small H⁺-catalyzed decomposition path (of A to $Cr^{3+}$-(aq) and Haa), they are equally consistent with the simultaneous occurrence of inner-sphere and outer-sphere paths.[12] This postulate of the presence of both mechanisms is further supported by a comparison of the relative rate data in Table II; these data suggest that the outer- and inner-sphere paths are in competition: the two oxidants that presumably go by an outer-sphere mechanism, $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$, have relative rates similar to $Co(aa)_3$, and very different from a typical inner-sphere reactant, $Co(NH_3)_5$-$Cl^{2+}$.[13]

### TABLE II
RATES OF REDUCTION OF Co(III) COMPLEXES BY Eu(II) AND V(II) RELATIVE TO THE RATE OF REDUCTION BY Cr(II)

| Complex | Cr(II) | V(II) | Eu(II) | Ref |
|---|---|---|---|---|
| $Co(aa)_3$ | 1 | 50 | 440 | This work |
| $Co(NH_3)_6^{3+}$ | 1 | 42 | 220 | a, b |
| $Co(en)_3^{3+}$ | 1 | 10 | 250 | b |
| $Co(NH_3)_5Cl^{2+}$ | 1 | $2.5 \times 10^{-7}$ | $2 \times 10^{-4}$ | b, c |

 a A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **83**, 793 (1961). b J. P. Candlin, J. Halpern, and D. L. Trimm, *ibid.*, **86**, 1019 (1964). c J. P. Candlin and J. Halpern, *Inorg. Chem.*, **4**, 766 (1965).

Finally, it is necessary to account for the difference in the results when $Cr^{2+}$(aq) is oxidized by $Co(aa)_3$ and $Co(en)_3^{3+}$. Considering just the outer-sphere term for the former oxidant, the rate constants differ by a factor of about $10^5$. Within the framework of the Marcus theory of outer-sphere electron-transfer reactions,[14] there are four factors that could account for the greater reactivity of $Co(aa)_3$: (1) a smaller electrostatic repulsion; (2) a larger $\Delta F°$; (3) a smaller solvent reorganization term; and (4) a smaller inner-sphere reorganization term. The first factor should increase the rate constant by about 200 upon the change from $Co(en)_3^{3+}$ to $Co(aa)_3$, while little can be said of factors (2) and (3). But the fourth factor, which is operable in both inner-sphere and outer-sphere reactions, may account for the majority of the remaining difference. In reactions in which the electron is transferred to an $e_g$ orbital (in octahedral notation for simplicity), the stretching of bonds—the inner-sphere reorganization free energy—is anticipated to be very important; thus the weaker bonding (lower ligand field) of O donor ligands relative to N donor ligands

(12) If the entire ionic strength effect is postulated to arise from the outer-sphere path, then at H⁺ = 2 *M* one expects 15% inner-sphere path (see Table I). There is no reason to believe that Na⁺ and H⁺ will have equal effects at 2 *M* ionic strength. Finally, there is good evidence that the $Cr^{2+}$ ion is bound to more than one oxygen of the Co(III) complex, at least in ethanol–water mixtures—$Cr(aa)_2^+$ is a product of the reaction.³ However, there is no compelling evidence that the position of the attack of $Cr^{2+}$(aq) is only at an oxygen and not also at the ring ⩾CH group, a known nucleophilic site. See C. Djordjevic, J. Lewis, and R. S. Nyholm, *Chem. Ind.* (London), 122 (1959); J. P. Collman, *Angew. Chem. Intern. Ed. Engl.*, **4**, 132 (1965).

(13) It is to be noted, in addition, that the value of the rate constant for the $V^{2+}$(aq) reduction of $Co(aa)_3$ is probably too fast for inner-sphere attack—there is not sufficient time to remove a water molecule from the first coordination sphere of $V^{2+}$(aq): W. Kruse, quoted in M. Eigen and R. G. Wilkens, "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, 1965; H. Taube, private communication.

(14) A review is available: R. A. Marcus, *Ann. Rev. Phys. Chem.*, **15**, 155 (1964).

leads to an increased rate in the former case. This is illustrated in the reactions of $Fe^{2+}$(aq) with $Co(H_2O)_5$-$Cl^{2+}$ ($k > 5000$ $M^{-1}$ sec$^{-1}$)[15] and $Co(NH_3)_5Cl^{2+}$ ($k = 16 \times 10^{-4}$ $M^{-1}$ sec$^{-1}$);[16] and $Cr^{2+}$(aq) with $Cr(H_2O)_5Cl^{2+}$ ($k = 9$ $M^{-1}$ sec$^{-1}$ at 0°)[17] and $Cr(NH_3)_5Cl^{2+}$ ($k = 0.051$ $M^{-1}$ sec$^{-1}$)[18,19] and in the data presented here.

**Acknowledgment.**—The authors wish to thank Dr. Leonard Spialter of Aerospace Research Laboratories for the use of the Cary Model 14 spectrophotometer.

(15) T. J. Conocchioli, G. H. Nancollas, and N. Sutin, *J. Am. Chem. Soc.*, **86**, 1453 (1964).

(16) H. Diebler and H. Taube, *Inorg. Chem.*, **4**, 1029 (1965).

(17) D. L. Ball and E. L. King, *J. Am. Chem. Soc.*, **80**, 1091 (1958).

(18) A. E. Ogard and H. Taube, *ibid.*, **80**, 1084 (1958).

(19) This comparison illustrates the argument with considerable rigor: the electrostatic term is identical; the $\Delta F°$ term favors the amine complex; the solvent reorganization term is expected to be as close to the same as one can achieve—same radii, $NH_3$ and $H_2O$ presenting roughly the same features toward the solvent, except for the unshared electron pair on the oxygen.

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## Polycyclic Group V Ligands. III. 2,6,7-Trimethyl-4-methyl-2,6,7-triaza-1-phosphabicyclo[2.2.2]octane. A Bidentate Donor[1]

BY B. L. LAUBE, R. D. BERTRAND, G. A. CASEDY,
R. D. COMPTON, AND J. G. VERKADE[2]

Two types of polycyclic aminophosphine and aminoarsine systems have appeared in the literature since 1960.[3,4] The first described is of the adamantane type, $M_4(NCH_3)_6$, and the second is of the bicyclo-[2.2.2]octane structure type, $M(N(CH_3)N(CH_3))_3M$, where M = P or As. We report here the first example of a monophosphorus bicyclic aminophosphine, 2,6,7-trimethyl-4-methyl-2,6,7-triaza-1-phosphabicyclo[2.2.2]-octane (I), a number of its derivatives, its arsenic analog, and some unusual bidentate donor properties of I not observed for the comparable open-chain system $P(N(CH_3)_2)_3$.

### Experimental Section

Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. Molecular weights were obtained on an Atlas CH4 single-focusing mass spectrometer using a source temperature at 200°, a high-temperature inlet system between 145 and 150°, and an energy of 70 ev. The analytical data are recorded in Table I. Proton nmr data shown in Table II were obtained on approximately 5–10% solutions in specified solvents employing either a Varian A-60 or HR-60 spectrometer using tetramethylsilane as an internal standard.

(1) For part II in this series see K. J. Coskran and J. G. Verkade, *Inorg. Chem.*, **4**, 1655 (1965).

(2) Alfred P. Sloan Fellow.

(3) J. Riess and J. R. Van Wazer, *Bull. Soc. Chim. France*, 1846 (1966).

(4) D. S. Payne, H. Noth, and G. Henniger, *Chem. Commun.*, 327 (1965), and references therein.

## Table I
### Analyses and Molecular Weights

| Compound | %C Calcd | Found | %H Calcd | Found | %N Calcd | Found | %P Calcd | Found | %Q Calcd | Found | Mol wt Calcd | Found |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_8H_{18}N_3P$ (I) | 51.30 | 51.50 | 9.69 | 9.71 | 22.44 | 22.38 | 16.54 | 16.51 | | | 187 | 187 |
| $C_8H_{18}N_3PO$ (II) | 47.28 | 47.16 | 8.93 | 8.88 | 20.68 | 20.72 | | | | | 203 | 203 |
| $C_8H_{18}N_3PS$ (III) | 43.82 | 43.90 | 8.27 | 8.23 | 19.12 | 19.09 | 14.12 | 14.33 | 14.61 | 14.53[a] | 219 | 219 |
| $C_8H_{18}N_3As$ (IV) | 41.57 | 41.70 | 7.85 | 7.90 | 18.18 | 18.22 | | | 32.41 | 32.25[b] | 231 | 231 |
| $C_8H_{24}B_2N_3P$ (V) | 44.71 | 45.00 | 11.24 | 11.11 | | | 14.41 | 14.42 | 10.07 | 10.06[c] | 215 | 187[d] |
| $C_8H_{21}BN_3P$ (VI) | 47.79 | 47.55 | 10.53 | 10.36 | 20.90 | 20.80 | 15.41 | 15.48 | 5.38 | 5.53[c] | 201 | 201 |
| $C_8H_{21}BN_3OP$ (VII) | 44.27 | 41.13 | 9.75 | 8.94 | 19.36 | 18.82 | 14.27 | 13.98 | 4.98 | 4.29[c] | 217 | 217 |
| $C_8H_{21}BN_3PS$ (VIII) | 41.24 | 41.23 | 9.08 | 9.06 | 18.05 | 18.20 | 13.30 | 13.16 | 4.66 / 13.73 | 4.56[c] / 13.99[a] | 233 | 219[e] |

[a] Q = S. [b] Q = As. [c] Q = B. [d] Although the mass spectrum of V revealed retention of the $BH_3$ group, that of VI showed only the parent ligand I. Details of the decomposition will be published later. [e] In contrast to VII, the highest peak in the mass spectrum of VIII corresponded to that found in the spectrum of III, indicating a more facile loss of the $BH_3$ moiety.

## Table II
### $^1H$ NMR Spectra[a]

$$\begin{array}{c} Y \\ \diagup \; N(CH_3)CH_2 \diagdown \\ XP\text{—}N(CH_3)CH_2\text{—}CCH_3 \\ \diagdown \; N(CH_3)CH_2 \diagup \end{array}$$

| | X | Y | $NCH_2$ | $NCH_3$ | $CCH_3$ |
|---|---|---|---|---|---|
| I[b] | $e^-$ pair | $e^-$ pair | 2.56 (3.5) | 2.52 (17) | 0.83 |
| II | O | $e^-$ pair | 3.02 (7.0) | 2.57 (12) | 0.87 |
| III | S | $e^-$ pair | 3.05 (7.5) | 2.68 (15) | 0.92 |
| V | $BH_3$ | $BH_3$ | 2.90–3.60[c] | 2.64 (13) | 0.93 |
| | | | | 2.74 (12) | |
| | | | | 2.78 (12) | |
| VI | $BH_3$ | $e^-$ pair | 2.81 (5.0) | 2.51 (14) | 0.88 |
| VII[c] | O | $BH_3$ | 3.10–3.80[d] | 2.76 (12) | 0.94 |
| | | | | 2.79 (11) | |
| VIII[c] | S | $BH_3$ | 3.14–3.90[d] | 2.74 (14) | 0.98 |
| | | | | 2.85 (14) | |
| | | | | 2.87 (13) | |

[a] Chemical shifts are reported in ppm downfield with respect to tetramethylsilane in $CDCl_3$ for I–III and $CH_2Cl_2$ for V–VIII. $J_{PNCH}$ coupling constants in Hertz are in parentheses. $BH_3$ proton resonances and couplings will be reported later. [b] The spectrum of the arsenic analog IV obtained neat consisted of an $NCH_2$ singlet at 2.61 ppm, an $NCH_3$ singlet at 2.53 ppm, and a $CCH_3$ singlet at 0.76 ppm. [c] Spectrum obtained at −60°. [d] Complex multiplet.

Tris(dimethylamino)phosphine was prepared according to the method of Burg and Slota.[5] Tris(dimethylamino)phosphine oxide was purchased from Aldrich Chemical Co., Inc., Milwaukee, Wis., and purified by distillation at 10 mm (bp 110–115°). Tris(dimethylamino)phosphine sulfide was prepared by slowly adding 2.05 g (64.0 g-atoms) of sulfur to 10 g (61.2 mmoles) of tris(dimethylamino)phosphine with stirring and cooling to maintain the temperature near 30°. The resulting yellow solution was diluted with ether, decolorized with Norit A, and distilled at 9 mm (bp 123°) after filtration.

For the boron Lewis acid absorption studies, commercially available diborane (Callery Chemical Co.) was purified as described earlier.[6] Solvents used in these studies were distilled from calcium hydride.

**$P(N(CH_3)CH_2)_3CCH_3$ (I).**—The triamine 1,3-bis(methylamino)-2-(methylaminomethyl)-2-methylpropane was prepared in two steps from the triol 2-(hydroxymethyl)-2-methyl-1,3-propanediol obtained from Eastman Kodak, Rochester, N. Y. The triol was converted to the corresponding tribromide in 55% yield by the method of Doering and Levy.[7] The tribromide was treated with methylamine to give the triamine by a modification of the method given by Mann.[8] A mixture of 20.0 g (65.0 mmoles) of tribromide, 24.0 g (0.78 mole) of anhydrous methylamine, and

25 ml of ethanol was placed under an atmosphere of dry nitrogen in an autoclave and heated at 180–190° for 12 hr. The resulting solution was evaporated to dryness under vacuum and the residue was refluxed for 6 hr with 19.2 g (0.294 mole) of potassium hydroxide in 250 ml of benzene. The benzene solution was filtered, dried with magnesium sulfate, and distilled under nitrogen at atmospheric pressure affording 8.2 g (80% yield) of triamine boiling at 207°.

Compound I was prepared following a general method for aminophosphines discussed by Burgada.[9] In a typical preparation, 8.1 g (52 mmoles) of the triamine was heated with stirring to 85° under nitrogen and 9.0 g (55 mmoles) of tris(dimethylamino)phosphine was added dropwise over a period of 45 min. After the evolution of dimethylamine ceased, the temperature was gradually raised to 170° and held there until dimethylamine evolution again ceased. Distillation at 10 mm afforded 8.8 g (90% yield) of I boiling at 82–86°.

**$OP(N(CH_3)CH_2)_3CCH_3$ (II).**—To a stirred solution of 7.5 g (47.1 mmoles) of triamine in 50 ml of ether held at 0° was added dropwise over a period of 30 min 8.5 g (55 mmoles) of phosphorus oxychloride dissolved in 40 ml of ether. The mixture was then refluxed for 6 hr and filtered, and the filtrate was evaporated to dryness to yield 2.5 g (26% yield) of crude II which was recrystallized from ether (mp 97–99°).

**$SP(N(CH_3)CH_2)_3CCH_3$ (III).**—To 9.5 g of I (51 mmoles) was added in small portions 1.7 g of freshly sublimed sulfur (54 g-atoms) while stirring. After the exothermic reaction ceased, the mixture was heated to 130° for 5 min. Cooling the reaction mixture produced a solid which was extracted with ether. The ether extract was decolorized with Norit A, filtered, and evaporated to dryness to produce 10 g (90% yield) of crude III. The crude product was sublimed under vacuum at 50° to yield colorless crystals (mp 92.5–94.5°).

**$As(N(CH_3)CH_2)_3CCH_3$ (IV).**—This compound was prepared in a manner similar to that described above for I except that tris(dimethylamino)arsine was used instead of tris(dimethylamino)phosphine. The product was obtained in 72% yield as a distillate obtained at 10 mm (bp 91–94°).

**Diborane Absorption Studies.**—Standard vacuum techniques were employed in condensing diborane onto solutions of specified ligands frozen at −196°. These solutions were then stirred at an equilibration temperature until a constant vapor pressure was obtained. Pertinent reaction conditions are given in Table III and Figures 1 and 2.

The solid compound V filtered cold from the reaction mixture of I and diborane described in Table III was found to lose diborane readily in moist air to produce the white compound VI which could be sublimed at 50° under vacuum (mp 74–76°). Adduct V was stable, however, on purging a chloroform solution for 2 hr with dry nitrogen. Compound VI could also be synthesized under the conditions used to make V using 0.5 mole of $B_2H_6$/mole of I.

Concentrating the solutions from the reactions of II with $B_2H_6$ and of III with $B_2H_6$ and cooling to −78° produced colorless

(5) A. Burg and P. J. Slota, Jr., *J. Am. Chem. Soc.*, **80**, 1107 (1958).

(6) C. W. Heitsch and J. G. Verkade, *Inorg. Chem.*, **1**, 392 (1962).

(7) W. von E. Doering and L. K. Levy, *J. Am. Chem. Soc.*, **77**, 509 (1955).

(8) G. M. Gibson, J. Harley-Mason, A. Litherland, and F. G. Mann, *J. Chem. Soc.*, 163 (1942).

(9) R. Burgada, *Ann. Chim.* (Paris), **8**, 347 (1963).

REACTION CONDITIONS FOR DIBORANE ABSORPTION STUDIES

| Ligand | Ligand concn, $M$ | Solvent (15 ml) | Equilibration temp, °C | Product | Mole ratio, ligand:$B_2H_6$ |
|---|---|---|---|---|---|
| $P(N(CH_3)_2)_3$ | 0.87 | Pentane | −78 | | 1:0.5[a] |
| $OP(N(CH_3)_2)_3$ | 0.73 | $CH_2Cl_2$, pentane | −45 | | 1:~0.7[b] |
| $SP(N(CH_3)_2)_3$ | 0.55 | $CH_2Cl_2$ | −45 | | None |
| I | 0.83 | $(C_2H_5)_2O$ | −78 | V, VI | 1:1[c] |
| II | 0.19 | $CH_2Cl_2$ | −45 | VII | 1:0.5[d] |
| III | 0.40 | $CH_2Cl_2$ | −45 | VIII | 1:0.5[e] |

[a] See Figure 1 for mole ratio *vs.* vapor pressure plot. [b] The ligand and solvent were scrupulously dried by distilling under an inert atmosphere from calcium hydride. In addition, on several runs the solvent was pretreated with diborane with subsequent removal of all unreacted diborane. In spite of these precautions, the first increment of diborane produced from 0.05 to 0.1 mmole of noncondensable gas with none in succeeding increments. The vapor tension *vs.* mole ratio plot is shown in Figure 1. [c] The vapor tension *vs.* mole ratio plot is shown in Figure 2. A run without I confirmed previous conclusions [H. E. Wirth, F. E. Massoth, and D. X. Gilbert, *J. Phys. Chem.*, **62**, 870 (1958)] that only negligible interaction between diborane and ether takes place in this temperature range. [d] In spite of rigorous precautions against moisture by distilling the solvent from calcium hydride, using freshly sublimed II, and carrying out all operations under dry nitrogen or on the vacuum line about 0.05 mmole of noncondensable gas was produced in several runs. The vapor tension *vs.* mole ratio plot is shown in Figure 2. [e] See Figure 2 for mole ratio *vs.* vapor pressure plot.
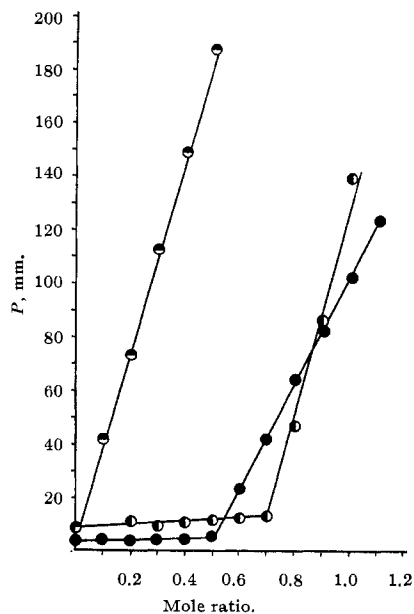


Figure 1.—Diborane partial pressures are plotted against mole ratios of diborane to $P(N(CH_3)_2)_3$ (●), $OP(N(CH_3)_2)_3$ (◐), and $SP(N(CH_3)_2)_3$ (◓) under conditions described in Table III.

VII and VIII, rsepectively. Both compounds are stable in halogenated hydrocarbons even on prolonged purging with dry nitrogen.

### Discussion

Although $P(N(CH_3)_2)_3$ was found to absorb 0.5 mole of $B_2H_6$ as noted previously,[10] I readily absorbed 1.0 mole of $B_2H_6$ to form adduct V. Compound V is quite stable at room temperature, but readily loses 0.5 mole of $B_2H_6$ in moist air to form the $BH_3$ adduct VI

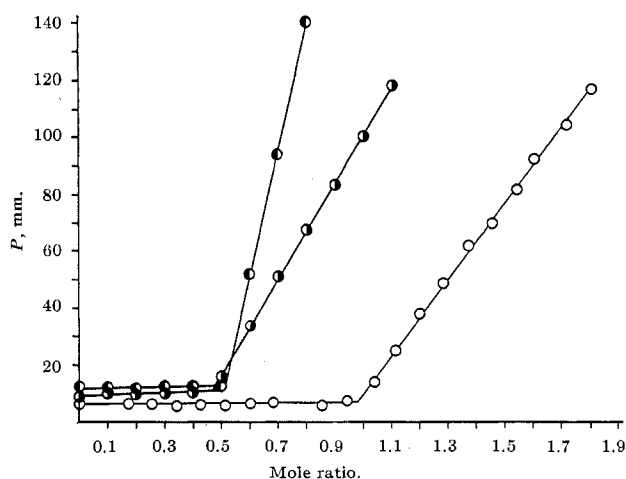(10) T. Reetz and B. Katlafsky, *J. Am. Chem. Soc.*, **82**, 5036 (1960).



Figure 2.—Diborane partial pressures are plotted against mole ratios of diborane to compounds I (○), II (◑), and III (◐) under conditions described in Table III.

which can also be prepared by limiting the $B_2H_6$:I ratio to 0.5. The $BH_3$ adduct VII was very stable in view of the fact that the product of a reaction between $OP(N(CH_3)_2)_3$ and $B_2H_6$ in a 1:0.5 mole ratio seems to decompose easily and has not as yet yielded tractable analyses. Adduct VIII was surprisingly stable in spite of the lack of adduct formation of $SP(N(CH_3)_2)_3$ with $B_2H_6$. The noncondensable gas (assumed to be hydrogen) produced in the reaction of $OP(N(CH_3)_2)_3$, $SP(N(CH_3)_2)_3$, and II with $B_2H_6$, although negligible, could not be avoided in spite of rigorous precautions (see Table III). If reactions similar to the one observed by Koster and Morita[11] at higher temperatures were taking place (see below), the hydrogen measured would account for a maximum of only about 2 mole % of the diborane used. The reason for the absorption of 0.20

$$3OP(N(CH_3)_2)_3 + {}^5/_2B_2H_6 \longrightarrow 3H_3BP(N(CH_3)_2)_3 + 3H_2 + B_2O_3$$

mole of $B_2H_6$ beyond theory for $H_3BOP(N(CH_3)_2)_3$ will be discussed in a later publication.

Proton nmr spectral data for I–VIII are listed in Table II. As shown in the example in Figure 3, spectra for I, II, III, and VI exhibit the required number of lines for the postulated structures if the only significant coupling is that of the $P^{31}$ nucleus to the $NCH_3$ and $NCH_2$ protons. No firm conclusions can be inferred from the proton spectra concerning the geometrical disposition of the $NCH_3$ groups and to this end X-ray studies are in progress. Since the $NCH_2$ and $NCH_3$ protons are apparently chemically equivalent, the $NCH_3$ groups may be effectively changing places with the nitrogen lone pair by a rapid inversion process taking place in spite of the locked configuration of the attached $CH_2$ and P substituents. Alternately, the σ-bonding framework on nitrogen may be essentially $sp^2$. Proton nmr spectral features observed at low temperature were only negligibly altered from those at room temperature and thus were of no value in possibly deciding the question of inversion. A structural indication of the bidentate nature of I is clearly seen from

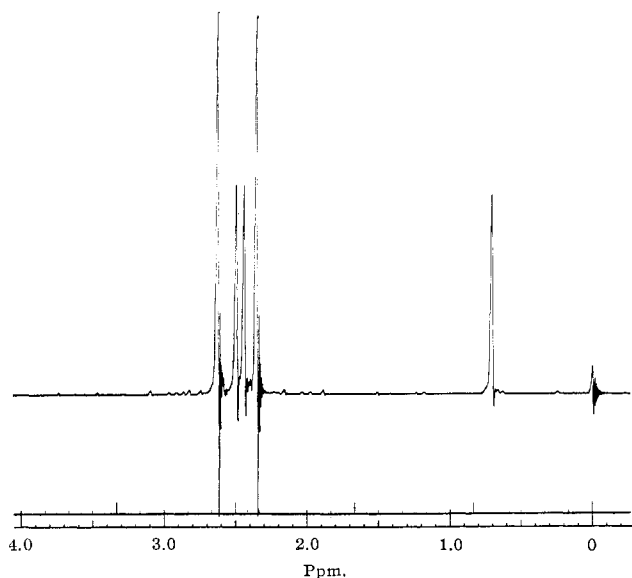(11) R. Koster and Y. Morita, *Angew. Chem. Intern. Ed. Engl.*, **4**, 593 (1965).

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 exchange 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.
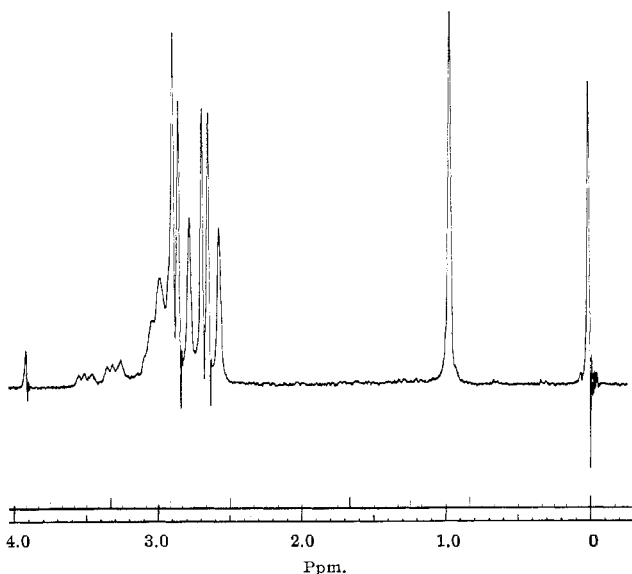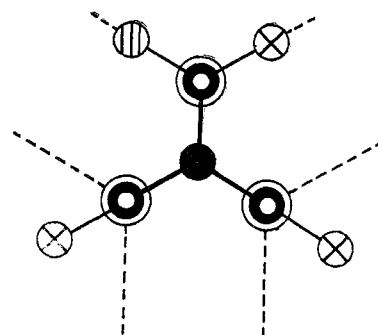


Figure 5.—A schematic partial projection of V, VII, or VIII as viewed from above the phosphorus bridgehead atom (●) toward the carbon bridgehead which is not visible. Represented are the nitrogens (◉), methyl groups (⊗), methylene carbons (○), methylene hydrogens (– – – –), and the borine group (◍) on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

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## The Reaction of Methylphosphine with Carbon Monoxide Borane

BY L. J. MALONE AND R. W. PARRY

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).



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