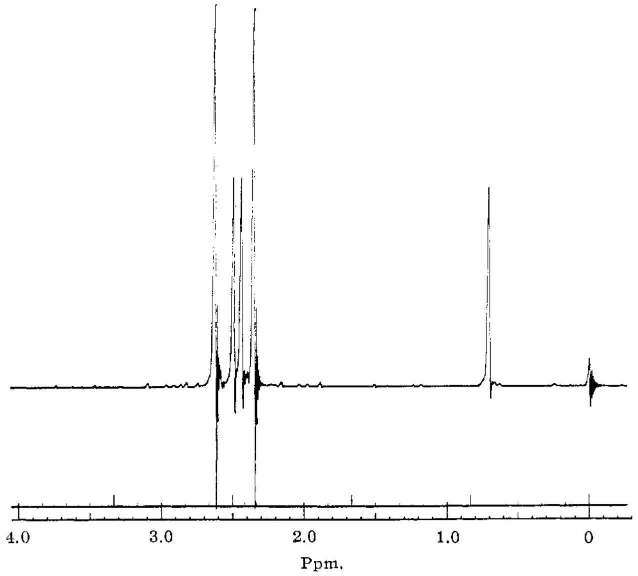

Figure 3.—The proton nmr spectrum of I obtained neat using tetramethylsilane as an internal standard.

the nmr data for V, VII, and VIII, an example of which is shown in Figure 4. The general asymmetry of the H^1 nmr spectra suggests bonding of the BH_3 moiety to a nitrogen in these compounds rather than a rapid exexchange of the Lewis acid among the nitrogens or its attachment to the oxygen or sulfur. In all cases, the NCH_2 resonance is quite complicated as might be expected because of quaternization of one of the nitrogens (see schematic partial projection in Figure 5). Similarly, three N-methyl doublets of equal intensity are expected and observed for V and VIII. In the spectrum of VII, intensity measurements reveal that two of the doublets are superimposed.

In contrast to I, $P(N(CH_3)_2)_3$ exhibited no observable bidentate properties. The main product in the reaction of $OP(N(CH_3)_2)_3$ with B_2H_6 is apparently a 1:1 adduct of BH_3 wherein the acidic moiety is attached to the phosphoryl oxygen rather than to a nitrogen as in VII.

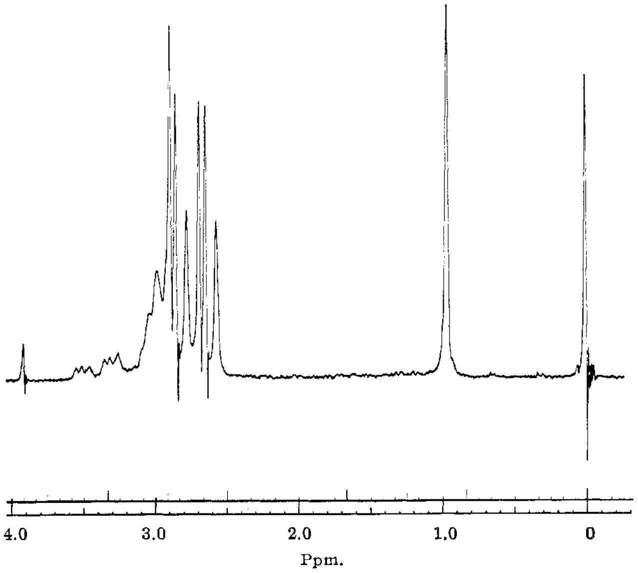

Figure 4.—The proton nmr spectrum of V under conditions described in Table II.

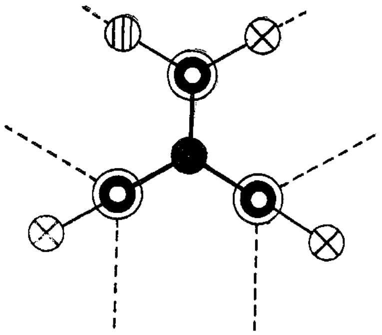

Figure 5.—A schematic partial projection of V, VII, or VIII as viewed from above the phosphorus bridgehead atom (●) toward the carbon bridgehead which is not visible. Represented are the nitrogens (◉), methyl groups (⊗), methylene carbons (○), methylene hydrogens (– – – –), and the borine group (◍) on nitrogen. The borine, oxygen, and sulfur on the phosphorus in V, VII, and VIII, respectively, are not shown.

Support for this suggestion stems from the observation of only one doublet N-methyl proton resonance upon adduct formation of $OP(N(CH_3)_2)_3$. In contrast to III, $SP(N(CH_3)_2)_3$ forms no BH_3 adduct under the conditions employed. In the present absence of precise structural data it is difficult to account for these observations in an entirely satisfactory manner. Dreiding models of these compounds, however, indicate that the free rotation of the $(CH_3)_2N$ groups around the N–P bonds in molecules of the type $P(N(CH_3)_2)_3$ makes adduct formation on nitrogen difficult whereas the constraint present in the molecules of polycyclic variety exposes a relatively unhindered site on the nitrogen to electrophilic attack. Work on the Lewis base properties of the arsenic compound IV and the coordination properties of these caged systems is in progress.

Acknowledgments.—Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research as well as to the National Science Foundation for a grant (NSF GP-2328) to J. G. V. The authors thank Mr. R. A. Martin for experimental assistance.

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The Reaction of Methylphosphine with Carbon Monoxide Borane

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Received August 19, 1966

In an earlier publication from this laboratory[1] it was shown that methylamine reacts with carbon monoxide borane to give a compound of formula $[H_3CNH_3]^+$-$[H_3BC(O)(NHCH_3)]^-$. The anion structure is that of an N-methylboranocarbamate.[1]

[1] J. C. Carter and R. M. Parry, *J. Am. Chem. Soc.*, **87**, 2354 (1965).

In view of the foregoing fact, it was of interest to consider the reaction of methylphosphine with carbon monoxide borane and to compare the reaction products with those of methylamine and carbon monoxide borane. The reaction observed was a simple base displacement process. The equation representing the observed reaction with methylamine is

$$H_3BCO + 2NH_2CH_3 \longrightarrow [H_3CNH_3]^+[H_3BC(O)(NHCH_3)]^-$$

For methylphosphine the equation representing the process observed is

$$H_3BCO + H_3CPH_2 \longrightarrow H_3BPH_2CH_3 + CO\uparrow$$

Experimental Section

Standard vacuum line techniques were used throughout. Infrared spectra were obtained on a Perkin-Elmer Model 21 double-beam instrument and on a Perkin-Elmer 337. Solids were prepared in KBr disks or in Nujol or Fluorlube mulls on NaCl plates. A 10-cm gas cell with NaCl plates was used for gas samples.

Preparation of H_2PCH_3.—A sample of Cl_2PCH_3, graciously donated by Edgewood Arsenal, was reduced with $LiAlH_4$ in diethyl ether. A 1.8-g sample of $LiAlH_4$, in a cold finger apparatus on the vacuum line, was dissolved in 10 ml of dry diethyl ether; then 6 mmoles of PCl_2CH_3 was distilled into the solution. The mixture was allowed to warm gradually from −196°. A Dry Ice–2-propanol slush in the cold finger permitted refluxing of the ether as the temperature rose slowly. When the reaction was complete (about 0.5 hr), ether was removed and water was distilled onto the reaction mixture. Gases formed were led through a trap at −78°, through a trap at −196°, and through the vacuum pump. The contents of the −196° trap were allowed to pass through a trap at −112° into a trap at −196°. A 3.4-mmole quantity of PH_2CH_3 was recovered in the −196° trap and identified by its vapor pressure[2] of 210 mm at −45° and by its gaseous infrared spectrum.[3]

The Reaction of PH_2CH_3 with H_3BCO. (a) In Diethyl Ether.—A 1.02-mmole sample of H_3BCO was dissolved in the vacuum system reactor in 10 ml of diethyl ether. A 3.41-mmole sample of PH_2CH_3 was frozen above the carbon monoxide borane solution and then allowed to melt and run down onto the frozen solution. The temperature was raised gradually from −196 to 0°. Above −78° CO evolved slowly. The solvent ether was removed at 0° leaving a clear liquid which was identified as $H_3BPH_2CH_3$.

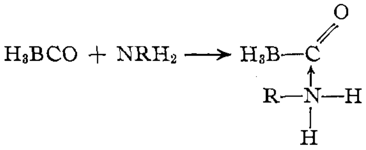
(b) **In the Absence of Solvents.**—A 1.00-mmole sample of H_3BCO and a 4.73-mmole sample of H_2PCH_3 were frozen together in a reaction tube and allowed to warm slowly from −196 to −78°. No CO was evolved at this point. After 2 days at −78° a 0.82-mmole quantity of CO was recovered along with 3.65 mmoles of unreacted CH_3PH_2. No unreacted H_3BCO was recovered. The liquid remaining in the reaction tube was identified as $H_3BPH_2CH_3$ on the basis of vapor pressure (3.5 mm at 23.6° *vs.* 3.6 mm at 23.6°[4]) and infrared spectrum. Values are indicated as absorption frequency, cm^{-1}, and relative peak height in parentheses: 2980 (100); 2870 (95); 2400 (60, broad); 1970 (15); 1450 (35); 1390 (60); 1360 (50); 1270 (35); 1140 (100, broad); 1095 (70); 997 (30); 990 (20); 965 (20); 950 (20); 905 (20); 820 (40, broad). The foregoing observations are consistent with the equation for the process

$$1.00H_3BCO + 1.08CH_3PH_2 \longrightarrow 0.82CO + 0.82H_3BPH_2CH_3 + \text{extra component}\begin{cases}0.18H_3BCO\cdot H_2PCH_3 + \\ 0.08H_2PCH_3\end{cases}$$

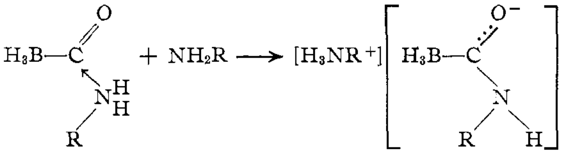
Clearly the major product was $H_3BPH_2CH_3$, but stoichiometry suggests that as much as 18% of unidentified products remain.[5]

Discussion

In the reaction of methylamine and carbon monoxide borane an initial nucleophilic attack by nitrogen on the carbon provides the simplest and most reasonable mechanism for rationalizing the products produced. The process can be formulated as

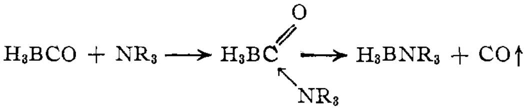


If another methylamine molecule or any suitable proton acceptor is present in the external system, transfer of a proton from the coordinated amine to the proton acceptor is to be expected.



Loss of a proton from methylamine gives the methyl amide ion which is a much stronger base than the free amine. Because the amide ion is a strong base, the carbamate structure is stabilized. Thus, under conditions where proton transfer can occur, the ionic solid is favored.

On the other hand, where proton transfer is rendered difficult or impossible by (1) the fact that the amine has no removable protons as in $N(CH_3)_3$ or (2) the fact that no suitable receiver is present, proton transfer does not occur and the adduct rearranges to give the simple borane adduct and free CO. For the case of $N(CH_3)_3$, reason 1 is represented as



It is suggested that methylphosphine illustrates reason 2. The compound H_2PR is very poor as a proton acceptor; the cation $[H_3PR^+]$ is not particularly stable at 25° and 1 atm, at least not with anions of the type considered here. Without proton transfer, rearrangement occurs as with NR_3 to give the more stable borane addition compound and free CO.

Acknowledgment.—This work was generously supported by the U. S. Public Health Service, under Grant No. CA-07989-02 from the National Cancer Institute.

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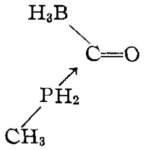
(2) E. C. Evers, E. H. Street, Jr., and S. L. Jung, *J. Am. Chem. Soc.*, **73**, 5088 (1951); K. W. Morse, unpublished results, University of Michigan, 1966.

(3) H. R. Linton and E. R. Nixon, *Spectrochim. Acta*, 146 (1959).

(4) A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **75**, 3872 (1953).

(5) Structures such as $[CH_3PH_3^+][H_3BC(O)PHCH_3^-]$ or



have not been eliminated in accounting for retention of H_3BCO in product.