enthalpy of activation (ΔH^*) of 13.3 ± 0.4 kcal mol^{-1} and a rate constant at 25°C of 1.1 ± 0.06 × 10^{-1} sec^{-1} by least-squares fitting.[12] The entropy of activation (ΔS^*) was −16 ± 3 cal deg^{-1} mol^{-1} as determined from $k^{25°\mathrm{C}}$. The half-lives of the trans molybdenum(0) and tungsten(0) complexes were 10 and 8 sec, respectively, at 20°C.

The similarity of the rate constants and the products of the reaction suggested that both the tungsten and molybdenum complexes reacted by a similar mechanism. Of the two most likely pathways, bond rupture and ligand twist, the latter was ruled out since the cis and trans isomers of [Mo(CO)$_2$dpe$_2$] are structurally rigid. George and Siebold[7] have reported that the ^{31}P NMR spectrum of a mixture of the molybdenum(0) isomers displayed separate resonances due to the cis and trans forms only and no intermediate or time-averaged signals were observed between 6 and 40°C.

The rate-determining step in the bond-rupture mechanism involves the intramolecular opening of one of the chelate rings. A dissociative process is in accord with the observed first-order kinetics and is supported by the decreased rate of isomerization of *trans*-[Mo(CO)$_2$dpe$_2$] in the tetrahydrofuran (THF) medium. Only if an associative mechanism were operative would the rate constant be expected to increase upon replacing CH$_2$Cl$_2$ in the electrolyte with THF since THF is a better ligand for early transition metals than CH$_2$Cl$_2$. Moreover, a transition state with a greater charge separation than in the reactant is predicted since the reaction rate decreases as the dielectric constant of the solvent decreases ($\epsilon^{20°\mathrm{C}}$ = 7.58[13] and 9.08[14] for THF and CH$_2$Cl$_2$, respectively).[15] A metal complex with a dangling phosphine ligand is consistent with an activated complex of increased polarity.

The studies of George and Siebold[7] imply that the rate of isomerization is even slower in benzene (conversion of *trans*-[Mo(CO)$_2$dpe$_2$] to the cis form requires 2 hr at 40°C) which agrees with the present results since benzene has a dielectric constant of 2.28 at 20°C.[14] Also, since benzene is a poorly coordinating solvent, the observed differences in rate between the various media cannot be attributed to coordination of the solvents.

The observed entropy of activation may appear to be somewhat negative for a dissociative mechanism. However, Dobson[16] reported that ΔS^* values for substitution reactions involving bond rupture mechanisms of complexes of the type [W(CO)$_4$(bidentate)] were very dependent upon the nature of the chelating group. For example, the reactions of [W(CO)$_4$(bidentate)], where bidentate = (CH$_3$)$_2$NCH$_2$CH$_2$CH$_2$N(CH$_3$)$_2$ (tmpa) or (CH$_3$)$_3$CSCH$_2$CH$_2$SC(CH$_3$)$_3$ (dto), with P (OC$_2$H$_5$)$_3$ proceeded via a reversible dissociation of one end of the bidentate ligand followed by nucleophilic attack of the Lewis base. The activation parameters for the dissociation step were ΔH^* = 31.0 and 25.7 kcal mol^{-1} and ΔS^* = +27.0 and +1.6 cal deg^{-1} mol^{-1} for tmpa and dto, respectively. Furthermore, it was observed that as ΔH^* decreased the values of ΔS^* followed. In the present case the enthalpy of activation is only one-half of that reported for the above reactions. When the bidentate ligand was a phosphine as in [Mo(CO)$_4$dpe] or [Mo(CO)$_4$(H$_2$PCH$_2$CH$_2$PH$_2$)], the substitution reactions with P (OC$_2$H$_5$)$_3$ involved dissociation of one of the carbonyl groups (ΔH^* = 38.0 kcal mol^{-1} and ΔS^* = +18.1 cal deg^{-1} mol^{-1})[17] for the former complex while the latter molybdenum complex reacted with rupture of a metal–phosphorus bond (ΔH^* = 32.9 kcal mol^{-1} and ΔS^* = +8.9 cal deg^{-1} mol^{-1}).[18] Although these results provide a good comparison for the present work, nevertheless, a limitation is introduced since the substitution reactions which followed a dissociative mechanism often showed a dependency on the nature of the nucleophile.[16]

A mechanism that involved the total dissociation of a bidentate phosphine ligand from *trans*-[M(CO)$_2$dpe$_2$] is unlikely since the reaction rate was unaffected (to within experimental error) by the addition of excess phosphine and since free phosphine ligand was not observed in the NMR spectrum.[7] Also, the dissociation of a carbonyl group seems equally unlikely since the activation parameters are very different from those reported for the loss of CO from other metal carbonyls.[17,19]

If the half-wave potentials of the couples, *cis*-[M(CO)$_2$dpe$_2$]/*cis*-[M(CO)$_2$dpe$_2$]$^+$ and *trans*-[M(CO)$_2$dpe$_2$]/*trans*-[M(CO)$_2$dpe$_2$]$^+$, are estimated from the peak potentials of the cyclic voltammograms ($E_{1/2} = E_\mathrm{p} \pm 0.029$ V)[9] and equated to the standard potentials of the couples, then it can be shown that isomerization stabilizes the cis metal(0) complexes with respect to oxidation by approximately 7 kcal mol^{-1}. This stabilization results from the reduced competition for the metal nonbonding electrons by the strongly π-withdrawing carbonyl ligands.

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Registry No. *trans*-[W(CO)$_2$dpe$_2$], 51202-31-4; *trans*-[Mo(CO)$_2$dpe$_2$], 40219-77-0; *trans*-[W(CO)$_2$dpe$_2$]BF$_4$, 57049-44-2; *trans*-[Mo(CO)$_2$dpe$_2$]BF$_4$, 57049-45-3.

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Preparation and Conformation of 1,2-Bis(tetrafluorophosphorano)dimethylhydrazine

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Structures of several compounds which contain P–N–N–P linkages have recently been reported.[1-5] In the P(III) derivatives P[N(CH$_3$)N(CH$_3$)]$_3$P and F$_2$PN(CH$_3$)N(CH$_3$)PF$_2$ x-ray diffraction[1] and NMR evidence,[2] respectively, indicate that the P–N–N–P moieties are planar. This would be consistent with a model in which the two P–N bonds contain considerable pπ–dπ bond character and form a delocalized conjugated π network similar to that found in 1,3-dienes. On the other hand, in the P(V) compounds OP[N(CH$_3$)N(C-

$H_3)]_3PO$,[3] $(C_6H_5)N{=}P[N(CH_3)N(CH_3)]_3P{=}N(C_6H_5)$,[4] and $(C_6H_5)O(S)P(NHNH)_2P(S)O(C_6H_5)$,[5] the hydrazine fragments adopt their more usual gauche configuration[6] and the P–N–N–P unit is nonplanar. In order to explore whether the conformational difference which appears to exist between cyclic P(III) and P(V) derivatives also pertains to acyclic compounds we have prepared $F_4PN(CH_3)N(CH_3)PF_4$, the first acyclic hydrazine derivative of a pentacoordinate phosphorane, and have investigated its stereochemistry using dynamic nuclear magnetic resonance (DNMR) spectroscopy.

Experimental Section

All manipulations were performed in a vacuum line or under a dry nitrogen atmosphere. PF_5 (Matheson Gas Products) was purified by distillation on the vacuum line. 1,2-Dimethylhydrazine was obtained from solutions of 1,2-dimethylhydrazine dihydrochloride (Aldrich Chemical Co.) in concentrated NaOH by vacuum-line distillation; it was purified by a reported procedure.[7] $[(CH_3)_3Si]N(CH_3)N(CH_3)[Si(CH_3)_3]$ was prepared by a reported procedure.[8]

NMR spectra were obtained using a Varian HA-100 spectrometer (^1H and ^{19}F) and a Varian XL-100 spectrometer (^1H and ^{31}P) operating in the Fourier transform mode. Spectra were obtained in Cl_2CF_2 (−120 to +30°), a Cl_2CF_2–$DCCl_3$ 3:1 mixture (−120 to +30°), and H_2CCl_2 (−20 to +80°). Chemical shifts are referenced to internal TMS (^1H), external trifluoroacetic acid (^{19}F), and external 85% H_3PO_4 (^{31}P). Ir spectra were obtained on a Beckman IR-10 spectrometer using a 10-cm gas cell with KBr windows. Mass spectra were run as gas samples on a Hitachi Perkin-Elmer RMU-6D spectrometer. Elemental analysis was run by Galbraith Laboratories, Knoxville, Tenn.

Preparation of $F_4PN(CH_3)N(CH_3)PF_4$. $F_4PN(CN_3)N(CH_3)PF_4$ was synthesized by the direct reaction between gaseous PF_5 and liquid $[(CH_3)_3Si]N(CH_3)N(CH_3)[Si(CH_3)_3]$. In typical preparations a 3–5-mmol aliquot of the silylhydrazine was placed in a cold finger attached to a 500-ml reaction flask. The cold finger was cooled to −196° and the flask was evacuated on the vacuum line. Two millimoles of PF_5 per millimole of $[(CH_3)_3Si]N(CH_3)N(CH_3)[Si(CH_3)_3]$ was then measured on the vacuum line and frozen into the reaction flask which was sealed and allowed to warm slowly to room temperature. After about 12 hr at ambient temperature the flask was reattached to the vacuum line, a break-seal was opened, and the volatile components were distilled through traps held at −22, −45, and −196°. $F_4PN(CH_3)N(CH_3)PF_4$ was retained in the −45° trap; typical yields were greater than 90%.

$F_4PN(CH_3)N(CH_3)PF_4$ is a colorless liquid. Samples stored in sealed, evacuated ampules show no sign of decomposition after more than 1 year at 0°. Anal. Calcd for $F_8P_2N_2C_2H_6$: C, 8.79; H, 2.19; N, 10.25. Found: C, 8.99; H, 2.09; N, 10.21. Its vapor pressure is about 20 Torr at 25°.

The ions observed in the 70-eV mass spectrum of $F_4PNCH_3NCH_3PF_4$, the percent of the ion current carried by the ions ($\%\Sigma_{30}$), and tentative assignments are as follows: 253, 3.3, $F_4PNCH_3NCH_3PF_3^+$; 165, 2.8, $F_4PNCH_3NCH_3^+$; 146, 4.6, $F_3PNCH_3NCH_3^+$; 145, 0.6, $F_3PN_2C_2H_5^+$; 117, 1.0, $F_3PNCH_4^+$; 116, 4.5, $F_3PNCH_3^+$; 107, 57.4, PF_4^+; 104, 2.2, $F_3PNH_2^+$, $F_3PCH_3^+$; 88, 1.3, PF_3^+; 85, 2.3, $F_2PNH_2^+$, $F_2PCH_3^+$; 81, 0.2, ?; 69, 1.6, PF_2^+; 59, 1.0, $N_2C_2H_7^+$; 58, 6.4, $N_2C_2H_6^+$; 57, 1.9, $N_2C_2H_5^+$; 43, 8.6, N_2CH_3. Its ir spectrum shows the following bands: 2980 (w), 2860 (w), 1440 (w), 1245 (mw), 1195 (mw), 1110 (m), 1055 (m), 965 (vs), 920 (vs), 890 (vs), 780 (w), 680 (w), 635 (mw), 540 (s) cm^{-1}.

Results and Discussion

The reaction of phosphorus pentafluoride with 1,2-trimethylsilyl-1,2-dimethylhydrazine

$$2PF_5 + [(CH_3)_3Si]N(CH_3)N(CH_3)[Si(CH_3)_3] \rightarrow F_4PN(CH_3)N(CH_3)PF_4 + 2FSi(CH_3)_3$$

closely parallels the reactions of PF_5 with aminosilanes which have proven to be easy synthetic routes to the aminotetrafluorophosphoranes.[9-12] This behavior again demonstrates the similarity between phosphorus–hydrazine and phosphorus–amine chemistry which has been commented on before.[13-15] Thermal decomposition of 1:1 adducts which form between PF_5 and many secondary amines has also proven to be a convenient route to the aminotetrafluorophosphoranes.[5,11,16] While we observed PF_5 to form a 1:1 adduct with $HN(CH_3)N(CH_3)H$, thermolysis, in our hands, led only to intractable solids which we were not able to characterize. This is probably not a surprising result because a nonvolatile, moderately unstable hydrazinium salt in which the nitrogen atom β to phosphorus is protonated is a reasonable product of the dehydrofluorination of the 1:1 adduct.

Table I. NMR Data

Chemical Shifts, Ppm

^{19}F: from external CF_3COOH

F(av)(+80°)	F_a(−80°)	F_a'(−80°)	F_e(−80°)	F_e'(−80°)
−7.97	−17.88	−8.36	−1.31	−0.62

^{31}P: from external 85% H_3PO_4	^1H: from internal TMS
+70.4 (+30 to −120°)	−2.78 (+30°)

Coupling Constants, Hz

PF(av)	PF_a	PF_a'	PF_e	PF_e'	F_eF_a	F_eF_e'	F_aF_a'	FH	$\lvert PH + P'H \rvert$
877	815	790	931	955	81	50	<5	2.3	8.4

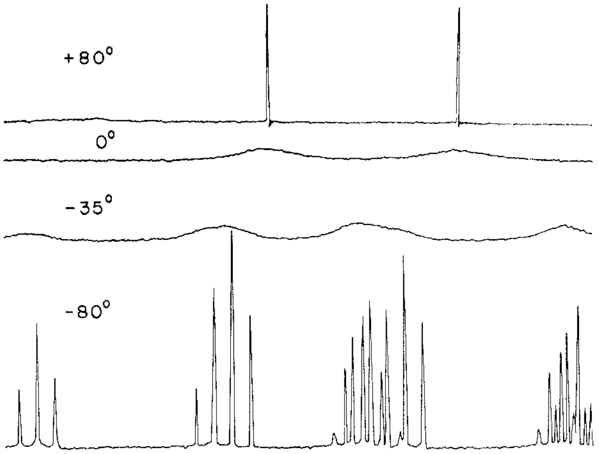


Figure 1. Variable-temperature ^{19}F NMR spectra.

$F_4PN(CH_3)N(CH_3)PF_4$ was characterized by elemental analysis and NMR, ir, and mass spectroscopy. Its ir spectrum is essentially a superposition of the spectrum of 1,2-dimethylhydrazine[17] from which the N–H modes have been removed plus very strong bands at 965, 920, and 890 cm^{-1} and a strong one at 540 cm^{-1}. The latter peaks can be assigned as P–F and P–N modes by analogy to the spectra of aminotetrafluorophosphoranes.[10,12,16] As observed[18,19] in the mass spectra of many other pentaccordinate phosphorus compounds, no parent ion is seen in the mass spectrum of $F_4PN(CH_3)N(CH_3)PF_4$. Rather, the highest *m/e* peak corresponds to the molecular ion less a single fluorine. The spectrum is consistent with the formulation of the compound as a hydrazinophosphorane and appears to be the result of a straightforward fragmentation, largely via P–F and P–N bond scission. One metastable peak, observed at $m^* \approx 46.7$, could tentatively be assigned to

$$\underset{(m/e\ 165)}{F_4PN(CH_3)N(CH_3)^+} \rightarrow \underset{(m/e\ 88)}{F_3P^+} + F\cdot + CH_3N{=}NCH_3$$

for which m^* (calcd) = 46.9.

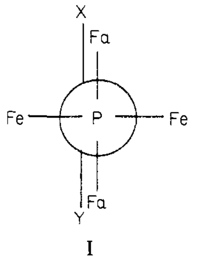
NMR Studies. The Conformation of $F_4PN(CH_3)N(CH_3)PF_4$. Variable-temperature ^{19}F, ^{31}P, and ^1H NMR data are summarized in Table I. At −80° the ^{19}F spectrum (Figure 1) consists of the ABMN portion of an ABMNX spectrum.[20] This non-first-order spectrum could be analyzed and gave the coupling constants and chemical shifts reported in Table I. Assignments have been made by analogy to other tetrafluorophosphoranes[11,12,21] and assume trigonal-bipyramidal geometry for the phosphorus. The two low-field doublets both of whose PF coupling constants are about 800 Hz (−17.88

ppm, J_{PF_a} = 815 Hz; −8.36 ppm, $J_{PF_{a'}}$ = 790 Hz) are attributed to axial fluorine resonances and the two high-field doublets (−1.31 ppm, J_{PF_e} = 931 Hz; −0.62 ppm, $J_{PF_{e'}}$ = 955 Hz) are in the correct chemical shift range and possess appropriate[11,12,21] coupling constants to arise from equatorial fluorines. Upon warming, the peaks coalesce and reappear by +80° as a single doublet of appropriately averaged chemical shift and coupling constant. The line shape of the ^{19}F spectrum near coalescence could be closely approximated by a theoretical spectrum calculated assuming that the rate at which the equatorial and axial fluorines become diastereotopic is identical with the rate at which F_e becomes inequivalent to $F_{e'}$ and F_a becomes inequivalent to $F_{a'}$. A value of $\Delta G^{\ddagger}_{253} \approx 12$ kcal/mol was calculated for the interchange which gives rise to this temperature dependency.[22]

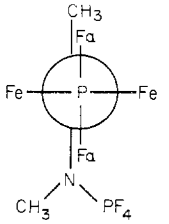
At −120° the ^{31}P spectrum is the X portion of the ABMNX spectrum. The coupling constants are the same as those extracted from the ^{19}F data. Between −120 and +30° the spectrum changes in the manner expected[21] for a tetrafluorophosphorane in which fluorine exchange is becoming fast on the NMR time scale. By +30° this exchange is rapid and the spectrum is the appropriate binomial quintet.

The ^{1}H spectrum is complex at +30° and could only be explained if coupling occurs between the two phosphorus atoms and the protons couple with both phosphorus atoms. Good fits were obtained between experimental and calculated spectra if $J_{F\text{-}H}$ = 2.3 Hz, $|J_{PNCH} + J_{PNNCH}|$ = 8.4 Hz, J_{PNCH} = 7–8 Hz, J_{PNNCH} = 1.4–0.4 Hz, and $J_{PP'}$ = 6–7 Hz. As temperature is lowered, the ^{1}H spectrum remains as a single resonance. At −90° and below the anticipated four different H–F couplings cannot be resolved and the signal consists of a broad triplet arising from proton–phosphorus virtual coupling, $|J_{PNCH} + J_{PNNCH}|$ = 8.6 Hz.

Discussion of NMR Results. All of the NMR spectra indicate that at low temperature both phosphorus atoms are isochonous, but within each PF$_4$ group all four fluorine atoms are nonequivalent. There is ample evidence[11,12,23] that the conformation of compounds of the type F$_4$PNXY is I, with the nitrogen either planar or time-average planar because of rapid inversion. Assuming this to be the conformation about the P–N bond in F$_4$PN(CH$_3$)N(CH$_3$)PF$_4$ (X = CH$_3$, Y = N(CH$_3$)PF$_4$ in I) the axial fluorines become diastereotopic only if both P–N rotation and intramolecular fluorine exchange become slow on the NMR time scale. For the equatorial fluorines also to be anisochronous F$_4$PN(CH$_3$)N(CH$_3$)PF$_4$ must not possess mirror symmetry through the plane containing the two axial fluorines, X, and Y as depicted in structure I. Most logically this asymmetry can be explained if the PNNP unit is nonplanar as in II and if N–N bond rotation, in addition to P–N torsion and fluorine exchange, slows at low temperature.



I



II

The simultaneous slowing of both P–N bond rotation and fluorine interchange has already been observed in several P–N compounds[11,12,23] (and analogous behavior has been reported in some P^V–S compounds[24]) and has been discussed[25] in terms of a lowering of the barrier to P–N rotation in a square-pyramidal intermediate which is predicted by the Berry[21] model for the permutational isomerism of tetrafluorophosphoranes. However the simultaneous slowing of three stereochemical processes as seen with F$_4$PN(CH$_3$)N(CH$_3$)PF$_4$ is unprecedented. While cogent arguments[25] can be made as to why P–N rotation and F exchange must be concerted, there seems to be no a priori reason to expect that N–N rotation must occur through a transition state common to the other two processes. In fact the 12-kcal/mol barrier obtained in this study is similar in magnitude to barriers previously reported[6] for N–N torsion in acyclic hydrazines. Thus, although the possibility clearly exists that all three of these processes are concerted, at this point it appears equally likely that at least N–N rotation proceeds by a path which is not inextricably linked to those followed by the other two processes. The only restriction would be that the activation energies of each of these events would have to be close to the 12-kcal/mol value mentioned above.

Registry No. F$_4$PN(CH$_3$)N(CH$_3$)PF$_4$, 57484-19-2; PF$_5$, 7647-19-0; [(CH$_3$)$_3$Si]N(CH$_3$)N(CH$_3$)[Si(CH$_3$)$_3$], 685-26-7; ^{31}P, 7723-14-0.

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