the 5σ play an important role in determining the trans CO's force constant will remain true.

The trend in the trans CO of the disubstituted species allows us to compare two opposing trends in the occupancies. The replacement of two bromine atoms by two iodine atoms causes the 5σ occupation to decrease, a change which tends to strengthen the CO bond, just as in the manganese monohalide complexes. However, because the species is disubstituted, each CO trans to one halogen is cis to another. Thus, there will be an increase in the occupancy of the 2π orbital in going from bromine to iodine due to increased direct donation. The results in Table III show that for $Mn(CO)_4X_2^-$ these two effects cancel each other to produce similar force constants, but, in $Fe(CO)_4X_2$ the increase in 2π occupation dominates because of the iron's smaller covalent radius; the overall effect is to produce considerably weaker force constants for the iodide.

Distributions.—In the previous two sections we have discussed both the mono- and disubstituted species with respect to changes in the metal and in the halogen; in this section we will discuss the specific changes which occur when a second halide is substituted for a carbonyl. From the force constants in Table III we can see that both the trans and cis CO bonds are weaker in the dihalide than in the corresponding monohalide. There are two major reasons for this trend. First, the replacement of a neutral carbonyl by a negative halide causes an increase in the energy of the 3d diagonal term relative to the 5σ and 2π terms. This increase in the 3d energy is due mainly to the crystal field of the additional halide and not to any additional electron donation to the metal. As the 3d level rises in energy, fewer electrons are donated to the 3d from the 5σ orbital and more are donated from the 3d to the 2π orbital. The overall effect is an increase in both the 5σ and 2π occupations, which results in a weaker CO bond and a lower force constant.

The second important effect is that of direct donation from the halogen p_z orbitals. Because these complexes are disubstituted with the halogens cis to each other, the cis carbonyl now has two halogens capable of donating to it, while the trans carbonyl now has one. Thus, we would expect a larger increase in the occupancy of those 2π orbitals which can receive electron density directly from the halogen. We may compare the occupancies of $Mn(CO)_4Br_2^-$ with those of $Mn(CO_5)Br$ (Table III). The small increase, average 0.015, in the $2\pi_x$ of the trans carbonyl and in the $2\pi_y$ of the cis carbonyl is due to the increased energy of the 3d metal orbital, but the larger increase, average 0.034, in the $2\pi_y$ of the trans carbonyl and in the $2\pi_x$ of the cis carbonyl is due to the combined effect of the direct donation and the higher 3d energy. Thus, direct donation is responsible for more than half of the increase in the 2π occupancy in the latter pair of orbitals.

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CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
UNIVERSITY OF HAWAII, HONOLULU, HAWAII 96822

1,2-Dimethylhydrazinochloro- and -fluorodiphosphines

BY MARY D. HAVLICEK AND JOHN W. GILJE*

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$P(NCH_3NCH_3)_3P$ and $ClP(NCH_3NCH_3)_2PCl$ react with PCl_3 to form $Cl_2PNCH_3NCH_3PCl_2$. The latter compound can also be prepared by hydrazinolysis of PCl_3 with $HNCH_3NCH_3H$. The corresponding 1,2-dimethylhydrazinofluorodiphosphines can be synthesized from the chloro derivatives by fluorination with SbF_3. These compounds form complexes with simple BX_3 Lewis acids. Direct reaction with B_2H_6 yields the bis-borane derivatives of each of these compounds except $Cl_2PNCH_3NCH_3PCl_2$, which undergoes decomposition. In the case of $F_2PNCH_3NCH_3PF_2$ a mono-borane adduct could also be isolated. In each of the compounds, BH_3 addition occurs exclusively at the phosphorus. With BF_3 unstable complexes form whose properties are reminiscent of the nitrogen-bonded BF_3 complexes of the aminohalophosphines.

While the aminolysis of PCl_3 was reported over 75 years ago[1] and the aminohalophosphines have received much attention since their first preparation 15 years ago,[2,3] little is known about halophosphine derivatives of other nitrogenous bases. The preparations of some hydrazino- and hydroxylaminochloro- and -fluorophosphines have been reported.[4] The reaction of PCl_3 with 1,1-dimethylhydrazine has been investigated,[5] and closely related trifluoromethyl-,[6] alkyl-,[7,8] and alkylaminophosphino[9] derivatives of several hydrazines have been synthesized and studied.

In a communication Payne, Noth, and Henniger reported[10] that $P[N(CH_3)_2]_3$ reacts with $HNCH_3NHCH_3 \cdot 2HCl$ to form $P(NCH_3NCH_3)_3P$, whose cage structure

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[1] A. Michaelis and G. Schroeter, *Ber.*, **27**, 490 (1895).

[2] A. B. Burg and P. J. Slota, *J. Amer. Chem. Soc.*, **80**, 1107 (1958).

[3] E. Fluck, *Top. Phosphorus Chem.*, **4**, 291 (1967).

[4] A. E. Goya, M. D. Rosario, and J. W. Gilje, *Inorg. Chem.*, **8**, 725 (1969).

[5] D. B. Whigan, J. W. Gilje, and A. E. Goya, *ibid.*, **9**, 1279 (1970).

[6] E. W. Ainscough, L. K. Peterson, and D. E. Sabourin, *Can. J. Chem.*, **48**, 401 (1970), and references therein.

[7] J. M. Kanamueller and H. H. Sisler, *Inorg. Chem.*, **6**, 1765 (1967), and references therein.

[8] S. F. Spangenberg and H. H. Sisler, *ibid.*, **8**, 1004 (1969).

[9] O. J. Sherer and J. Wokulat, *Z. Naturforsch. B*, **22**, 474 (1967).

[10] D. S. Payne, H. Noth, and G. Henniger, *Chem. Commun.*, 327 (1965).

was recently confirmed.[11] The reaction of $P(NCH_3NCH_3)_3P$ with PCl_3 to yield $ClP(NCH_3NCH_3)_2PCl$ was briefly mentioned.[10] These compounds are the first of a new series of potential multidentate, in some cases chelating, phosphine ligands, $X_nP(NCH_3NCH_3)_{3-n}PX_n$ (X = halogen, n = 0–2), of considerable potential interest. The preparation of the remaining members where X = Cl or F and their acid–base reactions with BH_3 and BF_3 are reported here. The ^{19}F nmr spectrum of $F_2PNCH_3NCH_3PF_2$ has already appeared[12] in a communication where its stereochemistry was discussed.

Experimental Section

All manipulations were performed in a vacuum line or under a dry nitrogen atmosphere. Starting materials, solvents, and reagents were of the highest purity available commercially. 1,2-Dimethylhydrazine was obtained from solutions of 1,2-dimethylhydrazine dihydrochloride (Aldrich Chemical Co.) in concentrated NaOH by vacuum line distillation and purified by a reported procedure.[13] Diborane was prepared by the method of Weiss and Shapiro;[14] its purity was checked by vapor pressure and ir. Other reagents and solvents were dried and/or purified by appropriate means before use. Elemental analysis was performed by Galbraith Laboratories, Knoxville, Tenn.

Nmr spectra were obtained using Varian A-60 (^1H) and HA-100 (^1H and ^{19}F) spectrometers equipped with variable-temperature probes. An NMR Specialities HD-60B ^{31}P spin decoupler together with the HA-100 was utilized for the double-resonance experiments. ^1H and ^{19}F spectra at ambient temperatures were run as solutions in $CHCl_3$, high-temperature spectra in *n*-undecane or 1,1,2,2-tetrachloroethane, and those at low temperatures in CF_2Cl_2 or 2-methylbutane. ^1H chemical shifts are relative to internal TMS, while ^{19}F chemical shifts were measured relative to several internal standards; they have been converted to trifluoroacetic acid reference.

Ir spectra were recorded on Beckman IR-5 and IR-9 and Perkin-Elmer 700 spectrometers. Solids were run as dispersions in KBr pellets and Nujol mulls and as solutions in CCl_4 and $CHCl_3$; liquids were run as films on KBr disks, and gases were run in a 10-cm gas cell fitted with KBr windows. Uv spectra were run on a Cary Model 14 spectrometer on acetonitrile solutions, and mass spectra, on a Hitachi Perkin-Elmer RMU-6D spectrometer.

Preparation of $Cl_2PNCH_3NCH_3PCl_2$.—(a) A mixture of 2.75 g (20.0 mmol) of PCl_3 and 1.00 g (4.24 mmol) of $P(NCH_3NCH_3)_3P$ dissolved in 10 ml of $HCCl_3$ was allowed to react for 1 hr at ambient temperature on a vacuum line. The $HCCl_3$ and excess PCl_3 were then distilled from the reaction vessel leaving 3.30 g (12.6 mmol) of $Cl_2PNCH_3NCH_3PCl_2$. At ambient temperature the compound disproportionates into PCl_3 and $ClP(NCH_3NCH_3)_2PCl$ ($P_{dis} \approx 1$ mm (30°)) and more slowly decomposes further into an uncharacterized yellow solid. It can be stored at −78° when dissolved in PCl_3 and can be purified (nmr spectra of freshly purified material show no noticable impurities) by recrystallization from $HCCl_3$ at low temperature (~0° or below). Molecular weight [260 (mass spectral), theoretical 260] and the isotope peaks of the parent ion in the mass spectrum which confirm the presence of four chlorines support the proposed formulation. Major ir peaks are 3000 (ms), 1480 (mw), 1275 (m), 1230 (m), 1160 (mw), 1105 (m), 1065 (ms), 965 (m), 920 (m), 760 (m), and 730 (s) cm^{-1}.

(b) After 36.0 g (0.262 mol) of PCl_3 and 3.64 g (0.0695 mol) of $HNCH_3NCH_3H$ were condensed together at −196°, the mixture was slowly warmed and held at 27° for 1 hr. The 5.54 g (0.0415 mol) of $HNCH_3NCH_3H \cdot 2HCl$ which had precipitated during this time was removed by vacuum-line filtration and excess PCl_3 was evaporated from the filtrate. The solid remaining in the reaction tube was recrystallized from $HCCl_3$ giving 2.01 g (0.0076 mol) of $Cl_2PNCH_3NCH_3PCl_2$.

Preparation of $P(NCH_3NCH_3)_3P$ and $ClP(NCH_3NCH_3)_2PCl$.—These compounds were prepared by the routes mentioned in the literature.[10] $ClP(NCH_3NCH_3)_2PCl$ can also be prepared *via* the reaction of stoichiometric amounts of $P(NCH_3NCH_3)_3P$ and $Cl_2PNCH_3NCH_3PCl_2$ in $HCCl_3$ solvent at ambient temperature. The infrared spectra of these two compounds have not been published; the principal peaks are as follows: $P(NCH_3NCH_3)_3P$: 2900 (m), 2850 (m), 1455 (m), 1420 (mw), 1215 (m), 1185 (s), 1090 (ms), 1055 (s), 915 (s), 760 (m), 745 (mw) cm^{-1}; $ClP(NCH_3NCH_3)_2PCl$: 2910 (s), 2880 (s), 1600 (w), 1465 (ms), 1390 (m), 1365 (m), 1260 (s), 1150 (w), 1110 (s), 920 (w), 750 (s) cm^{-1}.

Preparation of $F_2PNCH_3NCH_3PF_2$.—A 1.47-g (5.61 mmol) sample of $Cl_2PNCH_3NCH_3PCl_2$ was fluorinated with 3.5 g (20 mmol) of SbF_3 on the vacuum line. After about 2 hr at 27° (the initially vigorous reaction was moderated occasionally by cooling to −78°) the mixture was separated by distillation from 27° through a trap held at −78°, from which 0.63 g (3.2 mmol) of $F_2PNCH_3NCH_3PF_2$ was recovered, and one at −196°, which ultimately contained a trace of PF_3.

After a few minutes at room temperature pure colorless $F_2PNCH_3NCH_3PF_2$ began to cloud and evolve PF_3; however, it could be stored for several weeks at −78° and only slight decomposition occurred over several months when it was stored at 0° as a solution (about 10% v/v) in CCl_3F, toluene, isopentane, or 1,1,1-trichloroethane. As a consequence of this instability, good elemental analysis could be obtained. Typical data follow. *Anal.* Calcd for $F_2PNCH_3NCH_3PF_2$: C, 12.25; H, 3.06; N, 14.29 (mol wt 196). Found: C, 13.52; H, 3.23; N, 15.51 (mol wt 190 (vapor density), 196 (mass spectral); vapor pressure (P_{vap}) ~26 mm at 30°)). Ir peaks are 2930 (ms), 2900 (m), 1600 (vw), 1460 (ms), 1440 (ms), 1250 (s), 1175 (ms), 1070 (s), 1000 (sh), 990 (s), 930 (mw), 820 (ms, br), 770 (s, br), 700 (ms), 650 (mw) cm^{-1}.

Preparation of $FP(NCH_3NCH_3)_2PF$.—A mixture of 2.18 g (8.75 mmol) of $ClP(NCH_3NCH_3)_2PCl$ and several grams of SbF_3 contained in a sublimator attached to the vacuum line was heated to 50–70° for 6 hr. During this time 0.632 g (2.92 mmol) of white solid $FP(NCH_3NCH_3)_2PF$ was collected at −23° on the cold finger of the sublimator. Care must be taken in the preparation: if the reaction mixture is heated above 70° or the cold finger cooled lower than about −23°, it is nearly impossible to separate the $FP(NCH_3NCH_3)_2PF$ from impurities which collect with it.

The white $FP(NCH_3NCH_3)_2PF$ (mp 55–59°) decomposes at room temperature even under vacuum. It can be stored at −78° for reasonable periods and solutions in inert solvents appear to be moderately stable (as indicated by nmr). No good analysis could be obtained on the compound; however, typical values follow. *Anal.* Calcd for $FP(NCH_3NCH_3)_2PF$: C, 22.22; H, 5.56; N, 25.93. Found: C, 20.99; H, 5.89; N, 23.47. The main ir peaks are 2930 (ms), 2900 (sh), 1620 (vw), 1470 (sh), 1445 (w), 1215 (s), 1050 (s), 970 (s), 890 (w), 865 (w), 825 (s), 770 (s, br), 865 (w), 675 (w) cm^{-1}.

Reaction of $P(NCH_3NCH_3)_3P$ with Diborane.—$H_3BP(NCH_3NCH_3)_3PBH_3$ was prepared by reaction of $P(NCH_3NCH_3)_3P$ with tetrahydrofuran–borane as described by Payne, Noth, and Henniger.[10] The same adduct can also be obtained from the direct reaction of $P(NCH_3NCH_3)_3P$ with B_2H_6. The major peaks in its ir spectrum are 2920 (m), 2870 (sh), 2440 (s), 2390 (sh), 1390 (m), 1190 (sh), 1160 (s), 1080 (w), 1030 (s), 950 (m), 840 (w), 790 (s) cm^{-1}.

Reaction of $ClP(NCH_3NCH_3)_2PCl$ with Diborane.—A solution of 0.230 g (0.92 mmol) of $ClP(NCH_3NCH_3)_2PCl$ and 2.25 mmol of B_2H_6 in 1 ml of diethyl ether was allowed to react at −78° for about 12 hr. The diethyl ether and excess B_2H_6 were than distilled from the reaction flask and separated by vacuum line distillation. A 1.30-mmol amount of B_2H_6 was recovered; hence 0.95 mmol of B_2H_6 had reacted. The pale yellow solid material (mp 130° dec) remaining in the reaction flask was sparingly soluble in chloroform. Its ir spectrum shows peaks at 2950 (m), 2880 (sh), 2440 (s), 2370 (m), 1470 (s), 1400 (m), 1380 (m), 1270 (m), 1170 (w), 1130 (s), 1030 (w), 750 (s) cm^{-1}.

Reaction of $Cl_2PNCH_3NCH_3PCl_2$ with Diborane.—The direct reaction of $Cl_2PNCH_3NCH_3PCl_2$ with B_2H_6 and that in ethereal solutions were attempted several times at temperatures at and well below ambient. In all cases an irreproducible amount of H_2 and unidentified yellow solids were produced; molar ratios of consumed B_2H_6 to $Cl_2PNCH_3NCH_3PCl_2$ were usually a little less than 2:1. This reaction was not characterized further.

Reaction of $FP(NCH_3NCH_3)_2PF$ with Diborane.—A tube con-

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[11] W. Van Doorne, G. W. Hunt, R. W. Perry, and A. W. Cordes, *Inorg. Chem.*, **10**, 2591 (1971).

[12] T. T. Bopp, M. D. Havlicek, and J. W. Gilje, *J. Amer. Chem. Soc.*, **93**, 3051 (1971).

[13] J. R. Crook and K. Schug, *J. Amer. Chem. Soc.*, **86**, 4271 (1964).

[14] H. C. Weiss and I. Shapiro, *ibid.*, **81**, 6167 (1959).

taining 0.0473 g (0.220 mmol) of $FP(NCH_3NCH_3)_2PF$ and 1.26 mmol of B_2H_6 was kept at −126° for 2 hr and then at 27° until B_2H_6 consumption had ceased. Unreacted B_2H_6 (1.01 mmol) was distilled from the mixture; consequently 0.25 mmol of B_2H_6 was consumed. This consumption indicated a formula of $H_3BFP(NCH_3NCH_3)_2PFBH_3$ for the adduct. The major peaks in its ir spectrum are 3000 (mw), 2420 (ms), 2380 (ms), 1600 (w), 1470 (w), 1430 (w), 1210 (ms), 1080 (s), 1020 (sh), 935 (m), 835 (w) cm^{-1}.

Reaction of $F_2PNCH_3NCH_3PF_2$ with Diborane.—Depending on the molar ratio of reactants, a mono- or bis-borane adduct could be isolated from this reaction. In a typical preparation of $F_2PNCH_3NCH_3PF_2 \cdot BH_3$, 2.17 mmol of B_2H_6 and 0.723 g (3.69 mmol) of $F_2PNCH_3NCH_3PF_2$ were held at 27° for 12 hr. (During this time the mixture turned light yellow indicating some decomposition.) The mixture was then distilled through traps held at −78 and −196°. Excess diborane (0.45 mmol) was recovered in the −196° trap, and the $F_2PNCH_3NCH_3PF_2 \cdot BH_3$ ($P_{vap} \approx 12$ mm (27°)) was retained at −78°.

The bis-borane adduct could be obtained if an excess of B_2H_6 was employed. For example, after 0.260 g (1.33 mmol) of $F_2PNCH_3NCH_3PF_2$ and 1.91 mmol of B_2H_6 were allowed to react at 27° for about 15 hr and the reaction mixture was distilled through −78 and −196° traps, only 0.42 mmol of B_2H_6 was recovered, indicating a consumption of one B_2H_6 per $F_2PNCH_3NCH_3PF_2$. The $F_2PNCH_3NCH_3PF_2 \cdot 2BH_3$ ($P_{vap} \approx 3$ mm (27°)), which slowly decomposes at room temperature, was obtained from the −78° trap. The ir spectra of these two adducts are as follows: $F_2PNCH_3NCH_3PF_2 \cdot BH_3$: 2960 (m), 2930 (m), 2430 (s), 2360 (m), 1470 (ms), 1450 (ms), 1260 (ms), 1180 (ms), 1125 (m), 1075 (s), 1055 (ms), 1010 (s), 910 (sh), 885 (s, br), 835 (s), 810 (s), 775 (s), 680 (s), 655 (w) cm^{-1}; $F_2PNCH_3NCH_3PF_2 \cdot 2BH_3$: 2930 (mw), 2900 (mw), 2430 (s), 2400 (s), 1620 (w), 1490 (m), 1450 (ms), 1270 (ms), 1120 (sh), 1080 (s, br), 1020 (sh), 900 (s, br), 810 (w) cm^{-1}.

Reactions with BF_3.—Reactions of the various compounds with BF_3 were conducted on the vacuum line under a variety of conditions. Temperature was varied between −112° and room temperature, reactions with both excess phosphine and excess BF_3 were conducted, and reaction times of between several minutes and several days were employed. With $P(NCH_3NCH_3)_3P$, $ClP(NCH_3NCH_3)_2PCl$, and $Cl_2PNCH_3NCH_3PCl_2$ the consumption of BF_3 was not reproducible and yellow, uncharacterized products, which usually liberated some BF_3 upon warming, formed. Mass and nmr spectra of these products showed that decomposition of the ligands had taken place. Only in the case of $ClP(NCH_3NCH_3)_2PCl$, where peaks for a bis-BF_3 complex appeared in the mass spectrum, was possible complexation of an intact ligand indicated. With $FP(NCH_3NCH_3)_2PF$ no reaction was observed.

A complex of 1:1 $F_2PNCH_3NCH_3PF_2$:BF_3 ratio formed at low temperature. In a typical experiment, 0.676 g (3.54 mol) of $F_2PNCH_3NCH_3PF_2$ and 8.54 mmol of BF_3 were cooled to −78° until the pressure had equilibrated. The excess BF_3 (4.69 mmol) was drawn off leaving a colorless complex of nominal stoichiometry $F_2PNCH_3NCH_3PF_2 \cdot BF_3$. Upon warming the complex dissociates (P_{dis} = 122 mm (25°)). Nmr spectra at room temperature and −70° are almost identical with the spectra of the free ligand, with the exception of a peak at +74.0 ppm from BF_3 which appears in the ^{19}F spectrum.

Results and Discussion

1,2-Dimethylhydrazinohalophosphines.—The reactions of $P(NCH_3NCH_3)_3P$ and the preparation of $ClP(NCH_3NCH_3)_2PCl$ which have previously been reported[8,10] and preparations of the 1,2-dimethylhydrazinochlorophosphines reported in this paper

$$P(NCH_3NCH_3)_3P + 2nPCl_3 \longrightarrow (n+1)Cl_nP(NCH_3NCH_3)_{3-n}PCl_n$$

$$2PCl_3 + 2HNCH_3NCH_3H \longrightarrow Cl_2PNCH_3NCH_3PCl_2 + HNCH_3NCH_3H \cdot 2HCl$$

are entirely analogous to known reactions of $P[N(CH_3)_2]_3$ and the substitution reactions commonly used to synthesize aminochlorophosphines.[3] Likewise the fluorination reactions

$$Cl_nP(NCH_3NCH_3)_{3-n}PCl_n \xrightarrow{SbF_3} F_nP(NCH_3NCH_3)_{3-n}PF_n$$

closely resemble those used with the aminophosphines.[15] This behavior further demonstrates the chemical similarities between the halophosphine derivatives of various nitrogenous bases which have been commented on before.[4,5]

Ir Spectra.—In the 4000–1000-cm^{-1} region the ir spectra of all of these compounds are quite similar to one another and to a spectrum 1,2-dimethylhydrazine from which the bands arising from N–H vibrations have been removed.[16] P–N and P–F stretching modes are generally found[17] between 1000 and 650 cm^{-1} and, as observed, spectral differences between the various compounds should occur in this region. These data imply that no rearrangements have occurred in the hydrazine moiety during the reactions studied here.

Nmr Spectra.—Supporting the conclusion that the hydrazine unit is intact the ^1H nmr spectrum of each of the compounds (Figure 1 and Table I) consists of a single resonance which is only slightly shifted from the N-CH_3 signal in $HNCH_3NCH_3H$ or $P(NCH_3NCH_3)_3P$. The multiplicities of the resonances observed in the ^1H spectrum (Figure 1) of $ClP(NCH_3NCH_3)_2PCl$ and ^1H (Figure 1) and ^{19}F spectra (doublet of doublets of septets) of $FP(NCH_3NCH_3)_2PF$ are identical with

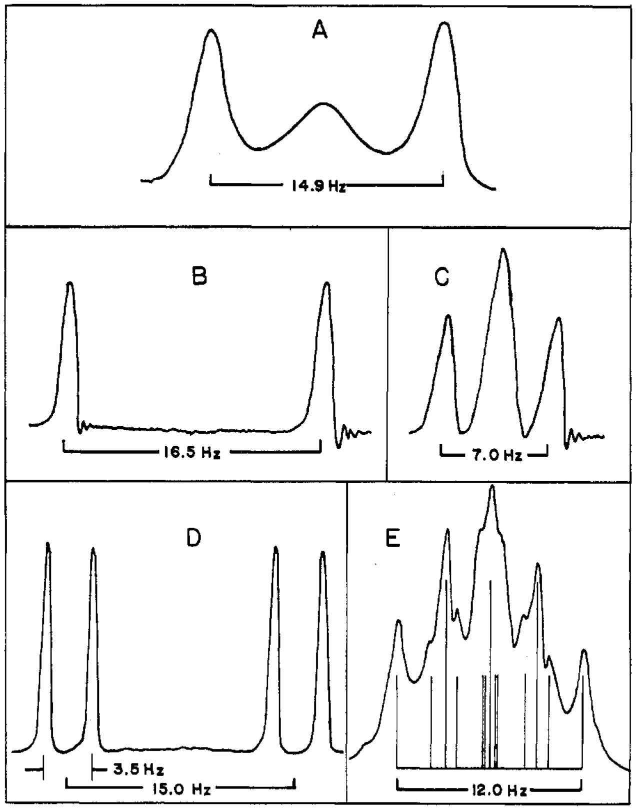

Figure 1.—Hydrogen-1 spectra: (a) $P(NCH_3NCH_3)_3P$; (b) $ClP(NCH_3NCH_3)_2PCl$; (c) $Cl_2PNCH_3NCH_3PCl_2$; (d) $FP(NCH_3NCH_3)_2PF$; (e) $F_2PNCH_3NCH_3PF_2$; compared to a line spectrum calculated using the parameters described in the text.

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[15] J. F. Nixon, *Advan. Inorg. Chem. Radiochem.*, **13**, 363 (1970).

[16] (a) R. H. Pearson, A. N. Fletcher, and E. St. C. Gantz, *Anal. Chem.*, **28**, 1218 (1956); (b) D. W. E. Axford, G. J. Janz, and K. E. Russell, *J. Chem. Phys.*, **19**, 704 (1951); (c) D. Hadzi, J. Jan, and A. Ocvirk, *Spectrochim. Acta, Part A*, **25**, 97 (1969).

[17] D. E. C. Corbridge, *Top. Phosphorus Chem.*, **6**, 235 (1969).

TABLE I

NMR DATA

Compound	Chem shifts, ppm		Coupling constants, Hz						
	^{1}H (from TMS)	^{19}F (from F_3CCO_2H)	PNC*H*	PNNC*H*	*PNCH* + *PN*-NC*H*	*F*PNC*H*	PF	*F*PNN*P*	Other
$P(NCH_3NCH_3)_3P$	−2.74				14.9				
$ClP(NCH_3NCH_3)_2PCl$	−2.98		16.5						
$Cl_2PNCH_3NCH_3PCl_2$	−3.18				7.0				
$FP(NCH_3NCH_3)_2PF$	−2.85	+26.3	15.0			3.5	1023	19	
$F_2PNCH_3NCH_3PF_2$	−2.87	*a*	3.5	2.5		3	*a*		3.5 (PP)
$H_3B\cdot P(NCH_3NCH_3)_3P\cdot BH_3$	−2.90 (C*H*$_3$)				13.3				
$H_3B\cdot ClP(NCH_3NCH_3)_2PCl\cdot BH_3$	−3.07 (C*H*$_3$)		10.5						
$H_3B\cdot FP(NCH_3NCH_3)_2PF\cdot BH_3$	−3.00 (C*H*$_3$)	+4.5	8.0			3.5	1159		
$H_3B\cdot F_2PNCH_3NCH_3PF_2\cdot BH_3$	−3.12 (C*H*$_3$)	−8.3	7.2			2.5	1197	20	104 (BH), 15 (*H*BPF)
	−0.67 (B*H*$_3$)								16 (PBH), 20 (BPF)
$\mathit{H_3B\cdot F_2PNCH_3}NCH_3PF_2$	−3.11 (C*H*$_3$)	*b*	8.4			3.2			87 (BH), 4 (PBH)
	−0.15 (B*H*$_3$)								
$H_3B\cdot F_2PNCH_3\mathit{NCH_3PF_2}$	−2.98 (C*H*$_3$)	*b*	5.8			3.0			
$HNCH_3NCH_3H$	−2.47 (C*H*$_3$)								

[a] Temperature dependent—see ref 12. [b] Temperature dependent—see text.

predicted simple first-order spectra. Coupling constants (Table I) are well within the ranges of about J_{PNCH} = 8–20 Hz, J_{FPNCH} = 2–5 Hz, and J_{PF} = 1000–1400 Hz reported previously[18] for couplings in other trivalent phosphorus compounds and compare well to J_{PF} = 971 Hz for $FP[NCH_3N(CH_3)_2]_2$.[19] (The assignment of ^{31}P–^1H and ^{31}P–^{19}F coupling was confirmed by ^{31}P double-resonance experiments.) The ^{19}F chemical shift of $FP(NCH_3NCH_3)_2PF$ (+26.3 ppm) is close to the values observed in $FP[N(CH_3)_2]_2$[18] (+22.3 ppm) and $FP[NCH_3N(CH_3)_2]_2$[19] (+23.8 ppm). While we could not obtain ^{31}P spectra with our spectrometer, a crude indor experiment was performed on $FP(NCH_3NCH_3)_2PF$ by systematically incrementing, at low power, the ^{31}P decoupling frequency. In this study, two decoupling regions, one centered at 1468 Hz and the other at 2348 Hz, were observed. The separation, 1120 Hz (compared to J_{PF} = 1123 Hz obtained from ^{19}F spectrum), confirms the expected doublet ^{31}P spectrum.

The ^1H spectra of the other compounds (Figure 1) are complex; nonetheless their interpretation is straightforward. The peculiar triplet observed for $P(NCH_3NCH_3)_3P$ has previously[8] been rationalized in terms of "virtual coupling" of the ^{31}P nuclei. Similarly the ^1H spectrum of $Cl_2PNCH_3NCH_3PCl_2$, which is also a triplet, can arise by coupling of the two ^{31}P nuclei. This interpretation was confirmed when the triplets in the spectra of both compounds collapsed into sharp singlets upon double irradiation of the ^{31}P. Unfortunately, neither J_{PNCH} nor J_{PNNCH} can be extracted from these spectra (the separation of the outer peaks of the triplets equals $|J_{PNCH} + J_{PNNCH}|$). Further, since appreciable PNNCH coupling occurs in $F_2PNCH_3NCH_3PF_2$ (see below), J_{PNNCH} cannot be ignored and J_{PNCH} be set equal to the separation of the outer peaks. For acyclic hydrazines,[20] aminophosphines,[21] and $F_2PNCH_3NCH_3PF_2$[12] the nmr spectra have been observed to be temperature dependent as a result of hindered P–N and N–N bond rotation. Likewise the ^1H spectrum of $Cl_2PNCH_3NCH_3PCl_2$ broadened at low temperatures, but as slow exchange had not been reached at −150°, the lower limit of our spectrometer, the exchange processes occurring in this molecule could not be determined.

The complex proton spectrum of $F_2PNCH_3NCH_3PF_2$ (Figure 1), obtained at ambient temperature, can be duplicated by a calculated spectrum based on the formulation of the compound as 1,2-bis(difluorophosphino)-1,2-dimethylhydrazine using the parameters J_{PNCH} = 3.5 Hz, J_{PNNCH} = 2.5 Hz, J_{PP} = 3.5 Hz, and J_{FPNCH} = 3.0 Hz. (These values compare with J_{FPNCH} = 3.5 Hz and J_{PP} = 3.5 Hz obtained[12] from the ^{19}F spectrum at −40°.) The spectrum is not extremely sensitive to small changes in the two PH coupling constants and hence their values may not be exact; it was possible to vary them by as much as 0.3 Hz and still obtain a reasonable calculated spectrum as long as the sign of the two coupling constants was the same and $|J_{PNCH} + J_{PNNCH}| = 6.0 \pm 0.2$ Hz. While J_{PNCH} usually is greater than 3–4 Hz, values as low as 0.8 Hz have recently been reported[22,23] in compounds containing a π-bonded group attached to the nitrogen. Since the P–N bonds in $F_2PNCH_3NCH_3PF_2$ may have appreciable pπ–dπ character, a similar effect may account for its low PNCH coupling constant. The ^1H spectrum broadens upon cooling, but at −150° the slow exchange limit had not been reached. The ^{19}F spectrum of $F_2PNCH_3NCH_3PF_2$, which has already been discussed,[12] is temperature dependent and indicates that the P–N–N–P framework is planar on the nmr time scale with restricted rotation about both the P–N and N–N bonds. Further confirmation of the compound's formulation comes from the ^{31}P spectrum which was determined to be a triplet, as expected for equivalent PF_2 groups, by indor experiments in which partial decoupling of both the ^1H and ^{19}F spectra occurred at three ^{31}P decoupling frequencies separated by about 1200 Hz ($J_{PF} \approx 1200$ Hz from the ^{19}F spectrum[12]).

Reactions with B_2H_6.—The dimethylhydrazinodiphosphines, like related aminophosphines,[24,25] form strong, phosphorus-bonded borane adducts. $H_3B\cdot P(NCH_3NCH_3)_3P\cdot BH_3$ has previously been reported,[10]

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(18) (a) G. S. Reddy and R. Schmutzler, *Z. Naturforsch. B*, **20**, 104 (1965); (b) J. F. Nixon and R. Schmutzler, *Spectrochim. Acta*, **22**, 565 (1966).

(19) M. D. Rosario and J. W. Gilje, unpublished data.

(20) M. J. S. Dewar and W. B. Jennings, *Tetrahedron Lett.*, 339 (1970).

(21) A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, **92**, 5206 (1970).

(22) D. C. H. Bigg, R. Spratt, and B. J. Walker, *Tetrahedron Lett.*, 107 (1970).

(23) J. Nelson, R. Spratt, and B. Walker, *J. Chem. Soc. D.*, 1509 (1970).

(24) H. Noth and H. J. Vetter, *Chem. Ber.*, **96**, 1298 (1963).

(25) (a) S. Fleming and R. W. Parry, *Inorg. Chem.* **11**, 1 (1972); (b) W. Van Doorne, Ph.D. Dissertation, University of Michigan, 1966.

and in this study bis-borane adducts of $ClP(NCH_3NCH_3)_2PCl$, $FP(NCH_3NCH_3)_2PF$, and $F_2PNCH_3NCH_3PF_2$ also were isolated, as was the mono-borane adduct of $F_2PNCH_3NCH_3PF_2$. Only $Cl_2PNCH_3NCH_3PCl_2$ did not form a stable adduct; instead its reaction with B_2H_6 invariably led to decomposition and the generation of uncharacterized yellow solids. It is interesting that this behavior parallels that of $Cl_2PN(CH_3)_2$ which, alone among the dimethylaminochloro- and fluorophosphines, decomposes when treated with B_2H_6.[24] Coordination of the other hydrazinophosphines without rearrangement is indicated by the ir spectra of the BH_3 complexes which closely resemble the spectra of the parent compounds with the exception of peaks at about 2400, 1100, and 800 cm^{-1} which can be attributed to B-H modes.

Nmr Spectra of BH_3 Complexes.—In common solvents the solubility of the BH_3 adducts is considerably less than that of the parent compounds. Since concentrated solutions could not be obtained in every case, the BH_3 signals, which are usually broad and low in intensity, could not be resolved in the proton spectra of several of the compounds. The N-CH_3 peaks, however, could be seen clearly and in all the bis-borane complexes appeared as a single resonance chemically shifted about 0.1–0.2 ppm downfield from their positions in the spectra of the parent ligands. The N-CH_3 peaks in $H_3B\cdot P(NCH_3NCH_3)_3P\cdot BH_3$, $H_3B\cdot ClP(NCH_3NCH_3)_2PCl\cdot BH_3$, and $H_3B\cdot FP(NCH_3NCH_3)_2PF\cdot BH_3$ qualitatively resemble the ^1H spectra of the uncomplexed ligands with coupling constants and chemical shifts as given in Table I. The ^{19}F spectrum of $H_3B\cdot FP(NCH_3NCH_3)_2PF\cdot BH_3$ is a single doublet, J_{PF} = 1159 Hz, δ +4.53 ppm, each member of which shows incipient but unresolved splitting. The magnetic equivalence of the NCH_3 and PF groups, the chemical shift changes occurring upon adduct formation, and the failure to observe coupling of the NCH_3 group with the BH_3 indicate that coordination has occurred at phosphorus. (A 0.05–0.20-ppm downfield shift occurs in the NCH_3 peak when BH_3 coordinates phosphorus in aminophosphines;[25] when nitrogen in a methylamine is complexed, this peak is shifted by about 1 ppm.[26] The 21.8-ppm downfield shift of the ^{19}F signal in $FP(NCH_3NCH_3)_2PF$ upon addition of BH_3 compares with an 18-ppm downfield shift for this resonance between $FP[N(CH_3)_2]_2$ and its phosphorus-bonded borane complex.[25] Spin coupling of the N-methyl groups with BH_3 is seen in the amine–boranes[26] but not the aminophosphine–boranes.[25])

In contrast to the complex splitting of the NCH_3 resonance in $F_2PNCH_3NCH_3PF_2$ the ^1H spectra of its two borane complexes are simple first order. With $H_3B\cdot F_2PNCH_3NCH_3PF_2\cdot BH_3$ the N-CH_3 signal is a double of triplets (J_{PNCH} = 7.2 Hz, J_{FPNCH} = 2.5 Hz, δ −3.12 ppm) and the BH_3 protons appear as a broad quartet of doublets (J_{BH} = 104 Hz, J_{PBH} = 16 Hz, δ −0.67 ppm). The temperature-independent (between +30 and −50°) ^{19}F spectrum of this compound is a doublet, J_{PF} = 1197 Hz, δ −8.3 ppm, each member of which is further split into a complex multiplet which can be duplicated by a spectrum calculated using the parameters J_{PNNPF} = 20 Hz, J_{BPF} = 16 Hz, J_{HCNPF} = 3 Hz, and J_{HBPF} = 15 Hz. These values of J_{BPF} and J_{PBH} are typical[25] of a $FPBH$ linkage and, along with the chemical shift the PF_2, which is near the value of −4.3 ppm observed in $H_3B\cdot F_2PN(CH_3)_2$,[25] and the chemical shift of the N-CH_3 group, indicate coordination of the phosphorus. Likewise coordination of the phosphorus in $H_3B\cdot F_2PNCH_3NCH_3PF_2$ is indicated by the chemical shifts and the P–B coupling constant. As expected the two N-CH_3 groups are magnetically nonequivalent; each appears as a doublet of triplets with the spectral parameters listed in Table I. The high-field signal (δ −2.98 ppm) can be assigned, by analogy to the chemical shifts in $F_2PNCH_3NCH_3PF_2$ and $H_3B\cdot F_2PNCH_3NCH_3PF_2\cdot BH_3$, to the NCH_3 group adjacent to the uncomplexed PF_2; likewise the resonance at −3.11 ppm is assigned to the NCH_3 bonded to the F_2PBH_3 moiety. The BH_3 group appears as a broad quartet of doublets. The 4-Hz HBP coupling constant is typical of this linkage.[25] The ^{19}F spectrum is temperature dependent; because of the compound's decomposition, we were unable to observe the fast-exchange region (somewhere above 25°) and consequently have been unable to interpret completely the low-temperature data. The stereochemical interchanges taking place in this and related compounds are currently under investigation in this laboratory.

Reactions with BF_3.—Only $F_2PNCH_3NCH_3PF_2$ forms a simple complex with the other common boron-containing Lewis acid BF_3. At −78° a 1:1 adduct forms which dissociates as temperature is increased. Of the other hydrazinodiphosphines $P(NCH_3NCH_3)_3P$, $ClP(NCH_3NCH_3)_2PCl$, and $Cl_2PNCH_3NCH_3PCl_2$ decompose to form uncharacterized yellow solids, while $FP(NCH_3NCH_3)_2PF$ does not react with BF_3. Similar behavior is encountered in the reactions between BF_3 and the aminophosphines where decomposition,[24] disproportionation,[27] and unstable complex formation, presumably through coordination of the nitrogen,[25,28,29] occur. In view of the similarities between the amino- and hydrazinophosphines the difficulties in characterizing the BF_3 reactions are probably not surprising, and with BF_3's tendency to complex nitrogen in the aminohalophosphines, quite complex behavior might be expected for the hydrazino analogs with their plethora of nitrogen donor sites.

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[26] C. W. Heitsch, *Inorg. Chem.*, **4**, 1019 (1965).

[27] R. R. Holmes and R. P. Wagner, *J. Amer. Chem. Soc.*, **84**, 357 (1962).

[28] R. G. Cavell, *J. Chem. Soc.*, 1992 (1964).

[29] R. W. Parry, "Coordination Chemistry," S. Kirschner, Ed., Plenum Press, New York, N. Y., 1969, p 207.