Cyanide and carbonyl complexes in which π back-bonding is important are indeed precisely where this assumption might be expected to break down. The extent of π overlap between M and C and between C and O (or N) are interrelated and depend sensitively on the nuclear coordinates. Table II shows that the eigenvectors for the high-frequency "C–O stretching" mode actually contain a $\sim$35% negative contribution from the M–C stretching coordinate. This seems surprising since we are accustomed to thinking of the C–O stretching modes as quite pure, and indeed they are pure from the point of view of the potential energy distribution,[2] in which the eigenvector elements are weighted by the force constants. It is characteristic of linear systems of this kind, however (see for example the thiocyanate ion[16]), that the higher frequency mode is badly mixed with respect to the eigenvector elements themselves. In other words, as the C–O bonds are stretched, in the high frequency A_{1g} mode, the M–C bonds are substantially compressed. The result should be a significant transfer of π overlap from C–O to M–C and a concomitant change in the molecular polarizability, which is not allowed for in bond polarizability theory. This synergistic effect could account for unreasonably high $\bar{\alpha}'_{CO}$ and $\bar{\alpha}'_{CN}$ values.

On the other hand, the eigenvectors for the M–C modes are quite pure. Table II shows that the contributions from C–O stretching are only about 8%, and they are positive (M–C and C–O bonds are stretched in phase). We might therefore hope that π-overlap synergism is slight for these modes. Table I shows that the M–C bond order estimates are indeed quite reasonable. While they exceed the theoretical maximum,[17] 1.5, for Cr–C and W–C, the discrepancies are within the error limits of the Long and Plane equation.[11] Furthermore, because the eigenvectors are nearly pure, the $\bar{\alpha}'_{M-C}$ magnitudes are substantially independent of the choice of sign for the $\bar{\alpha}'_Q$'s, and there is little to choose between the values in set 1 and set 2.

Significantly, the M–C bond order estimates fall in the same order, $W > Cr \gtrsim Mo$, as do the M–C stretching force constants, strengthening the inference that this is also the order of decreasing π back-bonding. It should be noted that the bond polarizability derivatives themselves do not have the same order. They fall into line when reduced to $n/2$ values because of the differences in the M–C bond distances and the importance of the r^3 term in the Long and Plane equation.

We conclude that the Raman intensity data support the well-accepted notion that π back-bonding is significant in the group VI hexacarbonyls, as well as the impression gained from the best force constants available and from bond energy estimates that the extent of such bonding decreases in the order $W > Cr \gtrsim Mo$. On the other hand the data give inflated results with regard to the C–O bonds, probably because of synergistic effects which are neglected in bond polarizability theory.

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The Preparation and Properties of Lithium Bis(borane)dimethylphosphide(1−)

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In 1955 Schaeffer and Basile[1] reported that the reaction of diborane with lithium amide in diethyl ether yields only aminoborane polymer and lithium borohydride

$$LiNH_2 + B_2H_6 \longrightarrow LiBH_4 + (NH_2BH_2)_x \qquad (1)$$

We have found that, unlike lithium amide, lithium dimethylphosphide reacts with diborane in ether solvents to produce lithium bis(borane)dimethylphosphide(1−) (I)

$$Li(CH_3)_2P + B_2H_6 \longrightarrow Li(CH_3)_2P(BH_3)_2 \qquad (2)$$

This paper reports the preparation, properties, and some of the reactions of I.

Experimental Section

General Data.—Reactions were carried out with the aid of a standard high-vacuum system. Air-sensitive materials were manipulated in nitrogen-filled drybags or in the vacuum line. Diethyl ether, monoglyme (1,2-dimethoxyethane), and dioxane were stored in evacuated bulbs over lithium aluminum hydride and, when needed, were condensed directly into the reaction vessel. Boron-11 nmr spectra were obtained using a Varian HA-100 spectrometer operating at 32.1 MHz; proton nmr spectra were obtained with Varian HA-100 and A-60 instruments. Boron-11 and proton chemical shifts are in ppm relative to diethyl ether–boron trifluoride and tetramethylsilane (TMS), respectively. Infrared spectra were obtained using Perkin-Elmer 137 and 337 spectrophotometers.

Reagents.—Diborane and B_2D_6 were prepared by the reaction of polyphosphoric acid with sodium borohydride and $NaBD_4$, respectively. Phenyllithium was prepared in diethyl ether from bromobenzene and lithium wire containing 1% sodium (Alfa Inorganics, Inc.) by the method of Gilman and Morton.[2] Dimethylphosphine was prepared from the reaction of tetramethyldiphosphine disulfide with lithium aluminum hydride in dioxane.[3] Lithium dimethylphosphide was prepared from phenyllithium and dimethylphosphine in diethyl ether.[4]

Reaction of $LiP(CH_3)_2$ with B_2H_6.—In a typical reaction, a 200-ml reaction vessel was charged with 2.69 mmol (determined from dimethylphosphine consumption) of lithium dimethylphosphide in 5 ml of monoglyme. A 3.10-mmol sample of diborane was condensed into the evacuated vessel, which was then warmed to room temperature and stirred magnetically for 1 hr. Separation of the volatile products produced only monoglyme and 0.32 mmol of diborane, implying a 2.78 mmol consumption of diborane. The involatile residue consisted of a viscous oil which, after treatment with 5 ml of anhydrous dioxane and evaporation of the solution under vacuum, yielded a colorless crystalline solid which was then washed with heptane and cold dioxane and dried under vacuum.

Analysis of the compound presented a problem because the material contained an appreciable, though evidently nonstoichiometric, quantity of lithium bromide[5] introduced from the phenyl-

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[5] W. Glaze and R. West, *J. Amer. Chem. Soc.*, **82**, 4437 (1960).

lithium preparation. Analysis was accomplished by acid hydrolysis according to

$$(CH_3)_2P(BH_3)_2^- + H^+ + 6H_2O \longrightarrow 2B(OH)_3 + 6H_2 + (CH_3)_2PH \quad (3)$$

Hydrogen was measured with a Toepler pump; boric acid was determined by complexing with D-mannitol and titration with standard base. The dimethylphosphine was determined by distilling the hydrolyzed solution into excess I_3^- followed by back-titration with thiosulfate. The dioxane of crystallization was recovered quantitatively by heating the solid to 80° under vacuum. Absolute percentages varied considerably between samples, but the elemental ratios remained essentially constant. In a typical analysis, the B:H:P ratio was found to be 1.9:5.8:1.0, compared to the calculated ratio of 2.0:6.0:1.0. In a separate experiment 0.96 mmol of dioxane was recovered per millimole of I.

Characterization.—I dissolves without reaction in glyme ethers, ethanol, toluene, neutral water, and aqueous base but is insoluble in diethyl ether, benzene, heptane, and chloroform. After 9 months, a solution of I in neutral D_2O had undergone only slight decomposition as indicated by its ^{11}B nmr spectrum. Acidification of an aqueous solution of I results in rapid hydrolysis (eq 3). Although I is reasonably air stable, it is quite hygroscopic. The proton nmr spectrum of I in D_2O (Figure 1) shows chemical shifts of δ(BH) 0.47 ppm and δ(CH) 1.08 ppm downfield from TMS with coupling constants J_{BH} = 88 Hz, J_{PCH} = 8 Hz, and J_{PBH} = 12 Hz. The boron-11 nmr spectrum of I in D_2O (Figure 2) shows a chemical shift of +34.5 ppm with coupling constants of J_{BH} = 88 Hz and J_{BP} = 107 Hz. Coupling constants and line widths are solvent dependent.

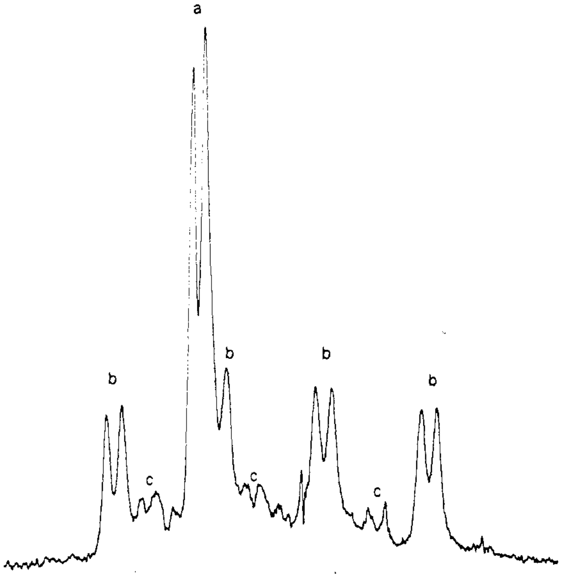

Figure 1.—The ^1H nmr spectrum of $(CH_3)_2P(BH_3)_2^-$ in D_2O.

The infrared spectrum (KBr matrix) shows the following bands (in cm^{-1}) not assigned to dioxane: 2970 (w), 2905 (w), 2865 (w), 2350 (s), 2280 (s), 2255 (s), 1420 (m), 1280 (m), 1060 (m), 940 (m), 920 (m), 708 (m).

The reaction of I with warm polyphosphoric acid yields only dioxane and hydrogen as volatile products. The reaction of I with hydrogen chloride in monoglyme yields methyl chloride, indicating probable cleavage of the solvent, and hydrogen. No volatile boron-containing material was detected.

To determine whether any dimethylphosphinoborane is formed in the reaction, a sample of I in monoglyme was hydrolyzed with a small amount of aqueous acid. The ^{11}B nmr spectrum of this solution showed only a single peak due to boric acid. The presence of any significant quantity of dimethylphosphinoborane would have been detected, since this compound is highly resistant to hydrolysis.[6]

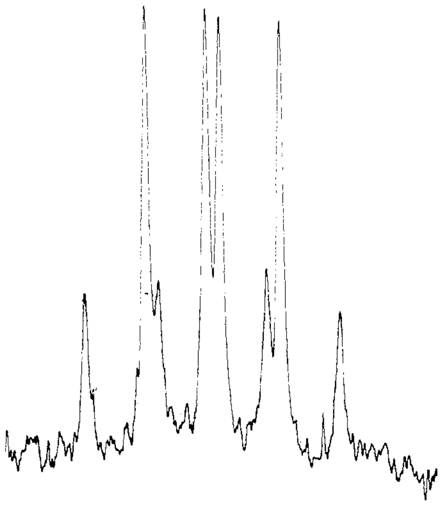

Figure 2.—The ^{11}B nmr spectrum of $(CH_3)_2P(CH_3)_2^-$ in D_2O.

Attempts to Detect the Intermediate Formation of $Li(CH_3)_2PBH_3$.—The stepwise addition of diborane to a monoglyme solution of lithium dimethylphosphide was studied in an nmr reaction vessel equipped with a Kontes high-vacuum stopcock. A 2.0-ml sample of 0.5 *M* phenyllithium in diethyl ether was injected into the vessel followed by 1.0 mmol of dimethylphosphine. The vessel was agitated occasionally, and after 2 hr all volatile products were removed. Diborane, 0.5 mmol, and about 1 ml of monoglyme were condensed into the vessel and the ^{11}B nmr spectrum was recorded. The resulting spectrum resembled that shown in Figure 2. Addition of another 0.5 mmol of diborane produced a stronger spectrum identical with the first. Addition of another 0.5 mmol of diborane resulted in a slight loss of resolution and the appearance of a broad peak at low field due to diborane. Removal of all volatiles and the addition of fresh monoglyme regenerated the original well-resolved spectrum.

In an attempt to detect the intermediate formation of $Li(CH_3)_2PBH_3$ by conversion to $(CH_3)_2PHBH_3$, 1 mmol of anhydrous methanol was condensed into an nmr reaction vessel containing the products of the reaction of 1 mmol of lithium dimethylphosphide and 0.5 mmol of diborane. No signal other than that assigned to I was detected in the ^{11}B nmr spectrum.

Deuterium Exchange between I and B_2D_6.—A 2.0-mmol sample of I was placed in a 200-ml reaction vessel. The vessel was evacuated and 2 ml of monoglyme was condensed in, followed by 0.5 mmol of B_2D_6. The solution was warmed to room temperature and stirred magnetically for about 2 hr. The infrared spectra of the recovered diborane and the solid residue clearly indicated deuterium exchange had occurred.

Results and Discussion

Formation of I.—The reaction of lithium dimethylphosphide with diborane in monoglyme yields only lithium bis(borane)dimethylphosphide(1−). No evidence for the presence of dimethylphosphinoborane could be found. In some isolated cases lithium borohydride was detected among the reaction products, but this was unequivocally attributed to the reaction of diborane with lithium ethoxide, an impurity in the phenyllithium. Since no $Li(CH_3)_2PBH_3$ was found, even in reactions where lithium dimethylphosphide was in excess, diborane may add to lithium dimethylphosphide as a unit to produce I directly. The reported low reactivity of dimethylphosphinoborane[6] makes its participation in the reaction as an intermediate very unlikely.

Properties of I.—The boron-11 and proton nmr spectra are consistent with the assigned structure. In

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[6] A. B. Burg and R. I. Wagner, *J. Amer. Chem. Soc.*, **75**, 3872 (1953).

the proton nmr spectrum, (a) is assigned to methyl protons which are split into a doublet of intensity six by ^{31}P; (b) arises from the BH_3 protons which are split by ^{11}B into a 1:1:1:1 quartet, each member of which is further split into a doublet by ^{31}P. The fine structure (c) is due to ^{10}B. The ^{11}B nmr spectrum of I consists of two overlapping quartets created by a similarity in the B–P and B–H coupling constants. The infrared spectrum of I compares favorably to the structurally related compounds $Na(CH_3)_2N(BH_3)_2$[7] and $KH_2P(BH_3)_2$.[8]

The thermal and hydrolytic stabilities of I are similar to those reported for $KH_2P(BH_3)_2$.[8,9] Attempts to prepare μ-dimethylphosphinodiborane from I and either polyphosphoric acid or hydrogen chloride failed. The compound $Na(CH_3)_2N(BH_3)_2$ has been shown to react with diborane in monoglyme to form μ-dimethylaminodiborane and sodium heptahydrodiborate (eq 4).[10] Treatment of I with diborane results only in recovery of the starting materials. The deuterium exchange of I

$$Na(CH_3)_2N(BH_3)_2 + B_2H_6 \longrightarrow \mu\text{-}(CH_3)_2NB_2H_5 + NaB_2H_7 \quad (4)$$

with B_2D_6 may possibly be explained by a process similar to eq 4. In this case (eq 5) the equilibrium may lie well to the left, while in the case of the nitrogen compounds, product formation is favored, perhaps owing to

$$Li(CH_3)_2P(BH_3)_2 + B_2H_6 \rightleftharpoons \mu\text{-}(CH_3)_2PB_2H_5 + LiB_2H_7 \quad (5)$$

steric effects. The possibility that deuterium exchange results from interchange of borane groups (eq 6) is unlikely in the light of the stability of I in aqueous solution for extended periods of time.

$$Li(CH_3)_2P(BH_3)_2 \rightleftharpoons Li(CH_3)_2PBH_3 + 0.5B_2H_6 \quad (6)$$

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Trifluoromethylsulfur Trifluoride Adducts. Adducts with Phosphorus Pentafluoride, Boron Trifluoride, Arsenic Pentafluoride, and Antimony Pentafluoride

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Trifluoromethylsulfur trifluoride was first reported by Tyczkowski and Bigelow in 1953.[1] More recently Sheppard has reported a convenient general preparative route to the monosubstituted derivatives of SF_4 through fluorination of the respective disulfides.[2] He suggested, in that report, that the chemistry of the monosubstituted derivatives is similar to that of SF_4.

In the present work the reactions of CF_3SF_3 with PF_5, BF_3,[3] AsF_5, and SbF_5 were investigated and in each case the 1:1 adduct was prepared and isolated. The Infrared spectra of the solids $CF_3SF_3 \cdot BF_3$, $CF_3SF_3 \cdot AsF_5$, and $CF_3SF_3 \cdot SbF_5$ are interpreted to indicate that they are ionic of the type $CF_3SF_2{}^+MF_{n+1}{}^-$ where MF_n represents the acceptor used. This fluoronium[4] type structure has been reported for a number of adducts involving SF_4[5] or other fluoride donors[6,7] with acceptors such as BF_3, AsF_5, and SbF_5.

Experimental Section

Materials.—Phosphorus pentafluoride (Matheson), boron trifluoride (J. T. Baker), and arsenic pentafluoride (Ozark Mahoning) were used directly from the cylinders. Antimony pentafluoride (Ozark Mahoning) was transferred to a glass container from the stock received, pumped down until rapid gas evolution ceased, distilled at atmospheric pressure, and then vacuum transferred to the reaction vessel. Trifluoromethylsulfur trifluoride was prepared and isolated using the procedure given in a previous communication.[3] All CF_3SF_3 samples were checked for the presence of SF_4 before use.

Apparatus.—The volatile materials were manipulated in a glass–metal vacuum system. All joints and stopcocks were lubricated with Halocarbon 25-5S grease. The $CF_3SF_3 \cdot BF_3$ preparation and dissociation pressure measurements were carried out in a 110-ml Monel–steel system equipped with a Heise Monel Bourdon tube absolute vacuum gauge. Pressure measurements were reproducible to ±1 Torr. The metal system was connected to the glass vacuum line through a Monel needle valve.

Infrared Spectra.—Infrared spectra were studied using a Perkin-Elmer Model 521 spectrometer. Gaseous samples were investigated in a 10-cm glass cell fitted with sodium chloride windows. Spectra of the solid $CF_3SF_3 \cdot BF_3$ and $CF_3SF_3 \cdot AsF_5$ adducts were obtained by examination of films deposited on a liquid nitrogen-cooled KBr support. This support window was positioned within a glass cell capped with KBr windows. The films were prepared by subliming the adducts directly onto the cold support. The $CF_3SF_3 \cdot SbF_5$ spectra were obtained at ambient temperature by studying a layer of powdered adduct between KBr plates. Sample plates were prepared in a drybox and the window edges were liberally coated with Halocarbon grease before exposure to the atmosphere. The samples remained colorless during the studies.

Preparation.—The $CF_3SF_3 \cdot PF_5$, $CF_3SF_3 \cdot BF_3$, and $CF_3SF_3 \cdot AsF_5$ adducts were prepared by direct combination of the reagents. Trifluoromethylsulfur trifluoride and an excess of the respective acceptor were transferred to a reactor held at −195°, and the reactor was warmed to −20° to promote contact and reaction; then the system temperature was lowered to a point at which the respective adduct showed a dissociation pressure less than 1 Torr [$CF_3SF_3 \cdot PF_5$ (−80°), $CF_3SF_3 \cdot BF_3$ (−65°), $CF_3SF_3 \cdot AsF_5$ (25°)], where the volatiles remaining in the system were removed, leaving the white solid adduct.

The $CF_3SF_3 \cdot SbF_5$ was obtained by warming a mixture of SbF_5 and an excess of CF_3SF_3 at 35° and then removing the unreacted CF_3SF_3 from the $CF_3SF_3 \cdot SbF_5$(s) by pumping at room temperature.

Properties.—**$CF_3SF_3 \cdot PF_5$** showed 1 atm decomposition pressure

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