to a 150-ml titration flask which was to serve as the cathode compartment of the electrolysis cell. Mercury was added to a depth of *ca.* 0.5 in. (surface area, 17 cm^2), a magnetic stirrer bar was added, and a Teflon cap was placed on the cell. The cap was fitted with a nitrogen inlet and outlet, a saturated calomel reference electrode, a cathode connection, and a 30-ml alundum cup which was positioned in the center of the cell, its bottom ~1 in. from the mercury. The alundum cup served as the anode compartment. The cell was made airtight. A few milliliters of electrolyte solution were added to the anode compartment and a platinum gauze anode inserted. The appropriate electrical connections were made to the Anatrol potential controller.

The current-voltage relationship of the system was determined by increasing the electrode potential in steps and recording the current. The cathode solution was magnetically stirred during these measurements. The cell was immersed in an ice bath, the magnetic stirrer was started, nitrogen was passed over the cathode solution, and the controlled potential electrolysis was carried out at an appropriate voltage.

During the electrolysis, the cathode compartment was continuously swept with N_2, and the sweepings were passed into a conventional glass, high-vacuum system and condensed in liquid nitrogen. These sweepings were then fractionated by low-temperature distillation *via* −78, −126, and −196° baths. The various fractions and the cathode solution were analyzed for NH_3, HNF_2, and F^- as required.

Formation and Decomposition of Complexes. All work was carried out in a conventional glass, high-vacuum system. Equimolar quantities (~3 mmoles) of HNF_2 and the solvent to be studied were measured separately and condensed together in a cold finger at −126°. The reagents were further mixed by allowing them to warm to room temperature and recooling to −126°. The dissociation pressures of the complexes were measured as they were allowed to warm slowly from −96 to 0°. Three or four points were taken on cooling the mixtures back to −96° at the end of each experiment to determine if the dissociation was completely reversible. Temperatures were measured to ±0.1° with an iron–constantan thermocouple, and pressures were read to ±0.2 mm. Equations were obtained through simple regression analysis of the data on a Bendix G-15 computer.

$HNF_2 + H_2O$. Some association of HNF_2 with H_2O was observed below −23°, but a true equilibrium expression was not obtainable.

$HNF_2 \cdot CH_3OH$. This complex exerts little or no measurable vapor pressure up to −55°. The reversible dissociation over the range −47.7 to 0.0° is described by the equation $\ln Kp = (-4143.2/T) + 23.22$, where $Kp = P^2/4$; $\Delta H = 8.24$ kcal $mole^{-1}$.

$HNF_2 \cdot CH_3CN$. This complex exerts little or no measurable vapor pressure up to −62°. The reversible dissociation over the range −56.6 to −1.2° is described by the equation $\ln Kp = (-6538.2/T) + 31.461$; $\Delta H = 13.01$ kcal $mole^{-1}$.

$HNF_2 + (CH_3)_2SO$ and $HNF_2 + (CH_3)_2NC(H)O$. These mixtures exerted little vapor pressure up to 0°. No equilibrium expressions were obtained: vapor pressure of $HNF_2 \cdot DMF$ at 0°, 5.0 mm; of $HNF_2 . DMSO$ at 0°, 5 mm.

Infrared Spectra. Spectra of the solvation complexes in the solid state at −196° were obtained by techniques similar to those described earlier.[13] The 1 *M* HNF_2 solutions were examined in conventional liquid cells. The spectra were obtained with a Perkin-Elmer Model 137 spectrometer.

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Trifluoromethylarsinophosphinoamines[1]

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Abstract: The new-type compounds $(CF_3)_2As(NH)P(CF_3)_2$ (mp −44°, bp estd 110°) and $(CF_3)_2As(NCH_3)P(CF_3)_2$ (mp −30°, bp estd 127°) are easily cleaved by HCl or NH_3, in contrast to the analogous P–N–P compounds. The point of cleavage is the As–N bond, which lacks π stabilization. BCl_3 is less effective than HCl for As–N–P cleavage and BF_3 still less; however, $[(CF_3)_2As]_2NH$ is more easily attacked than the As–N–P compounds. The novel compound $(CF_3)_2AsN[P(CF_3)_2]_2$ (mp 26°, bp estd 161°) also is cleaved at the As–N bond by HCl or NH_3, to form the well-stabilized $HN[P(CF_3)_2]_2$. The iminobisarsine $[(CF_3)_2As]_2NH$ with $(CF_3)_2PCl$ and $(CH_3)_3N$ catalyst exchanges groups to make $(CF_3)_2As(NH)P(CF_3)_2$ and finally $HN[P(CF_3)_2]_2$. The cacodyl oxide $[(CF_3)_2As]_2O$ with excess $(CF_3)_2PCl$ goes to $(CF_3)_2AsCl$ and $[(CF_3)_2P]_2O$ or with less $(CF_3)_2PCl$, to $[(CF_3)_2As]_2$ and oxidized phosphorus compounds; the unstable $(CF_3)_2AsOP(CF_3)_2$ probably is an intermediate in both cases. Accurate infrared spectra are reported for the three new arsinophosphinoamines.

Compounds containing the As–N–P chain should offer good opportunities for direct comparison of the π-acceptor strength of As_{4d} *vs.* P_{3d} orbitals, especially if fluorocarbon groups are placed on As and P to enhance their π-acceptor character. Accordingly, we have made the new arsinaminophosphines $(CF_3)_2As(NH)P(CF_3)_2$ and $(CF_3)_2As(NCH_3)P(CF_3)_2$ for a comparison of their chemical behavior with the previously known analogous As–N–As and P–N–P compounds. The syntheses were accomplished in a quantitative manner, by the established method whereby trimethylamine removes HCl from the appropriate mixture of reactants.[2,3] For the tertiary amine $(CF_3)_2AsN[P(CF_3)_2]_2$, however, it was necessary to employ the sodium salt $NaN[P(CF_3)_2]_2$ with $(CF_3)_2AsCl$—a process like that used for $N[P(CF_3)_2]_3$.[3] Attempts to make an As_2NP or As_3N compound did not succeed: like the phosphorus case, the As_2NH compound failed to react with $(CF_3)_2AsCl$ even in the presence of $(CH_3)_3N$; and attempts to make the sodium salt $NaN[As(CF_3)_2]_2$ failed for lack of protic acid character in the As_2N–H

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[1] This work was supported by National Science Foundation Grants GP-199 and GP-3812. Also, Grant G-14665 made available the Beckman IR7 instrument, required for this research.

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bond. Apparently the fairly easy formation of $NaN[P(CF_3)_2]_2$ from $HN[P(CF_3)_2]_2$ had depended upon a withdrawal of electrons into N_{2p}–P_{3d} π-bonds, loosening the proton more effectively than in the As_2N–H case. However, $(CF_3)_2As(NH)P(CF_3)_2$ forms a 1:1 $(CH_3)_3N$ adduct which, like the analogous P–N–P case,[3] could be a $(CH_3)_3NH^+$ salt.

The new As–N–P compounds, and $[(CF_3)_2As]_2NH$[4] as well, were easily cleaved by HCl, in sharp contrast to the extreme resistance of $HN[P(CF_3)_2]_2$ to such reactions.[3] Thus we could argue that the weak π-acceptor character of the As_{4d} orbital would permit the nitrogen to exert enough base action for HCl to attack both the As–N–P and As–N–As compounds. Moreover, the Lewis acid BCl_3, while slow to attack the As–N–P chain, very easily cleaved $[(CF_3)_2As]_2NH$, presumably through a more effective initial attachment to nitrogen. The difference must be electronic rather than steric, especially since BF_3 failed to attack either As–N–P compound but did appreciably cleave $[(CF_3)_2As]_2NH$ during extensive heating at 85°.

The cleavages of $(CF_3)_2AsN[P(CF_3)_2]_2$ by HCl and NH_3, like the analogous reactions of $N[P(CF_3)_2]_3$, gave equimolar yields of $HN[P(CF_3)_2]_2$. Thus the As–N bond here was the exclusive site of cleavage.

The ammonolyses of the As–N–P compounds also provide interesting comparisons. Whereas $HN[P(CF_3)_2]_2$ only formed an unstable NH_3 adduct and $CH_3N[P(CF_3)_2]_2$ ammonolyzed only in the liquid phase,[3] $(CF_3)_2As(NH)P(CF_3)_2$ was inert to ammonia in the vapor phase but cleaved even at −78° in the liquid phase, while $(CF_3)_2As(NCH_3)P(CF_3)_2$ ammonolyzed in either phase. The As(NH)P compound gave $(CF_3)_2PNH_2$ and $(CF_3)_2AsNH_2$ as expected, with the latter condensing to $[(CF_3)_2As]_2NH$ as it usually does.[4] The specific cleavage of $(CF_3)_2As(NCH_3)P(CF_3)_2$ at the As–N bond was demonstrated by the formation of $(CF_3)_2PNHCH_3$ but no $(CF_3)_2PNH_2$, while the arsenic aspect formed $(CF_3)_2AsNH_2$ and its condensation product $[(CF_3)_2As]_2NH$.

The ammonolytic cleavages can be rationalized by assuming that the arsenic 4d orbital, while much weaker than P_{3d} for π-acceptor bonding, is relatively effective as a σ-bond acceptor. Thus ammonia would form a dative σ-bond to arsenic without encountering much competition from π electrons in the original As–N bond, whereas the strong N→P π-dative bond would make phosphorus a poor site for such an SN2 invasion.

The weak π character of As_{4d} would not be fully explained by simple references to orbital diffuseness or electronegativity scales showing little difference between arsenic and phosphorus. Some importance might be attached to the change of sign beyond the node in the ψ_{4d} function, such that σ-bonding would be little affected, but some cancellation would occur in a π overlap with ψ_{2p}. A 4d–5sp hybrid would be little better; cancellation again would be serious. On the other hand, P_{3d} is described by a nodeless ψ function, offering excellent overlap with ψ_{2p} and advantageously combinable with P_{4s} and P_{4p}.

Closely related to the cleavage reactions are the group exchanges involving $(CF_3)_2PCl$. In the relatively simple case of $[(CF_3)_2As]_2NH$, there was first an exchange to form $(CF_3)_2As(NH)P(CF_3)_2$ and $(CF_3)_2AsCl$, and then a second exchange arriving at $HN[P(CF_3)_2]_2$ and a second $(CF_3)_2AsCl$. For both stages the driving force is obvious: a greater bond-energy difference between N–P and P–Cl than between As–N and As–Cl.

In the case of $[(CF_3)_2As]_2O$ with equimolar $(CF_3)_2PCl$, it may be assumed that the first stage was like that for the As_2NH compound, but the instability of the expected product $(CF_3)_2AsOP(CF_3)_2$ led to a prompt and quantitative formation of the cacodyl $(CF_3)_2As$–$As(CF_3)_2$ and nonvolatile material containing oxidized phosphorus. However, with a fair excess of $(CF_3)_2PCl$ it was possible to engage most of the As–O–P intermediate compound in further group exchange before it could disproportionate, so that a high yield of $[(CF_3)_2P]_2O$ was observed.

Experimental Methods

The experimental work described in the following sections was based upon modified Stock high-vacuum methods, whereby our new volatile compounds could be synthesized in a quantitative manner and chemically studied with an accurate account of reactants and products. Closure between U-traps was done by mercury float valves designed to serve also as differential (or low-range absolute) manometers. Numerous special devices such as stopcocked or sealable reaction tubes, steel cylinders, tube openers, weighing tubes, small fractionating columns, or vapor-phase infrared cells, could be attached to the main vacuum manifold through interchangeable ground-glass joints. Wherever a stopcock was necessary, its interior contact region was lubricated with a chlorofluorocarbon grease, and Apiezon grease T on the outside parts protected against leakage.

Literature methods were repeated for the synthesis of known starting materials not otherwise available—especially $(CF_3)_2AsCl$,[5] $[(CF_3)_2As]_2NH$,[4] $(CF_3)_2PNH_2$,[6] and $(CF_3)_2PNHCH_3$.[6]

The As–N–P Compounds

Syntheses. Either $(CF_3)_2PNH_2$ or $(CF_3)_2PNHCH_3$ was allowed to react with $(CF_3)_2AsCl$ and $(CH_3)_3N$ in appropriate proportions at 25°. The compound $(CF_3)_2As(NH)P(CF_3)_2$ formed easily enough in a stopcocked bulb, but the reaction was not quite complete after 12 hr. At 80° the mixture formed a trace of $HN[P(CF_3)_2]_2$, detectable by its very strong infrared band at 925 cm^{-1}. The formation of $(CF_3)_2As(NCH_3)P(CF_3)_2$ was slower, but could be brought to completion at 80°. Three experiments on these syntheses are described by the following equations with millimole stoichiometry.

$$\begin{array}{ccccccc}
(CF_3)_2PNH_2 & + & (CF_3)_2AsCl & + & (CH_3)_3N & \xrightarrow{12\text{ hr, }25°} & (CH_3)_3NHCl\ + \\
0.477 & & 0.804 & & 0.471 & & 0.414\text{ (wt)} \\
\underline{-0.055} & & \underline{-0.392} & & \text{(excess} & & 0.402\text{ (Cl detn)} \\
0.422 & & 0.412 & & \text{lost)} & & (CF_3)_2As(NH)P(CF_3)_2 \\
 & & & & & & 0.408
\end{array}$$

$$\begin{array}{cccccc}
(CF_3)_2PNHCH_3 & + & (CF_3)_2AsCl & + & (CH_3)_3N & \xrightarrow{48\text{ hr, }25°} \\
1.491 & & 1.284 & & 1.280 & \\
\underline{-0.366} & & \underline{-0.180} & & & \\
1.125 & & 1.104 & & &
\end{array}$$

$$\begin{array}{ccc}
(CH_3)_3NHCl & + & (CF_3)_2As(NCH_3)P(CF_3)_2 \\
1.131\text{ (wt)} & & 1.079 \\
1.123\text{ (Cl detn)} & &
\end{array}$$

$$\begin{array}{cccccc}
(CF_3)_2PNHCH_3 & + & (CF_3)_2AsCl & + & (CH_3)_3N & \xrightarrow{72\text{ hr, }80°} \\
0.649 & & 1.066 & & 0.644 & \\
 & & \underline{-0.427} & & & \\
 & & 0.639 & & &
\end{array}$$

$$\begin{array}{ccc}
(CH_3)_3NHCl & + & (CF_3)_2As(NCH_3)P(CF_3)_2 \\
0.638\text{ (wt)} & & 0.620 \\
0.628\text{ (Cl detn)} & &
\end{array}$$

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(5) G. R. A. Brandt, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 2552 (1952); E. G. Walaschewski, *Chem. Ber.*, **86**, 273 (1953).

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Where recovery of a reactant is indicated by a minus sign, it was isolated by high-vacuum fractional condensation and identified as pure by its infrared spectrum. Unused $(CF_3)_2AsCl$ passed through a trap at $-78°$ and either $(CF_3)_2PNH_2$ or $(CF_3)_2PNHCH_3$ passed at $-60°$; then the $-60°$ condensates were the pure As-N-P compounds.

Formulas. The molecular formulas of these compounds were confirmed by vapor-phase molecular weight determinations: for $(CF_3)_2As(NH)P(CF_3)_2$, 395 or 397 (calcd, 397); for $(CF_3)_2As(NCH_3)P(CF_3)_2$, 409 or 412 (calcd, 411). Basic hydrolysis of weighed samples at 25° gave $4.03HCF_3$ per molecule of the NH compound and $3.98HCF_3$ per molecule of the NCH_3 compound. Still further confirmation of the formulas is found in the stoichiometry of the HCl cleavage reactions, yet to be detailed.

Physical Properties. The As(NH)P compound melted in the range -44.8 to $-44.4°$ and the As-(NCH_3)P compound, -30.7 to $-30.0°$. Further evidence of their purity was found in the good conformity of their vapor tensions to reasonable equations, as shown in Tables I and II.

Table I. Volatility of $(CF_3)_2As(NH)P(CF_3)_2$
($\log P = 7.6860 + 1.75 \log T - 0.007T - 2548/T$)
($t_{760} = 110.5°$; Trouton constant = 21.5 eu)

Temp, °C	26.00	34.00	41.40	47.9	57.8	69.3
P_{obsd}, mm	25.73	39.46	56.86	77.8	121.0	193.1
P_{calcd}, mm	25.73	39.46	56.92	77.8	120.9	193.3

Table II. Volatility of $(CF_3)_2As(NCH_3)P(CF_3)_2$
($\log P = 6.2510 + 1.75 \log T - 0.005T - 2371/T$)
($t_{760} = 127.2°$; Trouton constant = 21.4 eu)

Temp, °C	24.10	36.70	48.0	55.5	64.2	73.3
P_{obsd}, mm	13.21	26.06	44.8	63.0	91.7	132.1
P_{calcd}, mm	13.35	26.02	44.7	63.1	91.5	132.3

Cleavage Reactions. Room-temperature reactions with dry HCl were performed in 150-ml weighed bulbs closed by stopcocks. The resulting volatile products, $(CF_3)_2PCl$ and $(CF_3)_2AsCl$, were separated by repeated high-vacuum fractional condensations involving traps at -95 and $-100°$. Their final purity and identity were proved by volatility measurements and infrared spectra. The results are summarized by the following equations with millimole stoichiometry.

$$\begin{array}{ccccccccc}
(CF_3)_2As(NH)P(CF_3)_2 & + & 3HCl & \longrightarrow & (CF_3)_2AsCl & + & (CF_3)_2PCl & + & NH_4Cl \\
0.739 & & 3.131 & & 0.750 & & 0.732 & & 0.721\ (wt) \\
 & & -0.896 & & & & & & \\
 & & \overline{2.235} & & & & & &
\end{array}$$

$$\begin{array}{ccccccccc}
(CF_3)_2As(NCH_3)P(CF_3)_2 & + & 3HCl & \longrightarrow & (CF_3)_2AsCl & + & (CF_3)_2PCl & + & CH_3NH_3Cl \\
0.838 & & 3.491 & & 0.834 & & 0.826 & & 0.839\ (wt) \\
 & & -1.014 & & & & & & 0.828\ (Cl\ detn) \\
 & & \overline{2.477} & & & & & &
\end{array}$$

$$\begin{array}{ccccccc}
[(CF_3)_2As]_2NH & + & 3HCl & \longrightarrow & 2(CF_3)_2AsCl & + & NH_4Cl \\
1.186 & & 4.046 & & 2.33 & & \\
 & & -0.468 & & & & \\
 & & \overline{3.578} & & & &
\end{array}$$

The compound $(CF_3)_2As(NCH_3)P(CF_3)_2$ with a 4 mole-ratio of BCl_3 reacted only slightly during 7 days at 25°, producing traces of BF_3 and $(CF_3)_2AsCl$. The recovery of BCl_3 was 98.1%. Only $[(CF_3)_2As]_2NH$ was attacked by BF_3, and then only at 85°, giving a 5.4% yield of $(CF_3)_2AsF$. The analogous BCl_3 reaction was almost complete after 12 hr at 25°, as shown by the following equation with millimole stoichiometry.

$$\begin{array}{ccccccc}
[(CF_3)_2As]_2NH & + & BCl_3 & \longrightarrow & 2(CF_3)_2AsCl & + & \text{“}(HNBCl)_n\text{”} \\
1.095 & & 4.142 & & 1.986 & & \text{nonvolatile} \\
-0.090 & & -3.388 & & & & \\
\overline{1.005} & & \overline{0.754} & & & &
\end{array}$$

Here the nonvolatile product could have been trichloroborazine or a higher polymer, but was not further investigated. However, at an early stage of the process it was possible to observe a component passing a trap at $-35°$ and condensing out at $-78°$—volatility behavior between $(CF_3)_2AsCl$ and the original As_2N compound. An Infracord scan of this transitory substance showed absorption peaks at frequencies (cm^{-1}) consistent with the formula $(CF_3)_2AsNHBCl_2$: N-H stretching near 3400 (w), a possible N-H bending mode near 1455 (w), the usual extremely intense C-F absorption in the 1100–1200 range, a possible B-N stretching near 1055 (w), B-Cl asymmetric stretching near 938 and 973, with the isotopic ratio of intensities, a probable As-N stretching near 810 (m), and CF_3 deformation near 733 (m). A pair of peaks near 1360 and weaker at 1385 would be interpretable as an $R-BF_2$ compound, arising from destruction of the CF_3 group. The further study of the probable $As-N-BCl_2$ compound, and others in the same class, would be of interest.

The absence of vapor-phase cleavage of the compound $(CF_3)_2As(NH)P(CF_3)_2$ by NH_3 was demonstrated by forming the mixture directly in an infrared cell without permitting any condensation to liquid. The spectrum of the mixture remained constant for at least 12 hr at 25°, showing only the original components. However, when the reaction was tried with a liquid phase present, a trace of white solid formed very rapidly and the volatiles were infrared-identified as $(CF_3)_2PNH_2$, $(CF_3)_2AsNH_2$, and $[(CF_3)_2As]_2NH$.

The vapor-phase ammonolysis of $(CF_3)_2As(NCH_3)P(CF_3)_2$ was observed by permitting gaseous ammonia to enter a relatively large bulb containing this As-N-P compound. A trace of white solid precipitated from the gas phase; then some of the gas was led into an infrared cell, for identification of the components as $(CF_3)_2PNHCH_3$, $(CF_3)_2AsNH_2$, and $[(CF_3)_2As]_2NH$. The last of these was isolated and found to represent 50% of the original arsenic. In a liquid-phase experiment, the results were quite similar except that the yield of the As_2N compound represented 70% of the arsenic. Separation difficulties prevented an accurate accounting of the yields of $(CF_3)_2PNHCH_3$ and $(CF_3)_2AsNH_2$; however, the infrared spectrum demonstrated their presence, and the absence of $(CF_3)_2PNH_2$ and $(CF_3)_2AsNHCH_3$.

The Trimethylamine Adduct. The absorption of $(CH_3)_3N$ by $(CF_3)_2As(NH)P(CF_3)_2$ was slow at $-78°$ but much faster in the range -40 to $-30°$; finally 0.546 mmole of $(CH_3)_3N$ (from a 1.209-mmole sample) was captured by 0.550 mmole of the As-N-P compound. The adduct seemed to be almost wholly dissociated in the vapor phase, showing an average molecular weight value 241; calculated for 100% dissociation, 228. Table III shows a range of dissociation pressures for the liquid.

Table III. Equilibrium Pressures:
$(CF_3)_2As(NH)P(CF_3)_2 \cdot (CH_3)_3N$ (Log P = 8.674 − 2102/T)

Temp, °C	−19.0	−14.2	4.4	0.0	8.3	11.8	16.4
P_{obsd}, mm	2.4	3.66	7.16	9.6	16.1	19.5	25.2
P_{calcd}, mm	2.5	3.62	7.11	9.4	16.0	19.7	25.9

The Arsiniminobisphosphine

Synthesis. A 1.467-mmole sample of $HN[P(CF_3)_2]_2$ was allowed to act upon sodium in excess, in 5 ml of tetrahydrofuran during 4 days at 25°, producing 0.548 mmole of H_2. The solvent was removed, finally with pumping at 100°, and the residue was treated during 12 hr at 0°, with 2.321 mmoles of $(CF_3)_2AsCl$, of which 1.157 mmoles was consumed. The yield of the expected $(CF_3)_2AsN[P(CF_3)_2]_2$ was roughly 1.0 mmole. It was purified by recrystallization from hexane, using a filtering Λ-tube attachable to the high-vacuum system.

Physical Properties. The new $AsNP_2$ compound melted in the range 25.2-25.9°. Its volatility behavior also indicated purity, as shown in Table IV.

Table IV. Volatility of $(CF_3)_2AsN[P(CF_3)_2]_2$
(Log P = 8.0350 + 1.75 log T − 0.0068 T − 2961/T)
(t_{760} = 161.2; Trouton constant = 21.2 eu)

Temp, °C	32.3	39.5	4.88	57.5	70.5	80.0	88.2
P_{obsd}, mm	4.15	6.40	10.92	17.6	33.3	51.6	72.6
P_{calcd} mm	4.10	6.40	10.95	17.6	33.4	51.3	72.7

Formula. The vapor-phase molecular weight of the $AsNP_2$ compound was determined as 557 or 564; calcd, 565. Its basic hydrolysis at 25° yielded 5.84 of the expected $6HCF_3$ per mole. Further confirmation of the formula came from the quantitative HCl cleavage, next described.

Cleavage Reactions. The following process (with millimole stoichiometry) occurred rapidly at 25°, but was allowed 12 hr for completion.

$$\begin{array}{ccccccc}
\mathrm{(CF_3)_2AsN[P(CF_3)_2]_2} & + & \mathrm{HCl} & \longrightarrow & \mathrm{(CF_3)_2AsCl} & + & \mathrm{HN[P(CF_3)_2]_2} \\
0.246 & & 1.244 & & 0.251 & & 0.242 \\
 & & -0.988 & & & & \\
\cline{3-3}
 & & 0.256 & & & &
\end{array}$$

The ammonolysis evidently would be described by the following account (in mmoles), although the immediate products were not isolated as such by direct distillation methods.

$$\begin{array}{ccccccc}
\mathrm{(CF_3)_2AsN[P(CF_3)_2]_2} & + & \mathrm{2NH_3} & \longrightarrow & & & \\
0.232 & & 0.746 & & & & \\
 & & -0.264 & & \mathrm{(CF_3)_2AsNH_2} & + & \mathrm{HN[P(CF_3)_2]_2 \cdot NH_3} \\
\cline{3-3}
 & & & & \text{(etc.)} & & 0.220 \\
 & & 0.482 & & & & (95\%)
\end{array}$$

After removal of the excess ammonia, the vapor-phase infrared spectrum of the mixture showed the absence of the $AsNP_2$ compound and the presence of $(CF_3)_2AsNH_2$ and its condensation product $[(CF_3)_2As]_2NH$, along with the adduct-dissociation products NH_3 and $HN[P(CF_3)_2]_2$. The quantity of the latter was determined by treating the mixture with 2.180 mmoles of HCl, of which 0.641 mmole was consumed. Then the arsenic compounds came out as 0.216 mmole of $(CF_3)_2AsCl$; recovery, 93%. The losses are regarded as mechanical.

As–P Group Exchanges

The Iminobisarsine with the Chlorophosphine. The reaction of $(CF_3)_2PCl$ with $[(CF_3)_2As]_2NH$ in the presence of $(CH_3)_3N$ did not produce any $[(CF_3)_2As]_2NP(CF_3)_2$, but the amine did have a catalytic action, causing the displacement of $(CF_3)_2As$ groups by $(CF_3)_2P$ groups. One experiment, running for 3 days at 25°, employed about $3(CF_3)_2PCl$ per $[(CF_3)_2As]_2NH$, forming $(CF_3)_2As(NH)P(CF_3)_2$ along with somewhat more $HN[P(CF_3)_2]_2$. These were not cleanly separable by distillation methods, but both were clearly identified by their infrared spectra. The fraction containing nearly all of the As–N–P compound was attacked by HCl (which would not affect the HNP_2 compound)[3] to form $(CF_3)_2AsCl$ and $(CF_3)_2PCl$ in amounts representing a 40% yield of $(CF_3)_2As(NH)P(CF_3)_2$.

A more nearly complete exchange occurred in an experiment running for 3 days at 80°, again using a trace of $(CH_3)_3N$ as a catalyst which had proved to be necessary. The millimole stoichiometry was as follows.

$$\begin{array}{cccccccc}
\mathrm{[(CF_3)_2As]_2NH} & + & \mathrm{2(CF_3)_2PCl} & \longrightarrow & \mathrm{HN[P(CF_3)_2]_2} & + & \mathrm{2(CF_3)_2AsCl} & + \\
0.670 & & 1.772 & & 0.622 & & 1.253 & \\
 & & 0.454 & & & & & \\
\cline{3-3}
 & & & & & & \mathrm{(CF_3)_2As(NH)P(CF_3)_2} & \\
 & & 1.318 & & & & 0.063 &
\end{array}$$

The Cacodyl Oxide with the Chlorophosphine. With a good excess of $(CF_3)_2PCl$ present, the oxide $[(CF_3)_2As]_2O$ reacted easily without a catalyst, developing the following millimole stoichiometry during 3 days at 25°.

$$\begin{array}{ccccccc}
\mathrm{[(CF_3)_2As]_2O} & + & \mathrm{2(CF_3)_2PCl} & \longrightarrow & \mathrm{2(CF_3)_2AsCl} & + & \mathrm{[(CF_3)_2P]_2O} \\
0.942 & & 2.328 & & 1.643 & & 0.826 \\
 & & -0.652 & & & & \\
\cline{3-3}
 & & 1.676 & & & &
\end{array}$$

However, with no excess of $(CF_3)_2PCl$, the assumed arsinoxyphosphine $(CF_3)_2AsOP(CF_3)_2$, unable to react further to make the diphosphoxane, disproportionated so that all of the oxygen went from weak As–O bonds to strong P–O bonds. Thus after 3 days at 25°

$$\begin{array}{cccccccc}
\mathrm{[(CF_3)_2As]_2O} & + & \mathrm{(CF_3)_2PCl} & \longrightarrow & \mathrm{(CF_3)_2AsCl} & + & \mathrm{[(CF_3)_2As]_2} & + \\
0.379 & & 0.383 & & 0.206 & & 0.208 & \\
 & & -0.186 & & & & & \\
\cline{3-3}
 & & & & & & & \text{nonvolatiles} \\
 & & 0.197 & & & & &
\end{array}$$

Infrared Spectra

The frequencies (cm^{-1}) of the vapor-phase infrared absorption maxima of the three new As–N–P compounds were recorded by the Beckman IR7 instrument, with calibrations assuring accuracy within 1 cm^{-1} for most of the sufficiently sharp peaks. For the lowest frequencies (not sought at the low pressure available to the $AsNP_2$ compound), the cell windows were 0.76-mm

Table V. Infrared Spectra of Three As–N–P Compounds

Suggested assignment	$\left.\begin{matrix}(CF_3)_2As\\(CF_3)_2P\end{matrix}\right>NH$	$\left.\begin{matrix}(CF_3)_2As\\(CF_3)_2P\end{matrix}\right>NCH_3$	$(CF_3)_2P\diagdown$ $(CF_3)_2P—N$ $(CF_3)_2As\diagup$
N–H or C–H stretching	3399 (1.5)	2978 (0.8)	. . .
	3365 (6.4)	2922 (0.35)	
		2853 (0.35)	
C–F overtones and combinations	2390 (0.16)	2267 (0.69)	. . .
	2290 (0.66)	2230 (0.38)	
	2264 (0.76)	1900 (0.14)	
C–H bending	. . .	1475 (0.43)	. . .
		1444 (0.30)	
C–F stretching (and satellites)	1289 (1.3)		
	1265 (1.9)	1264 (1.5)	
	1249 (6.2)		
	1210 (66)	1208 (32)	
	1182 (186)	1183 (97)	1197 (183)
	1172 (189)	1157 (280)	1167 (383)
	1159 (186)	1132 (82)	
	1134 (117)	1118 (47)	1107 (55)
	1059 (0.8)	1079 (9)	1064 (0.5)
P–N stretching (and CH_3 rock ?); satellites	973 (0.1)	984 (0.1)	
	943 (0.5)	921 (0.1)	927 (1.0)
	901 (26)	854 (2.5)	880 (33)
	845 (0.3)	827 (30)	802 (27)
	808 (0.2)		
CF_3, symm deformation	747 (0.4)	770sh (0.15)	
	744sh (—)		744 (5.4)
	734 (3.4)	732 (4.8)	734 (8.9)
As–N stretching	704 (3.7)		
	618 (0.8)	601 (0.7)	592 (3.8)
CF_3, asymm deformation	547 (4.8)	557 (0.4)	566 (2.6)
	532.5 (5.1)	543 (0.6)	547 (3.2)
	512.5 (7.3)	526 (0.4)	
P–CF_3 stretching	456 (4.3)	461 (6.1)	476 (12)
			455 (2.8)
			440.5 (2.8)
Uncertain	395 (0.3)		
	372 (0.3)	371.5 (0.7)	373 (3.2)
	352.5 (0.7)		
As–CF_3 stretching	328 (6.8)	325 (6.2)	331.5 (5)
			312 (3)
CF_3 rocking and wagging	281 (0.55)		
	255 (0.6)	252 (0.5)	. . .
	240 (0.4)		
	224 (0.3)	227 (0.3)	

thick annealed high-density polyethylene. For other ranges, the cell was wedge-shaped (of Pyrex glass) with four KBr windows 2 mm thick—providing a choice of two path lengths in a 10:1 ratio.

The results, given in Table V, include in parentheses the relative intensity at each frequency—calculated from the definition $k = (100/PL) \log I_0/I$ for pressure P (at 25°) and path length L, both in cm.

The assignments for most of the higher frequencies are clear enough, although some of the listed peaks or shoulders probably represent combinations or overtones, with most of the latter appearing as satellites of very intense fundamentals on account of the Fermi resonance principle. The weaker neighbors of the C–F stretching bands are good examples of this effect.

The As–CF_3 deformation modes are distinguishable by frequencies lower than for P–CF_3 deformations, but peaks in between might belong to either. Also uncertain of meaning are weak peaks between the P–CF_3 and As–CF_3 stretching modes; and the latter are distinguished from CF_3 rocking only by high intensities which would be unusual for the latter.