action. This intermediate could be formed in the same manner as in the radiolytic experiment, from reactions 1 through 5. The reaction would presumably be initiated by the thermal bond rupture of carbon tetrachloride. Reaction 6 is also highly probable in the thermal case. The chief difference between the thermal and radiolytic reactions occurs in the competitive reactions 7a–c. Only one of these (7b) involves ammonia as a reactant. It would therefore be relatively more rapid in the experiments of Watt and Hahn, owing to the higher concentrations of ammonia, and thus give rise to the observed predominant formation of guanidine. Ammonium dicyanamide and cyanoguanidine which are formed from the other two reactions (7a and 7c) were identified as major and minor products under radiolysis but were not found in the thermal reaction. It is possible that the failure of the earlier workers to identify these compounds was due to lack of a sufficiently sensitive analytical procedure, such as t.l.c., rather than their total absence.

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The New Phosphinoamines $HN[P(CF_3)_2]_2$, $CH_3N[P(CF_3)_2]_2$, and $N[P(CF_3)_2]_3$[1]

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The new bis(phosphino)amines $HN[P(CF_3)_2]_2$ *(m.p. −54°; b.p. 93° estd.) and* $CH_3N[P(CF_3)_2]_2$ *(m.p. −31°; b.p. 117° estd.) were made by using* $(CH_3)_3N$ *to force the action of* $(CF_3)_2PCl$ *upon* $H_2NP(CF_3)_2$ *or* $CH_3NHP(CF_3)_2$*. Both are stable up to 300° and resist acid cleavage at 100°.* $CH_3N[P(CF_3)_2]_2$ *forms no* $(CH_3)_3N$ *adduct but is cleaved by* NH_3 *or* CH_3NH_2 *(only in the liquid phase), whereas* $HN[P(CF_3)_2]_2$ *is not cleaved by* NH_3 *but exhibits acidity by forming vapor-dissociable* NH_4^+ *and* $(CH_3)_3NH^+$ *salts or by reaction with sodium to form* H_2 *and* $NaN[P(CF_3)_2]_2$*. Action by* $(CF_3)_2PCl$ *upon* $HN[P(CF_3)_2]_2$ *does not occur even with* $(CH_3)_3N$*, but the salt* $NaN[P(CF_3)_2]_2$ *reacts easily with* $(CF_3)_2PCl$ *to make the new volatile solid* $N[P(CF_3)_2]_3$ *(m.p. 37°; b.p. 152° estd.) stable to 150°. This is cleaved quantitatively by HCl to make* $(CF_3)_2PCl$ *and* $HN[P(CF_3)_2]_2$*, by* NH_3 *to make* $H_2NP(CF_3)_2$ *and* $HN[P(CF_3)_2]_2$*, by* H_2O *to make* $HN[P(CF_3)_2]_2$ *and* $(CF_3)_2POH$*, or by* $H_2NP(CF_3)_2$ *to make* $2HN[P(CF_3)_2]_2$*. The three new phosphinoamines are more resistant to cleavage than* $(SiH_3)_3N$*, and are presumed to have a similar π-enhanced planar bonding to N. Their infrared spectra have been recorded accurately and assigned.*

Introduction, Results, and Discussion

The stable aminophosphine $H_2NP(CF_3)_2$ has shown no sign of direct and easy convertibility to poly(phosphino)amines,[2] whereas all attempts to make $H_2NP(CH_3)_2$ have led rather to the poly(phosphino)amines $HN[P(CH_3)_2]_2$ and $N[P(CH_3)_2]_3$.[3,4] It can be understood that the disproportionation of $H_2NP(CH_3)_2$ to $HN[P(CH_3)_2]_2$ and NH_3 might not be resisted by the loss of two $N_{2p} \rightarrow P_{3d}$ two-atom π-bonds, for such π-bonding here would be relatively weak and the gain of one $N_{2p} \rightarrow (P_{3d})_2$ three-atom π-bond would more than half compensate the loss. However, when such π-bonding is considerably stronger, as in the corresponding $P(CF_3)_2$ compounds, the net loss of bond energy in such a conversion might be considerably greater. But no such ideas would predict actual instability for $HN[P(CF_3)_2]_2$ or $N[P(CF_3)_2]_3$. Rather, as suggested by Harris,[2] the difficulty of conversion of $H_2NP(CF_3)_2$ to poly(phosphino)amines has been the lack of an effective mechanism: the $N_{2p} \rightarrow P_{3d}$ π-bonding is so strong as to deactivate N as a base and P as a site for nucleophilic attack. Also, $H_2NP(CF_3)_2$ cannot be expected to react with $(CF_3)_2PCl$ without some means of HCl removal; and for that purpose no protic base (*e.g.*, R_2NH) can serve because P–N–P cleavage products would be favored.

Accordingly, we have made the new compound $HN[P(CF_3)_2]_2$ quantitatively from $H_2NP(CF_3)_2$ and $(CF_3)_2PCl$, using $(CH_3)_3N$ to remove HCl. Similarly, the new compound $CH_3N[P(CF_3)_2]_2$ was made from CH_3NH_2 and $(CF_3)_2PCl$, again using $(CH_3)_3N$ in a nearly quantitative process. In both syntheses it is probable that the $(CF_3)_2PCl$ was activated toward loss of Cl^- by the effect of a weakly N→P bonded complex with $(CH_3)_3N$, as seems reasonable in view of analogous experience with $(CF_3)_2PI$.[5]

Both of these new bis(phosphino)amines decomposed only slowly at 300° and resisted cleavage by protic or Lewis acids; thus neither would react with HCl at 100°, and $HN[P(CF_3)_2]_2$ was tried also with BCl_3 and

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(1) Supported by Grant No. GP-199 from the National Science Foundation, which contributed also through Grant No. G-14665 toward the purchase of the Beckman IR7 instrument.

(2) G. S. Harris, *J. Chem. Soc.*, 512 (1958).

(3) R. I. Wagner and A. B. Burg, *J. Am. Chem. Soc.*, **75**, 3871 (1953).

(4) A. B. Burg and P. J. Slota, Jr., *ibid.*, **80**, 1107 (1958).

(5) A. B. Burg and J. F. Nixon, *ibid.*, **86**, 356 (1964).

BF_3, again with no reaction at 100°. Neither would react with ammonia in the vapor phase at temperatures as high as 200°, but in the liquid phase their behavior toward ammonia and amines was quite different.

Ammonia cleaved liquid $CH_3N[P(CF_3)_2]_2$ quantitatively to an unresolvable mixture, the components of which were easily recognized by their unique infrared bands. One product was the expected $CH_3NHP(CF_3)_2$, which probably did not react further, since no methylamine was found. The equally expected $H_2NP(CF_3)_2$ appeared partly as such and partly as NH_3 and $HN[P(CF_3)_2]_2$. With methylamine, liquid $CH_3N[P(CF_3)_2]_2$ cleaved quantitatively to $2CH_3NHP(CF_3)_2$, but with $(CH_3)_3N$ it did not even form an adduct at any temperature between 0 and −78°.

With $HN[P(CF_3)_2]_2$, however, $(CH_3)_3N$ does form an adduct which must be interpreted as the salt $(CH_3)_3NH^{+-}N[P(CF_3)_2]_2$, for if it were an $N \rightarrow P$ bonded complex, the same kind of adduct should be formed by $CH_3N[P(CF_3)_2]_2$. Both this $(CH_3)_3NH^+$ salt and the corresponding NH_4^+ salt are dissociable into the vapor phase at 25°, presumably more on account of low lattice energies than protic-acid weakness of $HN[P(CF_3)_2]_2$. It is most interesting that the salt $NH_4^{+-}N[P(CF_3)_2]_2$ is not cleaved by ammonia, probably for two reasons: the anionic charge would repel the base and the π-bonding by two electron pairs from N to 2P would fully protect the P atoms from nucleophilic invasion by all but the strongest bases. However, a probable $H_3N\text{-}H\text{-}N[P(CF_3)_2]_2$ hydrogen bonding would make both of these effects less important.

The tris(phosphino)amine $N[P(CF_3)_2]_3$ could not be made by an extension of the amine–HCl method, for $HN[P(CF_3)_2]_2$ failed to react with $(CF_3)_2PCl$ and $(CH_3)_3N$ even at 100°. However, a product having the properties expected for the sodium salt $NaN[P(CF_3)_2]_2$ could be made by attacking $HN[P(CF_3)_2]_2$ with sodium in liquid ammonia, or better in tetrahydrofuran. The identity of this salt was indicated by its reaction with HCl to restore $HN[P(CF_3)_2]_2$; and with $(CF_3)_2PCl$ it gave a nearly quantitative yield of the desired $N[P(CF_3)_2]_3$.

This slightly volatile white solid could be heated at 100° without harm, but its extensive decomposition during 2 days at 160° showed it to be decidedly less stable than $HN[P(CF_3)_2]_2$. Its cleavage by water or ammonia at 25°, to produce $HN[P(CF_3)_2]_2$ and $(CF_3)_2POH$ or $H_2NP(CF_3)_2$, respectively, can be understood in terms of a three-way π-bond from N to 3P, whereby each P atom is less protected from nucleophiles than it would be even in $CH_3N[P(CF_3)_2]_2$, which also is cleaved by ammonia. Less obvious is the reason for the quantitative cleavage of $N[P(CF_3)_2]_3$ by HCl (at 100° but not at 25°), stopping with the formation of $HN[P(CF_3)_2]_2$ and $(CF_3)_2PCl$. However, the equally quantitative reaction of $N[P(CF_3)_2]_3$ with $H_2NP(CF_3)_2$ to make $2HN[P(CF_3)_2]_2$ suggests an interesting analogy to acid–base neutralization.

It is interesting to compare the new poly(phosphino)amines with the relatively well-known tris(silyl)amine, $(SiH_3)_3N$. The fast cleavage of this by HCl suggests some base character, implying weaker π-bonding than in the uncleavable $HN[P(CF_3)_2]_2$, wherein the strong π-bonding would work also against any nucleophilic attack. Then since the $N \rightarrow P$ π-electrons in $N[P(CF_3)_2]_3$ would be even less available for nitrogen-base action, the slow cleavage of this compound by HCl (requiring heat) might be due to less π-protection of phosphorus against nucleophilic attack. Finally, since $(SiH_3)_3N$ has a planar NSi_3 pattern,[6] it is reasonable to suppose that the NP_3, CNP_2, and HNP_2 structures here also are planar.

The experimental work described in the following sections was done by means of a glass high-vacuum manifold including a series of U-traps and mercury float valves for quantitative separations by high-vacuum fractional condensation. Where stopcocks were used, the grease was either halocarbon or Apiezon L. Special devices such as the vacuum tube opener, the microscale high-vacuum fractionating column,[7] or the stopcocked Λ-tube with filter for purification by low-temperature crystallization[8] were attached through 7/15 or 7/25 standard-taper ground joints.

The Bis(phosphino)amines

Syntheses. The initial experiment used equimolar amounts of $(CF_3)_2PCl$, $H_2NP(CF_3)_2$, and $(CH_3)_3N$ at 25°, giving not quite a 95% yield of $HN[P(CF_3)_2]_2$. Occlusion of reactants in the solid $(CH_3)_3NHCl$ was suspected. Accordingly, a quantitative synthesis was achieved by allowing 1 to 4 days for reaction in the sealed tube at 24° and then heating for 15–18 hr. at 100°. Thus from 2.71 mmoles of each reactant the yield of virtually pure $HN[P(CF_3)_2]_2$ was 955 mg. (2.705 mmoles) or 99.8%. Final purification was accomplished by refluxing at −60° in the high-vacuum microcolumn. The third experiment showed the millimole stoichiometry attached to the following equation, for which $(CH_3)_3NHCl$ was determined as chloride by silver nitrate titration.

$$\begin{array}{ccccc} (CF_3)_2PCl\ + & (CH_3)_3N\ + & H_2NP(CF_3)_2 \longrightarrow & & \\ 2.234 & 2.234 & 2.215 & & \\ \underline{-0.015} & \underline{-0.015} & & HN[P(CF_3)_2]_2\ + & (CH_3)_3NHC \\ 2.22 & 2.22 & & 2.23 & 2.225 \end{array}$$

The compound $CH_3N[P(CF_3)_2]_2$ was not quite so easily made: in either the gas or liquid phase the reaction of CH_3NH_2 with $(CF_3)_2PCl$ in excess gave none of it; and when equimolar quantities of $CH_3NHP(CF_3)_2$, $(CF_3)_2PCl$, and $(CH_3)_3N$ were mixed in the vapor phase, only a slight precipitation of solid material appeared during 2 days at 25°. The process was faster in the liquid phase, and was improved by heating, but remained far short of completion. For our best synthesis, the volatile mixture recovered from the 25° reaction of 11.01 mmoles of $(CF_3)_2PCl$ and 11.05 mmoles of CH_3NH_2 was mixed with 11.03 mmoles of $(CH_3)_3N$ (twice the calculated requirement) and heated in a 10-ml. sealed tube for 20 hr. at 60°. A volatile product was trapped *in vacuo* at −30°, and the more volatile components were again heated in a fresh 10-ml. sealed tube for 2 days at 60–80°; a slight brown color indicated an undesired side reaction. Again the most volatile components were removed and reheated, now producing very little solid. The combined product was purified by high-vacuum reflux at −50 to −40°; the yield of pure $CH_3N[P(CF_3)_2]_2$

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(6) K. Hedberg, *J. Am. Chem. Soc.*, 77, 6491 (1955).

(7) J. R. Spielman and A. B. Burg, *Inorg. Chem.*, 2, 1139 (1963).

(8) An improved version of that shown by A. B. Burg and R. Kratzer, *ibid.*, 1, 726 (1962).

was 5.14 mmoles, representing 93.3% of the initial $(CF_3)_2PCl$.

Confirmation of Formulas. The molecular weights of the two new bis(phosphino)amines were determined from their vapor densities: for $HN[P(CF_3)_2]_2$, 351 obsd. *vs.* 353 calcd.; for $CH_3N[P(CF_3)_2]_2$, 363 obsd. *vs.* 367 calcd. Basic hydrolysis gave $4.00HCF_3$ per $HN[P(CF_3)_2]_2$ at 25° or (requiring 100°) $3.97HCF_3$ per $CH_3N[P(CF_3)_2]_2$. Further evidence for the given molecular formulas, beyond the nearly quantitative syntheses, is provided by some quantitative reactions (yet to be described) equivalent to elementary analyses.

Physical Properties. The melting ranges of the new bis(phosphino)amines were observed visually, using vapor-tension thermometers. For $HN[P(CF_3)_2]_2$ the range was −55 to −54°; for $CH_3N[P(CF_3)_2]_2$, −32.4 to −31°. Representative equilibrium vapor pressures are shown in Tables I and II, with equations, derived normal boiling points, and Trouton constants consistent with good purity. The slightly high Trouton constant for the HNP_2 compound would be consistent with some small tendency toward hydrogen bonding.

Table I. Volatility of $HN[P(CF_3)_2]_2$
($\log P = 7.4256 + 1.75 \log T - 0.00680T - 2395/T$)
(t_{760} = 93.0°; Trouton constant = 22.1 e.u.)

Temp., °C.	0.00	23.9	34.8	52.0	63.2	73.5
P_{obsd}, mm.	11.60	46.7	81.3	176.2	274.9	402.4
P_{calcd}, mm.	11.59	46.8	81.2	175.8	275.4	402.1

Table II. Volatility of $CH_3N[P(CF_3)_2]_2$
($\log P = 7.240 + 1.75 \log T - 0.00650T - 2481/T$)
(t_{760} = 116.6°; Trouton constant = 21.0 e.u.)

Temp., °C.	0.00	9.6	25.0	36.9	47.0	60.9
P_{obsd}, mm.	4.46	8.41	17.3	38.9	63.3	114.3
P_{calcd}, mm.	4.47	8.37	17.5	38.7	63.0	114.5

Chemical Behavior. A small sample of $HN[P(CF_3)_2]_2$, heated in a sealed tube at normal pressure for 77 hr. at 250°, showed no change; but during 50 hr. at 300° it was partially decomposed to dark material and volatile products, among which HCF_3 and PF_3 were identified by their infrared spectra. A trace of gas not condensed at −196° might have been nitrogen. Similarly, $CH_3N[P(CF_3)_2]_2$ was unchanged during 24 hr. at 240° and showed only slight darkening during 60 hr. at 280–290°; the decomposition was too slight for identification of the products.

Addition of NH_3 in small portions to $HN[P(CF_3)_2]_2$ showed a rising initial melting temperature, to a maximum of +1.5° at $1.00NH_3$ per mole. With more NH_3, only solution effects were observed: no higher adduct could be recognized. The 1:1 adduct could not be separated from excess $HN[P(CF_3)_2]_2$ by distillation methods, but excess NH_3 could be removed through a high-vacuum trap at −65°, where the pure adduct condensed.

The analogous $(CH_3)_3N$ adduct was demonstrated first by a pressure–composition isotherm at 0°: as the amine was added, the pressure remained steadily near 12 mm., corresponding to $HN[P(CF_3)_2]_2$ with little solution effect, and began to drop sharply at ratios above $0.98(CH_3)_3N$ per mole; but above the 1:1 ratio there was a steep and steady rise toward the pressures expected for more and more dilute solutions in the liquid amine (at −78°, 0.5 to 5 mm.).

Both adducts were wholly dissociated in the vapor phase, as shown by their average molecular weights (184.5 and 214, *vs.* 185 and 206, respectively, calculated for complete dissociation). Also, the infrared spectra of the vapors showed only the bands characteristic of the two components in each case.

Representative dissociation pressures of these adducts are shown with Clapeyron–Clausius equations and derived free energies of dissociation in Tables III and IV. The melting point of $NH_3 \cdot HN[P(CF_3)_2]_2$ is calculated as 2.3°; observed range, 1.5–2.5°. For the fusion process, $\Delta F = 14.57 - 0.05288T$ kcal. The indicated high entropy of fusion would be reasonable for the conversion of an ammonium salt to a hydrogen-bonded liquid. The $(CH_3)_3N$ adduct was observed to be a white solid up to 75°, but its melting point was not determined.

Table III. Dissociation Pressures of $NH_3 \cdot HN[P(CF_3)_2]_2$

	Solid ($\log P = 13.8450 - 3473/T$) ($\Delta F = 31.80 - 0.09764T$ kcal.)			Liquid ($\log P = 8.0699 - 1882/T$) ($\Delta F = 17.23 - 0.04476T$ kcal.)		
Temp., °C.	−8.4	−5.5	0.1	7.4	32.1	42.9
P_{obsd}, mm.	5.34	7.33	13.81	23.0	79.9	131.0
P_{calcd}, mm.	5.34	7.41	13.65	23.0	80.3	130.4

Table IV. Dissociation Pressures of Solid $(CH_3)_3N \cdot HN[P(CF_3)_2]_2$
($\log P = 11.3481 - 3088/T$; $\Delta F = 28.27_5 - 0.07477T$ kcal.)

Temp., °C.	17.1	29.0	42.5	49.0	59.3	73.8
P_{obsd}, mm.	5.11	13.44	36.8	58.0	114.9	280.0
P_{calcd}, mm.	5.12	13.44	36.8	57.9	114.7	280.4

In accord with thermochemical prediction, HCl attacked the $(CH_3)_3N$ adduct, quantitatively restoring $HN[P(CF_3)_2]_2$. No cleavage occurred when 0.5 mmole of $NH_3 \cdot HN[P(CF_3)_2]_2$ was heated for 3 days in a 30-ml sealed tube at 200°.

The cleavage of $CH_3N[P(CF_3)_2]_2$ by methylamine was fairly simple, quantitatively forming $2CH_3NHP(CF_3)_2$. In the initial attempt, the 0.194-mmole sample was exposed to 0.225 mmole of CH_3NH_2 in a 4-ml. sealed tube for 60 hr. at 24°, but the infrared spectrum showed that the cleavage was incomplete. Hence a further 0.126 mmole of CH_3NH_2 was added and the whole mixture stood for 12 hr. at 0°. Then the excess CH_3NH_2 was removed by high-vacuum distillation through a U-trap at −78° and measured as a gas. The condensate at −78° then showed a 0° volatility of 26.4 mm., corresponding to pure $CH_3NHP(CF_3)_2$ (calcd. from literature equation, 26.1 mm.).[2] The infrared spectrum also was identical with our own records for this pure compound. Thus the following equation, with stoichiometry in millimoles, completes the proof of the formula $CH_3N[P(CF_3)_2]_2$.

$$\begin{array}{ccccc} CH_3N[P(CF_3)_2]_2 & + & CH_3NH_2 & \longrightarrow & 2CH_3NHP(CF_3)_2 \\ 0.194 & & 0.351 & & 0.385 \\ & & -0.155 & & (\text{calcd., } 0.388) \\ \cline{3-3} & & 0.196 & & \end{array}$$

The cleavage of $CH_3N[P(CF_3)_2]_2$ by ammonia was more complex, so that only a qualitative account of the products could be obtained. The 24° reaction of an equimolar mixture was only half complete (presumably because much was in the vapor phase), and the products were not readily separable by distillation methods. However, the infrared spectrum of the more volatile portion showed bands characteristic of NH_3, $HN[P(CF_3)_2]_2$, $H_2NP(CF_3)_2$, and $CH_3NHP(CF_3)_2$. A similar mixture resulted when the cleavage was brought to completion by a threefold excess of ammonia.

Mixing either ammonia or methylamine with $CH_3N[P(CF_3)_2]_2$ in the vapor phase, without permitting any condensation, led to infrared spectra showing only the bands of the components at their known intensities. The ammonia mixture was heated in a sealed tube for 3 days at 210°, again with no effect upon the spectrum. Since the cleavage reactions thus are shown to occur only in the liquid phase, it may be suggested that the process begins with either a P–H–N bond or a weak N→P dative bond, neither of which would be effectively possible in the vapor phase.

A conjectured cleavage of $CH_3N[P(CF_3)_2]_2$ by $H_2NP(CF_3)_2$ did not occur: after 40 hr. in the vapor phase and 24 hr. in the liquid phase, at 24°, the equimolar mixture had undergone no change of infrared spectrum.

The Tris(phosphino)amine

Synthesis through the Sodium Salt. The salt $NaN[P(CF_3)_2]_2$ was sought first by the action of $HN[P(CF_3)_2]_2$ on molten sodium at 100°. The reaction was quite limited, but the resulting white crystals reacted with HCl to produce some $HN[P(CF_3)_2]_2$, proving the survival of some $N[P(CF_3)_2]_2$ groups. An attempt to increase the salt formation by heating to 120° led to dark brown, tarry material. A better result came from the reaction of sodium with $HN[P(CF_3)_2]_2$ in liquid ammonia, but even though vacuum-sublimed sodium was employed, some HCF_3 appeared. Cleavage to $H_2NP(CF_3)_2$ also occurred, and the complete removal of excess ammonia required evacuation at 100°. However, the dry nonvolatile residue evidently included a useful yield of the salt, for its reaction with $(CF_3)_2PCl$ (fivefold excess) gave a 50% yield of the desired $N[P(CF_3)_2]_3$. A moderate parallel yield of $(CF_3)_2PF$ indicated that some of the original CF_3 groups had been destroyed during the sodium reaction, accounting for a very low yield of H_2 from that initial stage of the process. An attempt to make the sodium salt more cleanly by using diglyme as the solvent failed because the diglyme was too easily cleaved; however, tetrahydrofuran proved more suitable.

Accordingly, an unmeasured amount of vacuum-sublimed sodium was dissolved by a solution of 3.975 mmoles of $HN[P(CF_3)_2]_2$ in 5 ml. of tetrahydrofuran during 3 days in a sealed tube at 24°, producing slightly yellow crystals and solution. Hydrogen was measured as 0.807 mmole, indicating the formation of 1.614 mmoles of $NaN[P(CF_3)_2]_2$; and 0.078 mmole of HCF_3 also appeared. The THF and excess $HN[P(CF_3)_2]_2$ were removed as thoroughly as possible during 10 hr. *in vacuo* at 100°, but the recovery of the latter was only 1.65 mmoles. Hence, if the HCF_3 indicated the destruction of roughly 0.08 mmole of $HN[P(CF_3)_2]_2$, the nonvolatile residue would contain 2.245 mmoles of $N[P(CF_3)_2]_2$ groups instead of the expected 1.614 mmoles. Thus it could be suggested that 0.63 mmole of $HN[P(CF_3)_2]_2$ remained in hydrogen-bonded combination with $N[P(CF_3)_2]_2^-$ anions; and, in fact, 0.578 mmole of $HN[P(CF_3)_2]_2$ could be recovered after being released during the action of $(CF_3)_2PCl$ upon the solid (3 days at 0°) to form the desired $N[P(CF_3)_2]_3$. Taking all data into account, we can summarize the whole process by means of the following stoichiometric equations, with quantities in millimoles.

$$\begin{array}{llll}
2HN[P(CF_3)_2]_2 + Na \longrightarrow & H_2 & + & NaN[P(CF_3)_2]_2 + \\
\quad 3.97 \qquad \ldots & 0.807 \times 2 & = & 1.614 \\
\underline{-1.73} & & & 0.58HN[P(CF_3)_2]_2 \\
 & & & \text{occluded} \\
\quad 2.24 - 0.58 = 1.66 & & &
\end{array}$$

$$\begin{array}{lll}
NaN[P(CF_3)_2]_2 + & (CF_3)_2PCl \longrightarrow & N[P(CF_3)_2]_3 + NaCl \\
\quad 1.61 & \quad 4.73 & \quad 1.6 \\
 & \quad \underline{-3.0} & \\
 & \quad 1.7 &
\end{array}$$

The final yield of $N[P(CF_3)_2]_3$ could be estimated only roughly because it was difficult to remove from it the last trace of $HN[P(CF_3)_2]_2$; and for the same reason the 0.58 mmole of $HN[P(CF_3)_2]_2$, recovered from the second reaction, is a low estimate of what was occluded in the sodium salt. The $N[P(CF_3)_2]_3$ finally was purified by crystallization from a clean mixture of isohexanes, using the stopcocked filtering Λ-tube at temperatures as low as −78°. The disappearance of the strong infrared band at 925 cm.$^{-1}$ (P–N–P stretching) demonstrated the effectiveness of this method. Finally, the basic hydrolysis of a 195.4-mg. sample (0.375 mmole) yielded 2.225 mmoles of HCF_3, indicating 5.93 CF_3 groups per molecule. The vapor-phase molecular weight approached the calculated value, as described below. The final confirmation of the formula is based upon the quantitative cleavage reactions, also described below.

Physical Properties. The tris(phosphino)amine $N[P(CF_3)_2]_3$ forms colorless plates or prisms having a possibly distorted hexagonal appearance. The melting range was observed as 36.5–36.8°. The equations accompanying the volatility data of Tables V and VI would imply a melting point near 35°, and for the fusion process $\Delta F = 5433 - 17.64T$ cal.

Table V. Volatility of Solid $N[P(CF_3)_2]_3$
($\log P = 12.466 - 3570/T$)

Temp., °C.	0.00	10.5	23.6	29.2	36.3
P_{obsd}, mm.	0.24	0.76	2.71	4.58	8.51
P_{calcd}, mm.	0.25	0.76	2.73	4.56	8.51

Table VI. Volatility of Liquid $N[P(CF_3)_2]_3$
($\log P = 6.4393 + 1.75 \log T - 0.004681T - 2611/T$)
($t_{760} = 149.7°$; Trouton constant = 22.6 e.u.)

Temp., °C.	38.0	48.1	55.5	65.2	79.9	94.2
P_{obsd}, mm.	8.98	15.72	23.0	36.7	70.8	126.2
P_{calcd}, mm.	9.00	15.67	22.95	36.75	70.8	126.2

The somewhat higher than normal Trouton constant suggests a slight tendency toward association, and this was confirmed by the initial determination of the molecular weight in the vapor phase: 544 at 85° and

81 mm. At 94° and 72 mm. the result was 530, and at 97° and 73 mm. it was 525, obviously approaching the calculated value, 521.

Cleavage Reactions. A mixture of 72.5 mg. (0.139 mmole) of $N[P(CF_3)_2]_3$ and 0.227 mmole of HCl failed to react in a sealed tube during 12 hr. at 24°, but cleavage was complete after 65 hr. at 100°. The mixture was separated by high-vacuum fractional condensation, using U-traps at −78, −100, and −196°. The products were identified by their known volatilities and infrared spectra identical with our own recorded scans for the same compounds. The results are summarized by the following equation with quantities in millimoles.

$$\begin{array}{cccc} N[P(CF_3)_2]_3 + & HCl \longrightarrow & HN[P(CF_3)_2]_2 + & (CF_3)_2PCl \\ 0.139 & 0.227 & 0.139 & 0.139 \\ & \underline{-0.089} & & \\ & 0.138 \text{ used} & & \end{array}$$

This quantitative cleavage represents our most accurate confirmation of the molecular formula $N[P(CF_3)_2]_3$; the other cleavage reactions offer further confirmation with less precision.

An equimolar mixture of $N[P(CF_3)_2]_3$ and NH_3 reacted at 24° according to the following equation (quantities in millimoles).

$$\begin{array}{cccc} N[P(CF_3)_2]_3 + & NH_3 \longrightarrow & HN[P(CF_3)_2]_2 + & H_2NP(CF_3)_2 \\ 0.231 & 0.231 & 0.234 & 0.228 \end{array}$$

The two products were clearly recognized by their characteristic infrared bands, and foreign bands were not detected; however, complete separation by vacuum distillation methods was not feasible. Hence the quantity of $HN[P(CF_3)_2]_2$ was determined by the intensity of its P–N–P asymmetric stretching band at 925 cm.$^{-1}$, and the $H_2NP(CF_3)_2$ was estimated by difference. The indicated 1.3% error would be normal for such a method.

The analogous cleavage by just the calculated proportion of water seemed to be complete after 12 hr. at 24° and the products $HN[P(CF_3)_2]_2$ and $(CF_3)_2POH$ were recognizable, but the quantitative isolation of the latter would have been too difficult; hence the observations here remained qualitative. The absence of HCF_3 suggested a clean process.

The cleavage of $N[P(CF_3)_2]_3$ (0.189 mmole by weight) by $H_2NP(CF_3)_2$ (0.193 mmole by vapor–volume measurement) occurred in a U-trap between two mercury float valves. During 3 days at 23° the mixture evaporated completely, exerting 22 mm. pressure at 25°, as would not have been possible except for cleavage of the $N[P(CF_3)_2]_3$ (volatility, 3.06 mm. at 25°). The standard gas volume now was equivalent to 0.383 mmole; expected, 0.382. The complete infrared spectrum of the vapor proved to be identical with that of $HN[P(CF_3)_2]_2$. The extremely strong band for $N[P(CF_3)_2]_3$ at 858 cm.$^{-1}$ was undetectable and the strongest isolated band for $H_2NP(CF_3)_2$, at 1569 cm.$^{-1}$, was no more than slightly recognizable. Hence the $N[P(CF_3)_2]_3$ had reacted completely with an equimolar proportion of $H_2NP(CF_3)_2$ to form $2HN[P(CF_3)_2]_2$.

Infrared Spectra

The observed infrared fundamental modes of the three new poly(phosphino)amines are listed as frequencies of band maxima in Table VII. They were recorded for the vaporized samples by the Beckman IR7 instrument, using NaCl or CsI optics and windows of NaCl, KBr, or high-density annealed polyethylene, as appropriate, and path lengths ranging from 1.15 to 11.5 cm. Calibrations based upon known fine structures ensured accuracy within 1 cm.$^{-1}$ for frequencies below 2000 cm.$^{-1}$. The relative intensities, computed by the arbitrary definition $k = (100/PL) \log I_0/I$ for pressure P at 25° and path L, both in cm., were virtually independent of slit width; hence they are recorded (number in parentheses after each frequency) as roughly reproducible data. For this purpose the transmittance values I_0 and I were taken literally, leading to overestimated intensities for partially superposed bands.

Table VII. Main Infrared Peaks (cm.$^{-1}$) of Three Poly(phosphino)amines[a]

Suggested assignment	$HN[P(CF_3)_2]_2$	$CH_3N[P(CF_3)_2]_2$	$N[P(CF_3)_2]_3$
N–H or C–H stretching	3351(8.3)	2987(0.45)	. . .
		2927(0.23)	
		2862(0.23)	
CH_3, δ–a	. . .	1474(0.55)	. . .
CH_3, δ–e	. . .	1373(0.07)?	. . .
C–F stretching	1208sh(47)		
	1200(60)	1205(29)	1202(95)
	1180(116)	1187(78)	1169(330)
	1161(125)	1159(182)	1158(149)
	1132(55)	1131(53)	1140(54)
			1132(91)
C–N stretching, or CH_3 rocking, or CF_3, δ–a Fermi overtone	972(0.7)	1047(0.7)	939(0.4)
		923(0.34)	900(0.4)
P–N–P, a-stretching	925(25)	869(33)	859(103)
P–N–P, e-stretching	808(5.3)	647(0.7)?	. . .
CH_3 wagging?	. . .	822(0.19)	. . .
CF_3, δ–e, in and out of phase	$\left.\begin{matrix}750\\745\\743\end{matrix}\right\}(1.1)$	741(2.5).	745(6.7)
	728(0.3)	. . .	731sh(0.7)
CF_3, δ–a, in and out of phase	590(12)	564sh(0.8)	563(2.1)
	. . .	545.5(1.9)	550.5(3.8)
P–N–P out-of-plane bending?	525(0.8)	. . .	. . .
P–CF_3, a-stretching	473.5(3.7)	471.5(12)	486.5(8.3)
			468.5(2.0)
P–N–P scissors?	447(0.45)	. . .	. . .
P–CF_3, e-stretching	373(9.1)	398.5(12)	361.5(5.6)
CF_3 rocking and wagging	298(0.24)		
	280(0.11)	277(0.16)	. . .
	242.5(0.54)	239(0.24)	. . .

[a] Abbreviations: sh, shoulder; δ, deformation; a, asymmetric; e, symmetric.

Table VII omits many peaks regarded as overtones or combinations, or otherwise uncertain of assignment. Their frequencies and intensities are listed (sometimes with discussion) in the following paragraphs.

For $HN[P(CF_3)_2]_2$ a peak at 3379(0.31) probably represents the first overtone of the N–H bending mode, intensified by Fermi resonance with N–H stretching at 3351 cm.$^{-1}$. The observed frequencies 1699(0.13) and 1730(0.43) seem too high for the N–H bending fundamental, which may not have been seen at all. The C–F stretching overtones and combinations were obvious, at 2272(0.56), 2294(0.9), 2386(0.18), and 2554(0.11). A band consisting of a sharp spike at 1294(22) and a shoulder at 1290(16) might represent the combination 473.5 + 808, intensified by coupling with a C–F stretching mode; however, a fundamental in this region may be required to explain the combination or overtone at 2554 cm.$^{-1}$. Minor peaks appeared at 392(0.24), 771(0.09), 848(0.8), 882(0.7), 1010(0.09), 1052(0.08), 1250sh(1.5), 1329(0.34), 1367 (0.12), 1899(0.3), and 2094(0.17).

For $CH_3N[P(CF_3)_2]_2$ the C–F stretching overtones and combinations were 2267(1.1), 2290(0.32), 2306 (0.34), 2325(0.10), and 2397(0.26). A strong peak at 1079(9.7) may well represent an overtone of the CF_3 deformation at 545.5, intensified by Fermi resonance with C–F stretching; and similar origins might be ascribed to weaker absorptions at 1235sh(2.0), 1270 (1.1), and 1291(0.9). Other minor peaks were 950 (0.05), 985(0.05), 1400(0.2), 1514(0.3), 1680(0.07), 1791(0.07), 1857(0.07), 1879(0.2), 1901(0.2), and 1948 (0.2). The assignment of the relatively weak 647-cm.$^{-1}$ band to P–N–P symmetric stretching seems reasonable in relation to the strong 808-cm.$^{-1}$ band for the HNP_2 case, because the CH_3N unit contributes far more to the reduced mass than the HN unit could; also, the methyl group would partially balance the phosphorus units and hinder the motion of N, thus limiting the variation of polarity and so leading to relatively low intensity. For the NP_3 planar form, of course, the threefold symmetric N–P stretching mode would be infrared forbidden.

For $N[P(CF_3)_2]_3$ there was less observation of very weak bands because the pressure was limited to 10 mm. at the cell chamber temperature of 40°. The C–F stretching overtones and combinations appeared at 2256(1.0), 2275(0.8), 2298(0.6), 2321(0.46), 2358(0.23), and 2404(0.23). The peaks at 1095(2.3) and 1108(6.2) probably represent overtones of the in-phase and out-of-phase asymmetric CF_3 deformation (at 550.5 and 563), intensified by Fermi resonance with C–F stretching. Other satellites of the C–F stretching bands appeared at 1232sh(4.6) and 1276sh(1.4). The peaks at 900(0.4) and 939(0.4) probably belong to overtones of the P–CF_3 stretching modes at 468.5 and 486.5 cm.$^{-1}$, enhanced somewhat by the very intense asymmetric P–N–P stretching at 859 cm.$^{-1}$. Weaker and less assignable peaks were observed at 980(0.28), 1026(0.42), 1366(0.6), 1487(0.09), 1714(0.6), 1877(0.23), 1907(0.23), and 1947(0.06).

Most of the assignments in Table VII are securely based upon analogies to other compounds, but in some cases it is appropriate to indicate uncertainties by question marks or to consider alternatives.

The Nuclear Magnetic Resonance of Some Paramagnetic Transition Metal Acetylacetonates

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The n.m.r. spectra of the paramagnetic acetylacetonates of Ti(III), V(III), Cr(III), Mn(III), Fe(III), Mo(III), Ru(III), Tb(III), Eu(III), Mn(II), Fe(II), and Co(II) have been measured. Spectra were not observed for the Cu(II) and VO(II) compounds. Data on a number of diamagnetic acetylacetonates which were measured for comparison are also reported. The widths of the lines in the different compounds are discussed in relation to the relative rates of electron spin relaxation inferred from e.s.r. data. It is concluded that the isotropic shifts in line frequency in the first transition row compounds arise predominantly from contact interactions. In this series, spin can be delocalized to the ligand both by metal-to-ligand and ligand-to-metal charge-transfer processes with the latter becoming progressively more important in complexes of the later group metals. In the second transition series pseudo-contact effects become important, and in the rare earth compounds they are probably dominant. The interpretation of the contact shifts is discussed in terms of the electronic structures of the complexes and in relation to the chemistry of the metal ions.

Introduction

The interactions between unpaired electrons on transition metal ions and nuclei with magnetic moments on ligands coordinated to these ions have been the subject of a number of recent n.m.r. studies.[1–5] These studies have yielded a considerable amount of useful information on the electronic structures and magnetic properties of transition metal complexes. However, a number of questions regarding the extent of the applicability of this n.m.r. technique and the interpretation of the results still remain. Thus, the condition for observing nuclear resonances in paramagnetic compounds of this type is usually stated[6] as $1/T_1 \gg a_N$,

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