by filtration, under a stream of dry nitrogen, and subsequently washed with three 25-ml portions of dry benzene. The product, which formed in 76% yield, based on the amount of P_2Se_5 used, was dried *in vacuo* over phosphorus pentoxide.

Tetraphosphorus Heptaselenide-Bis(4-methylpyridine). This adduct was prepared in the manner described for tetraphosphorus heptaselenide-bis(pyridine) except that 25 ml of 4-methylpyridine was allowed to react with 1.5 g (3.3×10^{-3} mol) of finely ground P_2Se_5 at 100° for 3.5 hr. The insoluble orange product, which formed in 85% yield, was isolated and dried *in vacuo* over phosphorus pentoxide.

Tetraphosphorus Octaselenide-Hexakis(4-ethylpyridine). By allowing 25 ml of 4-ethylpyridine to react with 1.5 g (3.3×10^{-3} mol) of finely ground P_2Se_5 in the manner described for the preparation of the bis(pyridine) adduct, at 100° for a period not greater than 2 hr, tetraphosphorus octaselenide-hexakis(4-ethylpyridine) was isolated from the reaction mixture as an insoluble orange powder, in 45% yield.

Tetraphosphorus Heptaselenide-Tris(4-ethylpyridine). By allowing the reaction time to be extended to 12 hr and otherwise employing the same set of conditions as described for the preparation of the octaselenide, tetraphosphorus heptaselenide-tris(4-ethylpyridine) was isolated, as an insoluble orange powder, in 81% yield.

Triisoquinolinium Pyroselenophosphate. A reaction flask equipped with a mechanical stirrer, reflux condenser, and a nitrogen inlet was charged with 50 ml of isoquinoline, and stirring was initiated, followed by the addition of 1.5 g (3.3×10^{-3} mol) of finely ground P_2Se_5. The reaction was allowed to continue, at a temperature maintained between 27 and 35° for 12 hr. The insoluble orange powder, triisoquinolinium pyroselenophosphate, was collected by filtration under a stream of dry nitrogen, washed with three 25-ml portions of dry toluene, and dried *in vacuo* over phosphorus pentoxide. The yield, based on the weight of P_2Se_5 used, was 91%.

Registry No. P_2Se_5, 1314-82-5; $P_4Se_7 \cdot 2C_5H_5N$, 40827-84-7; $P_4Se_7 \cdot 2CH_3C_5H_4N$, 40827-85-8; $P_4Se_7 \cdot 3C_2H_5C_5H_4N$, 40900-75-2; $P_4Se_8 \cdot 6C_2H_5C_5H_4N$, 39310-00-4; $[C_9H_7NH^+]_3 \cdot [HP_2Se_7{}^{-3}]$, 39310-03-7.

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Reactions of Dimethylaminodifluoroarsine. Coordination with Boron Acids and Cleavage by Hydrogen Chloride[1]

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Reactions of dimethylaminodifluoroarsine with boron trifluoride, diborane, and borane-carbonyl were studied. Evidence for coordination of boron trifluoride at the nitrogen atom and of borane at the arsenic atom is presented. The reaction of dimethylaminodifluoroarsine with hydrogen chloride resulted in cleavage of the arsenic-nitrogen bond. Evidence for the formation of chlorodifluoroarsine is presented.

The compound dimethylaminodifluorophosphine has proved to be a most interesting compound both as a synthetic intermediate and as a Lewis base. Its reactions include cleavage by hydrogen halides to give mixed halophosphines[2,3] and coordination to various Lewis acids through either the phosphorus or nitrogen donor site.[4-7] It was the object of this study to determine to what extent these roles might differ in the arsenic analog, $(CH_3)_2NAsF_2$.[8]

I. Reactions of Dimethylaminodifluoroarsine with Boron Acids

1. Reaction of $F_2AsN(CH_3)_2$ with Trifluoroborane.

$(CH_3)_2NAsF_2$ undergoes reaction with excess trifluoroborane to give a 1:1 adduct. The product is a white solid with dissociation pressure at room temperature (25°) of 1 mm. Coordinated trifluoroborane can be removed slowly with pumping. On standing at room temperature for an extended period of time, decomposition other than by dissociation apparently occurs as indicated by the formation of a solid residue, slightly yellowed, which does not move under extended pumping in the vacuum line.

The infrared spectrum of $F_3B \cdot (CH_3)_2NAsF_2$ was obtained by preparing the compound on the KBr windows of a low-temperature cell. The resulting spectrum was very similar to that observed for $F_3B \cdot (CH_3)_2NPF_2$. In the arsine adduct, the peak observed in pure, solid $(CH_3)_2NAsF_2$ at 2800 cm^{-1} had disappeared and a very weak peak at 2880 cm^{-1} was observed. The entire spectrum in the C-H region was dramatically reduced in intensity from that of the uncoordinated compound. This is apparently a result of constraint on vibrational motion in the solid phase and was also observed in the phosphine case.[9] The spectra of the free arsine ligand and of the BF_3 adduct were also obtained in CCl_4 solution at room temperature. Some decomposition of the adduct is expected under the latter conditions but there was nonetheless clear evidence of a dramatic reduction of intensity of the 2800-cm^{-1} peak in the coordinated species. This peak at about 2800 cm^{-1} appears to be a reliable indicator of whether the nitrogen in a CH_3N group is coordinated.[5,7,10] Its

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(1) Presented in part at the 161st National Meeting of The American Chemical Society, Los Angeles, Calif., 1971.

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disappearance (or shift to higher frequency) is indicative of coordination at the nitrogen site. The result obtained is thus highly suggestive of formation of an N-B bond in the BF_3 adduct. In addition, a marked shift to higher frequency on coordination was observed in the region of the As-F stretching frequency. Two main peaks were observed in the free ligand at −196°: a peak at 620 cm^{-1} and one at 555 cm^{-1}. In the adduct, peaks at 655 and 680 cm^{-1} are observed with a medium-intensity shoulder peak at 610 cm^{-1}. Such shifts have also been noted in the phosphine case.[7]

The ^{11}B nmr spectrum of the adduct, obtained in toluene at −20°, is consistent with but not supportive of the assignment of the N-B bond. The broad 1:3:3:1 quartet due to BF_3 is observed at +103 ppm from triethylborane. The lack of detectable splitting in addition to this is not surprising due to the fact that both nitrogen and arsenic have quadrupole moments which, in combination with the ^{11}B nucleus, is likely to give an unresolved broad peak. The ^{19}F nmr of the adduct displayed a singlet at +88 ppm from $CFCl_3$ (-AsF_2) and a poorly resolved 1:1:1:1 quartet centered at +148 ppm from $CFCl_3$ (BF_3, $J_{B-F} \approx 15$ Hz). No appreciable broadening of the AsF_2 singlet was observed relative to free $(CH_3)_2NAsF_2$ (δ +78 ppm) in the same sample when the ratio of $(CH_3)_2NAsF_2$ to BF_3 was 2:1. On brief warming or standing in the probe at −65° the sample decomposes as indicated by the appearance of a sharp singlet at +43 ppm (AsF_3) and a very well-defined quartet at +153 ppm ($J = 20$ Hz). Continued warming brought about considerable complication of the spectrum: collapse of most of the peaks of the spectrum but continued growth of the quartet at +153 ppm.

2. Reactions of $(CH_3)_2NAsF_2$ with B_2H_6 and $BH_3 \cdot CO$. $(CH_3)_2NAsF_2$ underwent reaction with excess B_2H_6 in CH_2Cl_2 at −78° to give a 1:1 $(CH_3)_2NAsF_2 \cdot BH_3$ adduct. The compound was a white solid at −78°. On warming to −45°, gradual discoloration began. On warming further, rapid decomposition occurred to give metallic arsenic. (The reaction looked much like the Marsh test for As giving first a yellow color and finally a metallic mirror on the walls of the container.) The $H_3B \cdot (CH_3)_2NAsF_2$ adduct obtained from this reaction with B_2H_6 had no apparent dissociation pressure as high as −45°. The reduction reaction proceeded so rapidly above this temperature that no estimate could be made of its stability to dissociation relative to the BF_3 adduct.

The stoichiometry of the reaction with $BH_3 \cdot CO$ was not as definitive as in the B_2H_6 reaction, but it appeared that a 1:1 complex also formed in which the ligand displaced CO. The two reactants were mixed in 1:1 ratio in CH_2Cl_2 at −78°. A gradual pressure buildup was noted. Fractionation of the reaction mixture gave a noncondensable gas, CO possibly contaminated with H_2, a small quantity of unreacted $(CH_3)_2NAsF_2$ and $BH_3 \cdot CO$. A white solid remained in the reaction flask. Addition of excess $(CH_3)_3N$ to the solid to displace $(CH_3)_2NAsF_2$ and then removal and measurement of the excess amine indicated that about 1.0 mmol of BH_3 was present in the solid. This quantity and the $BH_3 \cdot CO$ recovered (0.40 mmol) very nearly total the amount of $BH_3 \cdot CO$ charged (1.35 mmol). The 1.0 mmol of BH_3 apparently combined compares favorably with 1.34 mmol of $(CH_3)_2NAsF_2$ charged initially. The white solid remaining in the flask behaved identically on warming with the B_2H_6 reaction product.

The infrared spectrum of $H_3B \cdot (CH_3)_2NAsF_2$ was obtained by condensing $(CH_3)_2NAsF_2$ and B_2H_6 as a thin film on the KBr plate of a low-temperature cell at −196°. After reaction and removal of excess diborane the free diborane peaks at 2480 and 2580 cm^{-1} observed in the unreacted solid had disappeared entirely and a strong, broad peak at 2350 cm^{-1} corresponding to the bound BH_3 was observed. The C-H peak at 2800 cm^{-1} remained undiminished. There was a small but detectable shift to lower frequency in the AsF_2 peaks originally at 623 and 555 cm^{-1}. This is in contrast to the large shifts to higher frequency of the BF_3 adduct. Other peaks remained relatively free of position shift relative to those in the uncoordinated arsine though there was some change in relative intensity. Repeated experiments in no case indicated diminution of the 2800-cm^{-1} peak and were highly reproducible. There was no indication that unreacted $(CH_3)_2NAsF_2$ was present in any appreciable amount. In marked contrast was the BF_3 adduct already discussed in which the whole C-H structure between 2800 and 3000 cm^{-1} was reduced dramatically in relative intensity and the peak at 2800 cm^{-1} disappeared completely. Therefore, an As-B bond seems indicated in the BH_3 adduct as opposed to the BF_3 adduct.

The ^{11}B nmr spectrum of $(CH_3)_2NAsF_2 \cdot BH_3$ was obtained in diethyl ether at −45° and displayed a 1:3:3:1 quartet at +86.9 ppm from triethylborane with J_{B-H} approximately 100 Hz. No additional splitting was observed. Binding to As could have resulted in observable splitting due to the fluorine nuclei of AsF_2 but the broadness due to nuclear quadrupoles can easily account for its lack of detection. The ^{19}F spectrum obtained at −65° in $(C_2H_5)_2O$ showed a broad peak (unresolved multiplet ?) at +52 ppm from CCl_3F. When an excess of $(CH_3)_2NAsF_2$ (2:1) was present, a sharp singlet was also observed at +81 ppm from CCl_3F. The half-height width to height ratios clearly showed a great degree of broadening of the AsF_2 signal on coordination to borane: 4.1 Hz/spectrum amplitude unit for the adduct signal and 0.33 Hz/spectrum amplitude unit for the free ligand. The ^{19}F signal is shifted by 29 ppm downfield from that of the free ligand. This compares with a 10-ppm shift upfield in the BF_3 adduct. This contrast in chemical shifts and signal breadths supports the conclusion of different binding sites for the boron atom in the two complexes.[11] The relatively unchanged breadth and position in the BF_3 adduct is consistent with an N-B bond in that there is relatively little effect on the AsF_2 resonance. The broadening and substantial shift of the AsF_2 resonance in the BH_3 adduct is suggestive of a more direct interaction with boron, thus of an As-B bond.

II. Cleavage of $(CH_3)_2NAsF_2$ by Hydrogen Chloride

$(CH_3)_2NAsF_2$ undergoes reaction with anhydrous hydrogen chloride in the gas phase to give a product identified as dimethylammonium chloride by comparison of its infrared spectrum with that of an authentic sample and chlorodifluoroarsine, AsF_2Cl. Conclusive evidence for the formation of AsF_2Cl lies in its mass spectrum; this assignment is supported by its nmr and ir spectra and its vapor-phase molecular weight. The product is a colorless, volatile liquid which is retained as a solid at −78° in the vacuum line.

The ready tendency of the product to disproportionate is well illustrated by the mass spectral study. The mass spectrum of this −78° fraction displays peaks at *m/e* 150 and 148 in the 1:3 ratio expected of the molecular ions $AsF_2{}^{37}Cl^+$ and $AsF_2{}^{35}Cl^+$. Also present are the appropriate major fragmentation peaks due to AsF_2, $AsFCl^+$, $AsCl^+$, and AsF^+. However, there are also peaks appropriate to $AsFCl_2$, AsF_3, and $AsCl_3$. After periods at room temperature in the mass spectrometer ranging up to 1 hr, the relative intensities

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[11] We are grateful to a referee for bringing this possibility to our attention.

of the peaks due to AsF_2Cl and AsF_3 did not change significantly. After standing at room temperature overnight, an increase in the relative intensities of the AsF_3 and $AsCl_3$ peaks to those due to AsF_2Cl is noted. Redistillation of the sample produced pure AsF_3 in the more volatile fraction and pure $AsCl_3$ in the less volatile as indicated by the mass spectra. Repetition of the mass spectrum of the $-78°$ fraction gave essentially the same results as before: all the mixed species were present and quite constant in relative intensity. The ratios did vary from sample to sample, however. This indicated that the product obtained in the $-78°$ fraction was not an equilibrium mixture. Continued redistillation and observation in the mass spectrometer produced increasing quantities of AsF_3 and $AsCl_3$ and a diminishing quantity of the $-78°$ fraction until it became negligible. The disproportionation is apparantly sufficiently rapid in the condensed phase that the mixture of halo-substituted products is invariably obtained as the substance warmed to vaporize, though at low pressures ($\sim$5 mm) in the vapor disproportionation was relatively slow. It was not possible to obtain a pure sample to study in the vapor phase by fractional distillation in the vacuum line using a wide variety of low-temperature bath combinations.

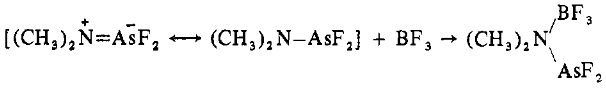
That some separation did occur was suggested by the vapor density molecular weight, which indicates that a dominant species in the fraction was AsF_2Cl: calcd, 148.5; found, 139. The low value is probably due to the presence of some excess of AsF_3 (mol wt 132) or may be a result of the very small masses measured. The vapor density would, of course, be the same for pure AsF_2Cl as for a mixture of AsF_2Cl, $AsFCl_2$, $AsCl_3$, and AsF_3 obtained by its disproportionation, but this does suggest at least an enrichment of AsF_2Cl in this fraction.

The infrared spectrum of AsF_2Cl displayed peaks at 752 and 740 cm^{-1}, a broad, intense peak at 715-695 cm^{-1}, and a peak at 375 cm^{-1} in the range 4000-300 cm^{-1}. The broad peak can be attributed to an overlap of a band at 702 cm^{-1} due to AsF_3 impurity with AsF_2Cl bands at 710 and 695 cm^{-1}. Such a doublet would be expected in this region due to the lowering of symmetry from C_{3v} to C_s on going from MX_3 to MX_2Y.[12] Comparison to other similar systems where M = P and X, Y = F, Cl[13] supports this assignment. Further comparison with analogous systems rationalizes the band at 375 cm^{-1} as probably due largely to F_2As-Cl deformation. That the band at 752 cm^{-1} is higher than any band in AsF_3 appears anomalous compared with the analogous phosphorus systems and with $AsCl_2Br$ and $AsClBr_2$.[13] If it is indeed due to AsF_2Cl, it remains unexplained. The peaks observed do not correspond to the most likely contaminants except for that at 702 cm^{-1} (AsF_3). These include $(CH_3)_2NAsF_2$ and $(CH_3)_2NH_2Cl$. The peaks do lie in the region expected for AsF_2Cl.

The ^{19}F nmr spectrum was obtained with a sample prepared by combining the product of several preparations, testifying to the difficulty found in preparing and isolating the compound. Three singlets were observed in the spectrum: at 45.2 ppm from CCl_3F, 76.0 ppm, and 88.2 ppm. The lowest field peak was the largest and was assigned to AsF_3 on comparison with an authentic spectrum (41.5 ppm). In the PF_xCl_{3-x}[14] and NF_xCl_{3-x}[15] systems, ^{19}F resonance is observed at progressively higher field on substituting Cl for F (decreasing x). By analogy the higher field peaks observed are most likely due to AsF_2Cl (+76.0 ppm) and $AsFCl_2$ (+88.2 ppm).

Discussion

I. As in the case of $(CH_3)_2NPF_2$, $(CH_3)_2NAsF_2$ provides two potential donor sites, N and As. In contrast to the phosphine analog, however, the parent AsF_3 seems to display very little ligand character while quite extensive ligand behavior, especially π-acid behavior, is exhibited by PF_3.[16] The experimental evidence obtained in this work strongly suggests that the coordination of $(CH_3)_2NAsF_2$ is qualitatively analogous to that of the corresponding phosphorus compound. In Pearson's terminology[17] the hard acid BF_3 coordinates at the hard base site, N, while the soft acid, BH_3, coordinates at the soft base site, As. The planar geometry and short P-N bond of $(CH_3)_2NPF_2$ has suggested an explanation for the relatively weak nitrogen basicity in that compound in terms of $(p \rightarrow d)\pi$ bonding between N and P.[7] According to this model, the lone pair on nitrogen is involved to some extent in bonding to the phosphorus atom d orbitals to give the planar geometry and the lowered basic character of nitrogen. The increased electron density on phosphorus in turn gives rise to enhanced basicity at phosphorus. AsF_3 appears to have negligible σ-donor basicity but has been reported to be an excellent π acceptor.[18] No complexes have been reported in which AsF_3 is bound to either BH_3 or BF_3, a feature consistent with its weak σ-donor character. That the BH_3 group attaches to As in preference to N in $(CH_3)_2NAsF_2$ may thus be interpreted in terms of substantial enhancement of the σ-donor character through the mechanism suggested for $(CH_3)_2NPF_2$. An alternate mechanism would involve a hyperconjugation argument involving the π-acceptor character of $-AsF_2$. If no BH_3 adduct is stable with AsF_3, this argument would not appear to have a great deal of merit. That no such adduct has been reported may be due to this lack of stability or may be due to rapid reduction of AsF_3 precluding observation of such an adduct. The AsF_2 stretching frequencies in the infrared spectrum support the view of a significant N-As π bond. The shift of the As-F stretching frequencies at 623 and 555 cm^{-1} in the free ligand to 680 and 650 cm^{-1} in the BF_3 adduct suggest substantial strengthening of the As-F bond,[7,19] although it may also be due to vibrational coupling. According to the π-bonding model, this should arise through destruction of the $(p \rightarrow d)\pi$ bond on coordination of the nitrogen's nonbonding pair with BF_3. The diminished electron density on arsenic resulting from destruction of this dative π bond (loss of a formal negative charge) then allows a stronger As-F bond



$$[(CH_3)_2\overset{+}{N}{=}\overset{-}{As}F_2 \longleftrightarrow (CH_3)_2N{-}AsF_2] + BF_3 \rightarrow (CH_3)_2N\begin{smallmatrix} BF_3 \\ AsF_2 \end{smallmatrix} \qquad (1)$$

The coordination of BH_3 at the arsenic site need not result in destruction of the π bond and a much smaller effect on the AsF symmetric stretch is noted (623 to 605 cm^{-1}) in the opposite direction even though the coordination occurs

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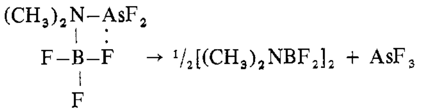
closer to the As-F bond. This is quite consistent with the small shift to lower frequency of the symmetric As-F stretching frequency in $C_5H_5Mn(CO)_2AsF_3$ (694 to 683 cm^{-1}).[18] For the BF_3 adduct of $(CH_3)_2NPF_2$, comparable changes were observed:[7] from 764 (ν_a) and 728 (ν_s) cm^{-1} in the free ligand to 880 and 827 cm^{-1}, respectively, in the adduct. A comparably small shift was noted in the symmetric P-F stretch on coordination to BH_3 (728 to 753 cm^{-1}) but in the direction of higher frequency rather than lower frequency as in the arsenic case. This may imply a greater degree of π bonding between As and B than in the phosphorus case, but this is by no means certain. With regard to the relative basicities of the arsenic and phosphorus sites in the two ligands, it would be of value to study the donor properties of $(CH_3)_2NAsF_2$ toward nonreducing acids which might be more amenable to comparative stability studies.

The decomposition of the BF_3 adduct may also lend support to the assignment of an N-B bond in that case. A probable decomposition is provided again by analogy to the phosphorus case.[7] The presence of AsF_3 in the nmr sample can be understood by means of



$$\begin{array}{l} (CH_3)_2N{-}AsF_2 \\ \quad\ \ | \quad\ \ \vdots \\ \quad F{-}B{-}F \quad \rightarrow {}^1/_2[(CH_3)_2NBF_2]_2 + AsF_3 \\ \qquad\ | \\ \qquad F \end{array}$$

The clearly defined quartet observed at 154 ppm in the ^{19}F nmr spectrum is likely a precursor to the dimer $[(CH_3)_2NBF_2]_2$ as it is identical with that observed in the decomposition of the $(CH_3)_2NPF_2 \cdot BF_3$ adduct at low temperature.[20]

II. The data obtained for the reaction of $(CH_3)_2NAsF_2$ with HCl are consistent with the reaction scheme

$$(CH_3)_2NAsF_2 + 2HCl \rightarrow AsF_2Cl + (CH_3)_2NH \cdot HCl \tag{2}$$

$$2AsF_2Cl \rightarrow AsFCl_2 + AsF_3 \tag{3}$$

followed by similar scrambling of $AsFCl_2$ to give the $AsCl_3$ observed. Supporting this are the formation of a white solid in the reaction, identified as $(CH_3)_2NH \cdot HCl$, observation of AsF_2Cl in the mass spectrum, and the gradual increase, in time, of the relative quantities observed in the vacuum line of $AsCl_3$ and AsF_3 compared with AsF_2Cl. That the reaction observed was not due to halogen exchange to produce $(CH_3)_2NAsCl_2$ was made clear by its total absence in the mass spectrum. That AsF_3 was not formed by scrambling of $(CH_3)_2NAsF_2$ was indicated by its absence in the mass and ir spectra of $(CH_3)_2NAsF_2$ taken after standing at room temperature.

Although this is the first report of preparation of a mixed haloarsine other than by halogen interchange,[21] Ruff and Paulett[22] observed the species AsF_2Cl in an nmr and mass spectrometry study of scrambling in a mixture of $AsCl_3$ and AsF_3. It is of some concern that the value observed in their work for the ^{19}F chemical shifts in the mixture of AsF_3, AsF_2Cl, and $AsFCl_2$ with $AsCl_3$ (40.4, 49.0, and 67.4 ppm relative to CCl_3F) are not in good agreement with those observed in this work (45.2, 76.0, and 88.2 ppm). There is no obvious explanation for this discrepancy, but our values have been double checked. The CCl_3F standard was external in this work and internal in the previous work. A substantial solvent effect was noted in the earlier work but not clearly sufficient to account for the difference observed. By means of both their mass and nmr studies, Ruff and Paulett obtained positive values for the free energy of formation of AsF_2Cl and $AsFCl_2$ from AsF_3 and $AsCl_3$ ($\Delta G \approx 1.5$ kcal/mol). This would indicate that scrambling of AsF_2Cl and $AsFCl_2$ as suggested above should be expected thermodynamically. The product obtained clearly disproportionates as indicated. A recent report[23] has suggested that the rate of scrambling in PF_2Cl is very sensitive to the presence of moisture. Consequently, our system was dried by flaming the vacuum line and conditioning with $SOCl_2$ or with AsF_3, and in no case were we able to obtain the pure AsF_2Cl. While this may be in part due to very similar volatilities of AsF_2Cl and its disproportionation products, it is also clearly true that the disproportionation is rapid at least in the condensed phase.

Experimental Section

General Techniques. Standard high-vacuum techniques were used throughout. Infrared spectra were obtained using a low-temperature infrared cell[24] and a 75-mm path gas cell with KBr or polyethylene windows on a Beckman IR-20-A spectrometer. ^{11}B and ^{19}F nmr spectra were obtained at 32.1 and 94.1 MHz, respectively, with a Varian Associates XL-100-12 instrument. External standards were used for chemical shift measurements. Chemical shifts are given in ppm from $(C_2H_5)_3B$ or $CFCl_3$. Mass spectra were obtained with an Hitachi Perkin-Elmer RMU-6E spectrometer.

Materials. Commercial BF_3 (Matheson), AsF_3 (Alfa), and $(CH_3)_2NH$ and HCl (Matheson) were vacuum distilled before use. Diborane was prepared by the reaction of 85% H_3PO_4 with KBH_4[25] (Alfa). $BH_3 \cdot CO$ was prepared by the reaction of 85% H_3PO_4 with $Na_2H_3BCO_2$[26] (supplied by the laboratory of R. W. Parry). Solvents were reagent grade and were vacuum distilled before use.

Preparation of $(CH_3)_2NAsF_2$. The reaction equation is

$$2AsF_3 + 3(CH_3)_2NH \rightarrow 2(CH_3)_2NAsF_2 + (CH_3)_2NH \cdot HF_2 \tag{4}$$

An 8.6-mmol sample of $(CH_3)_2NH$ was condensed into a 100-ml bulb attached by a stopcock to a 500-ml bulb. The stopcock connecting the two bulbs was closed and a 5.7-mmol sample of AsF_3 was then condensed into the 500-ml bulb. The AsF_3 and $(CH_3)_2NH$ were allowed to warm to room temperature at which they were entirely in the vapor phase. The connecting stopcock was opened and the two reactants mixed in the gas phase. (Mixing in the condensed phase, in benzene, or in toluene solution gave little or no recoverable product.[8]) A white fog formed immediately. The mixture was allowed to stand at room temperature for about 15 min after which the product was distilled through a 0° trap and retained in a −45° trap: yield 50%; vapor pressure (at 23°) 11 mm; mp 2–4°. The $(CH_3)_2NAsF_2$ was identified by its vapor density molecular weight 164 (calcd 157, low vapor pressure gives large uncertainty) and its infrared, mass, and nmr spectra. The infrared spectrum was very similar to that of $(CH_3)_2NPF_2$.[27] It was as follows for the gas phase (25°) (in cm^{-1}): 2920 (s), 2820 (ms), 1450 (m), 1280 (m), 1190 (m), 1070 (w), 1030 (w), 960 (s), 730 (m), 630 (s), 580 (ms); for the solid film (−196°): 2970 (w), 2910 (m, sh), 2890 (s, ν(C–H)), 2840 (w, sh), 2800 (m, ν(C–H)), 1550 (vw), 1480 (m), 1460 (ms), 1440 (s, $\delta(CH_3)$), 1280 (s, $\delta(CH_3)$), 1190 (s, $\rho(CH_3)$), 1135 (w), 1065 (m, ν(C–N)), 955 (s, $\nu((CH_3)_2NAs)$), 623 (vs, ν(AsF)), 555 (vs, ν(As–F)). Mass spectrum (70 eV) [*m/e* (ion, relative intensity)]: 157 ($C_2H_6NAsF_2^+$, 5), 156 ($C_2H_5NAsF_2^+$, 8), 138 ($C_2H_6NAsF^+$, 6), 113 (AsF_2^+, 8), 94 (AsF^+, 3), 81 (?, 7), 58 (?, 3), 47 (SiF^+, 3), 45 ($C_2H_6NH^+$, 45), 44 ($C_2H_6N^+$, 100), 43 ($C_2H_5N^+$, 46), 42 ($C_2H_4N^+$, 79), 41 ($C_2H_3N^+$, 18), 40 ($C_2H_2N^+$, 10), 39 (C_2HN^+, 9), 38 (C_2N^+, 3), 30 (CH_3NH^+, 13), 29 (CH_3N^+, 19), 28 (CH_2N^+, N_2^+, 90), 27 (CHN^+, 25), 26 (CN^+, 3), 15 (CH_3^+, 43), 14 (N^+, CH_2^+, 8). No other peaks of relative intensity greater than 2 were observed except a strong H_2O^+ peak at 18. Nmr spectra: ^{19}F, δ +80 ppm (s, AsF_2, neat liquid), +78 ppm (s, AsF_2, toluene solution) ($\delta(^{19}F) = (\nu(CCl_3F) - \nu)/94.1$); ^1H, δ ∼2.5 ppm from TMS (s, H_3C, neat liquid).

Preparation of $F_3B \cdot (CH_3)_2NAsF_2$. A 0.92-mmol amount of

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$(CH_3)_2NAsF_2$ and 2.01 mmol of BF_3 were frozen in a reaction tube with a magnetic stirrer. On standing at −78° the BF_3 pressure slowly decreased. The mixture was then allowed to warm slowly until the $(CH_3)_2NAsF_2$ began to melt (2°) at which time the BF_3 pressure dropped rapidly. The mixture was stirred until no further pressure change was noted. It was then cooled to −78° and excess BF_3 was removed with pumping to a −196° bath. A 0.92-mmol amount of BF_3 was found to be consumed in the reaction to give a 1:1 ratio of reactants in the product. The infrared spectrum of $F_3B \cdot (CH_3)_2NAsF_2$ was obtained by condensing $(CH_3)_2NAsF_2$ and a large excess of BF_3 on the KBr window of the low-temperature infrared cell. They were then allowed to stand at room temperature for about 5 min after which the cell was chilled to −78° and the excess BF_3 removed. The spectrum of the mixture was recorded at each stage of the operation. The ir spectrum of the final product (solid film, −78°) was as follows (in cm^{-1}): 3290 (vw), 3030 (vvw), 2980 (vw), 2940 (vw), 2870 (vvw), 1475 (m), 1460 (sh), 1445 (w, $\delta(CH_3)$), 1415 (vw), 1345 (vw), 1250 (w, sh), 1200 (m, $\rho(CH_3)$), 1155 (s, ν(C–N) and/or ν(B–F)), 1130 (m, sh), 1090 (m, ν(C–N) and/or ν(B–F)), 1060 (w, ν(C–N) and/or ν(B–F)), 1015 (m, $\nu((CH_3)_2NAs)$), 950 (m), 910 (s, ν(B–F)), 890 (s, ν(B–F)), 820 (w), 805 (sh), 760 (m), 710 (m), 680 (s, ν(As–F)), 650 (s, ν(As–F)) 610 (m), 515 (w). The infrared spectrum was also obtained in CCl_4 solution in a NaCl cell with a CCl_4 blank and compared with a spectrum of free $(CH_3)_2NAsF_2$ under the same conditions. The region between 2750 and 3000 cm^{-1} was scanned particularly carefully. It displayed substantially more intense absorption in this region than in the solid phase but gave the same qualitative spectrum otherwise.

Nmr samples were prepared by carrying out the reaction in CH_2Cl_2 at −78° in a reaction tube to which an nmr tube was sealed above the liquid level of the reaction mixture. The solution was stirred with a magnetic stirrer until the pressure above the solution dropped to <1 mm. The entire assembly was then immersed in a Dry Ice bath and the solution was poured into the attached tube. The tube was then sealed. Samples were prepared both with a 1:1 ratio and with a 2:1 ratio of $(CH_3)_2NAsF_2$ to BF_3. Two samples were prepared, each at the 2:1 ratio with concentrations of the two samples in a 4:3 ratio. The ^{11}B nmr spectrum was observed at −45° as a broad 1:3:3:1 quartet at +103 ppm (J_{B-F} = 20 Hz). The ^{19}F spectrum gave much sharper signals and was observed in more detail. In all three samples, peaks were observed (−65°) at 43 (s, AsF_3), 88 (s, AsF_2), 148 (q, BF_3, $J_{B-F} \approx$ 15 Hz), and 153 ppm (q, J = 20 Hz). In addition the free ligand peak was observed at 78 (s) ppm in the samples containing excess ligand. The 43- and 153-ppm peaks grew with time indicating the decomposition of the samples. The appropriate 3:2 area ratio was observed for the peaks at 148 and 88 ppm ($BF_3 \cdot AsF_2$).

Preparation of $H_3B \cdot F_2AsN(CH_3)_2$. A 0.97-mmol sample of $(CH_3)_2NAsF_2$ was distilled into a reaction tube together with 0.85 mmol of B_2H_6. Five milliliters of dry CH_2Cl_2 was then added by distillation and the mixture was allowed to warm to −78° where it was held with stirring. A rapid pressure drop occurred as stirring commenced and a pale yellow precipitate formed. Stirring continued until no further pressure drop was noted. The excess B_2H_6 and the solvent were then removed by distillation from the reaction tube at −78°. There was no evidence of H_2 formation. A 0.35-mmol amount of unreacted B_2H_6 was recovered leaving 0.50 mmol combined with $(CH_3)_2NAsF_2$. Since 0.50 mmol of B_2H_6 is equivalent to 1.00 mmol of BH_3, the adduct ratio was 1:1. The infrared spectrum of $H_3B \cdot F_2AsN(CH_3)_2$ was obtained as described for the BF_3 adduct in the low-temperature ir cell except that the reaction was quenched to −196° as quickly as it occurred as was evident by the formation of a yellow coloration on the KBr window. Excess diborane was removed from the cell at −78°. To ensure that the spectrum obtained was not a composite with unreacted ligand, the procedure was repeated several times with excellent reproducibility. The ir spectrum is as follows (solid film, −78°) (in cm^{-1}): 3220 (m), 3160 (w, sh), 3000 (w), 2970 (w), 2950 (w, sh), 2880 (m, ν(C–H)), 2860 (w, sh), 2800 (m, ν(C–H)), 2400 (m, ν(B–H)), 2370 (w, sh), 2310 (w, sh), 2290 (m, ν(B–H) or 2 × 1150), 2240 (w, sh), 1465 (s, $\delta(CH_3)$), 1445 (s, $\delta(CH_3)$), 1440 (s), 1400 (w), 1355 (m, $\delta(CH_3)$), 1340 (w, sh), 1280 (m), 1190 (s), 1160 (s, $\rho(CH_3)$), 1085 (m, sh), 1070 (m, ν(C–N) and/or $\delta(BH_2)$), 1020 (w), 960 (s, $\nu((CH_3)_2NAs)$), 905 (m), 790 (mw), 605 (s, ν(As–F)), 577 and 540 (both s, ν(As–F)?). An nmr sample was prepared by carrying out the preparative reaction in diethyl ether in a reaction tube as described above. Approximately 0.24 mmol of adduct and 0.5 ml of diethyl ether were used. A second sample was prepared in the same manner with a 2:1 ratio of ligand to BH_3. During the course of the measurements substantial browning of the sample occurred indicating some significant reduction of the arsenic. This seemed to be unavoidable. The ^{19}F spectrum of the pure adduct gave a broad peak at 52 ppm (s, AsF_2) at −45°. A very weak, broad peak at about 90 ppm was observed to form in time. The spectrum of the sample containing excess ligand gave a broad peak at −65° at 52 ppm ($-AsF_2$, bound) and a sharp signal at 81 ppm ($-AsF_2$, free). The ^{11}B spectrum (−45°) gave broad peaks at 87 ppm (q, J_{B-H} = 100 Hz).

Reaction of $(CH_3)_2NAsF_2$ with $BH_3 \cdot CO$. A 1.34-mmol sample of $(CH_3)_2NAsF_2$ was condensed into a reaction tube followed by 6 ml of CH_2Cl_2. After stirring and chilling to −196°, 1.33 mmol of $BH_3 \cdot CO$ was added. The reaction tube was kept at −78° for a 6-day period with occasional stirring. A slight continuing pressure buildup was noted due to formation of CO. When this increase ceased to be observed, the mixture was fractionated (from −63°) to give 0.75 mmol of CO and 0.40 mmol of $BH_3 \cdot CO$, accounting for 1.15 of the 1.33 mmol charged. To the solid remnant was added 1.54 mmol of $(CH_3)_3N$. The resulting mixture was stirred at −78° for 3 days and fractionated giving 0.53 mmol of $(CH_3)_3N$. The difference of 1.01 mmol should correspond to the BH_3 coordinated. This is in good agreement with the 0.75 mmol of CO recovered and the 0.93 mmol of $BH_3 \cdot CO$ which was not recovered.

Reaction of $(CH_3)_2NAsF_2$ with HCl. A 0.129-g (0.824-mmol) sample of $(CH_3)_2NAsF_2$ and 1.65 mmol of HCl were allowed to react in the gas phase in a manner like that used in preparing $(CH_3)_2NAsF_2$. A white cloud formed immediately with crystalline material forming on the walls of the reaction vessel. The crystalline material gave an ir spectrum identical with that of an authentic sample of $(CH_3)_2NH \cdot HCl$. After the cloud was allowed to settle 2 min, the mixture was condensed in a trap at −196° and then distilled from −45° through traps at −64, −78, and −196°. $AsCl_3$ was retained at −64°, product at −78°, and AsF_3 at −196°. A variety of temperature combinations was tried with no improvement over this series. The compound at −78° was characterized as predominantly AsF_2Cl using the following data. The vapor density molecular weight was found to be 139 (calcd 148). Infrared spectrum (cm^{-1}, 25°): 752 (s), 740 (vs), 715–695 (vs), 375 (m). ^{19}F nmr spectrum (−45°) (ppm from CCl_3F): +45.2, +76.0, +88.2 (all singlets) with area ratio 10:1.3:1.0. Mass spectrum (at 70 eV) [*m/e* (ion, relative intensity)]: 186 ($As^{37}Cl_3^+$, 0.1), 184 ($As^{35}Cl^{37}Cl_2^+$, 0.4), 182 ($As^{35}Cl_2{}^{37}Cl^+$, 1.0), 180 ($As^{35}Cl_3^+$, 1.0), 168 ($As^{37}Cl_2F^+$, 0.15), 166 ($As^{37}Cl^{35}ClF^+$, 0.6), 164 ($As^{35}Cl_2F^+$, 1.0), 150 ($AsF_2{}^{37}Cl^+$, 2.0), 149 ($As^{35}Cl_2^+$, 0.6), 148 ($AsF_2{}^{35}Cl^+$, 4.6), 147 ($As^{37}Cl^{35}Cl^+$, 2.0), 145 ($As^{35}Cl_2^+$, 3.0), 132 (AsF_3^+, 52.5), 131 ($AsF^{37}Cl^+$, 1.5), 129 ($AsF^{35}Cl^+$, 4.0), 113 (AsF_2^+, 100), 112 ($As^{37}Cl^+$, 0.3), 110 ($As^{35}Cl^+$, 1), 94 (AsF^+, 5.9), 85 (SiF_3^+, 4.3), 75 (As^+, $AsF_2{}^{37}Cl^{2+}$, 5.9), 66 (SiF_2^+, 0.6), 56.5 (AsF_2^{2+}, 1.5), 47 (AsF_2^+, 4.9), 37.5 (As^{2+}, 1.5), 37 ($^{37}Cl^+$, 0.4), 36 ($H^{35}Cl^+$, 1.3), 35 ($^{35}Cl^+$, 1.2), 20 (HF^+, 0.6), 19 (F^+, 4.0).

Registry No. $(CH_3)_2NAsF_2$, 758-23-6; AsF_3, 7784-35-2; $(CH_3)_2NH$, 124-40-3; $F_3B \cdot (CH_3)_2NAsF_2$, 40544-37-4; BF_3, 7637-07-2; $H_3B \cdot F_2AsN(CH_3)_2$, 40544-38-5; B_2H_6, 19287-45-7; $BH_3 \cdot CO$, 13205-44-2; HCl, 7647-01-0; AsF_2Cl, 40544-39-6; boron-11, 14798-13-1.

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