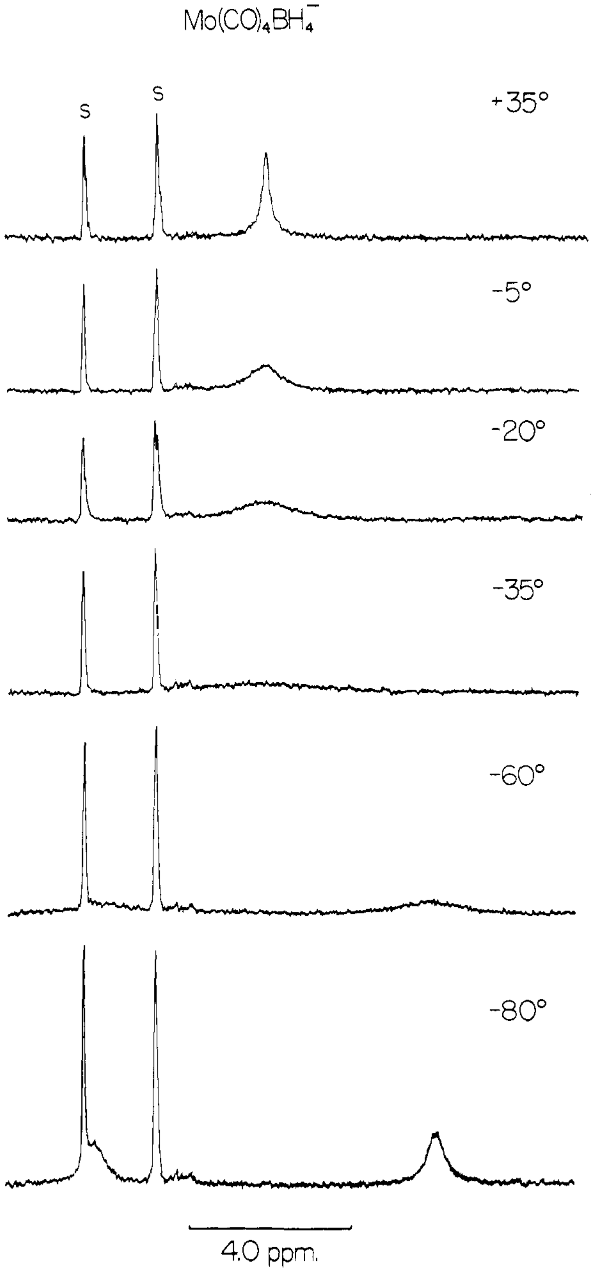


Figure 3. Variable temperature $^{1}H\{^{11}B\}$ spectra of $[PPN][Mo(CO)_4BH_4]$ at 60 MHz. The symbol S denotes traces of THF-d_7 in the solvent, THF-d_8.

droborate bonding,[48] eq 16 should be regarded as highly speculative.

$[PPN][Mo(CO)_4BH_4]$ provides an unusual opportunity to probe some of the energetic and mechanistic uncertainties discussed above because the structure is coordinatively rather saturated (quasi-octahedral $L_2Mo(CO)_4$) and because metal carbonyl complexes in this region of the periodic table usually conform to the 18-electron rule.[49] Furthermore, ^{13}C NMR of the carbonyl groups should provide a means of determining whether stereochemical changes in the metal coordination sphere occur in concert with H_t–H_b exchange. Five- and seven-coordinate metal polyhedra of mono- and tridentate intermediates are likely to be stereochemically nonrigid.[43b,50] Likewise, the manifestations of a boron-bound C_{4v} intermediate (eq 16) or a $\pi/4$ rotation of the $B(H_b)_2$ bonding plane about the B–Mo axis[51] could be detected.

Figure 3 presents variable temperature ^{1}H NMR spectra of I with decoupling of ^{11}B. At room temperature, a singlet centered at δ −2.7 is observed; without ^{11}B irradiation, a

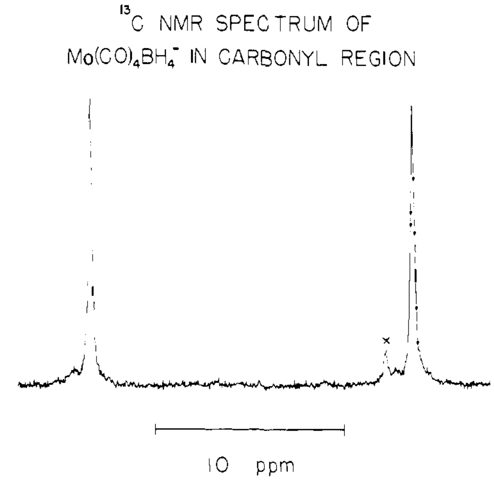
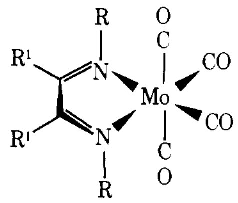


Figure 4. Room temperature 20-MHz ^{13}C NMR spectrum of $[PPN][Mo(CO)_4BH_4]$ in the carbonyl region. A trace of $Mo(CO)_5I^-$ is denoted by X.

quartet ($J_{^{11}B\text{-}H} \approx 80$ Hz) severely broadened by ^{11}B quadrupolar relaxation[7a] is seen. The singlet integrates in a ratio of ca. 4:30 with respect to the PPN aromatic resonances. Upon lowering the temperature, the BH_4 singlet collapses and at lower temperatures resonances at δ −9.8 and 4.3 grow in. These signals are in relative intensities of 2:2. The higher field peak is assigned to the H_b protons, with the resonance position attributable to diamagnetic and paramagnetic shielding[52] by the proximate transition metal. The low-field resonance is assigned to the H_t protons. The field position of H_t is comparable to values found for analogous terminal protons in several other bidentate transition metal tetrahydroborates ($\delta \approx$ 3.9–7.8[9a,36]) and in diborane ($\delta \approx 4.0$[53]). No spin-spin coupling could be resolved in what is expected to be an AA′XX′ pattern of multiplets (a maximum of ten lines is expected per multiplet[54]). This lack of resolution is attributable to the small expected magnitudes of the coupling constants,[55] low temperature viscosity line broadening, and possible incomplete decoupling (rf and/or correlation time[7a]) of ^{11}B. Taking the spectral coalescence point to be -42 ± 3 °C and employing the modified Bloch equations[56] yields a free energy of activation ($\Delta G_c^{\ddagger}$) for bridge-terminal hydrogen exchange in I of 10.0 ± 0.2 kcal/mol.

For carbon-13 studies of the carbonyl ligands it was necessary to synthesize a derivative ca. 15% enriched in ^{13}CO (see Experimental Section). The room temperature spectrum of this derivative in THF-d_8 exhibits two carbonyl resonances[57] in an intensity ratio of 1:1 at δ 209.8 and 226.2 ppm vs. Me_4Si (Figure 4). The field positions are similar to analogous $Mo(CO)_4$ compounds.[57,58] The line widths of the ^{13}CO resonances in I are invariant to broad band ^{1}H decoupling, indicating rather small C–H coupling constants. Based upon data from analogous tetracarbonylmolybdenum systems,[57,58] the low-field resonance is assigned to the CO groups in the plane of the H_b ligands. Variable temperature studies from −65 to 70 °C produced a surprising result: *the $Mo(CO)_4$ portion of the molecule is completely rigid over this temperature range.* That is, *bridge-terminal hydrogen interchange within the tetrahydroborate ligand does not permute the environments of the two kinds of carbonyl ligands.* Assuming that the minimum chemical exchange line broadening which could be discerned at 70 °C (above this temperature thermal decomposition becomes rapid) is 3 Hz, then the free energy of activation for axial-equatorial carbonyl interchange at 70 °C is $\gtrsim 18.6$ kcal/mol, which is at least 9 kcal/mol greater than the $\Delta G_c^{\ddagger}$ for the fluxional process in the tetrahydroborate moiety. It is of interest to note that nonrigidity has only been observed in



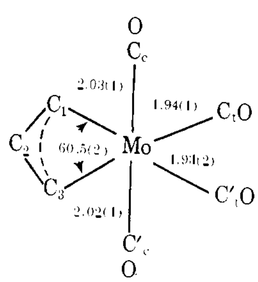
D

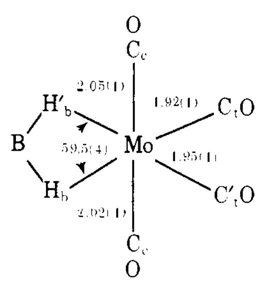
one *cis*-$L_2Mo(CO)_4$ system to date: that where L_2 = substituted diazabutadienes, D.[58] Here $\Delta G_c^{\ddagger} \approx 10$–13 kcal/mol.

Conclusions

This work demonstrates that metal tetrahydroborates of the middle transition elements are accessible with carbonyl groups as the only other ligands. As noted in the synthetic and mechanistic discussion, the formation of such products, as opposed to metal hydrides, depends critically upon the reaction conditions. Our results indicate that it may be possible to synthesize carbonyl tetrahydroborates of a number of other metals under the proper conditions of solvent and leaving group; this hypothesis is under investigation.

Since zerovalent molybdenum carbonyls conform rather closely to the noble gas formalism,[49] $Mo(CO)_4BH_4^-$ provides an opportunity to more accurately assess the number of electrons formally donated by a bidentate BH_4^- ligand. From simple electron counting and analogy to the η^3-allyl ligand in a number of early transition metal compounds, it was previously suggested[7a] that the bidentate BH_4^- ligand was a four-electron donor. Electron counting in I reveals that tetrahydroborate indeed acts as a formal four-electron donor. As has been shown elsewhere,[7a] the reasons for the similarity in ligation patterns of BH_4^- and η^3-allyl can be understood in terms of ligand bite angle as well as molecular orbital symmetries and energies. This similarity and its manifestation in the $Mo(CO)_4$ fragment is especially apparent when the structure of $Mo(CO)_4BH_4^-$ is compared to that of the allyl, $Mo(CO)_4[\eta^3\text{-}C_3H_4P(C_6H_5)_3]$,[59] as shown below.





Two features revealed by the dynamic NMR studies of bridge-terminal hydrogen exchange in $Mo(CO)_4BH_4^-$ are noteworthy. First, the barrier to hydrogen interchange ($\Delta G_c^{\ddagger} \approx 10$ kcal/mol), though high for a covalent metal tetrahydroborate,[7a] seems to be qualitatively rather low for a tetracarbonylmolybdenum complex undergoing formal 18 $\rightleftharpoons$ 16 electron configurational oscillations[49,60] as in a bidentate $\rightleftharpoons$ monodentate equilibrium.[61] These energetic observations coupled with the finding that the $Mo(CO)_4$ coordination polyhedron is immobile on the NMR time scale place restrictions on the range of operational BH_4^- rearrangement mechanisms and the lifetime of plausible nonrigid intermediates. For example, the intermediate of eq 12 or eq 13 must be sufficiently short lived that carbonyl positional scrambling[43b,50] does not occur about the metal before re-formation of the ground state bridge structure. Especially in the case of a five-coordinate, 16-electron $LMo(CO)_4$ moiety, this is likely to be a stringent restriction.[43b,50,63] There are in principle two differentiable rearrangement modes for bidentate tetrahydroborates, viz., reactions A ((12)(2)(4)) and B((13)(24)). Though we are not as yet able to rule out all mechanistic variants of the latter permutation, it is now possible to exclude a process such as eq 16 where either there is a C_{4v} intermediate with free rotation about the Mo–B bond or in which the metal coordination polyhedron "follows" by deformation of OC–M–CO angles (essentially pseudorotation) the bridge-terminal hydrogen interchange.[64] Theoretical studies of this interesting problem are also in progress.[65]

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Supplementary Material Available: A listing of structure factor amplitudes for the x-ray data set (Table V) (14 pages). Ordering information is given on any current masthead page.

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(66) Note Added in Proof. Infrared spectra of $[PPN][Mo(CO)_4BD_4]$ confirm the assignments of the MoH_2BH_2 normal modes. A medium intensity $\nu B-D_t$ absorption is observed at 1753 cm^{-1} (the other $\nu B-D_t$ mode is apparently obscured by the intense $\nu C-O$ transitions), $\nu H/\nu D \approx 1.36$; a weak $\nu B-D_b$ band is observed at 1422 cm^{-1}, $\nu H/\nu D \approx 1.35$; and a broad BD_2 deformation occurs at 925 cm^{-1}, $\nu H/\nu D \approx 1.24$; the bridge expansion mode is anticipated[7a] to occur in the region of a number of strong PPN^+ absorptions and could not be unambiguously identified.