On the other hand, the two C_5H_4 moieties could also be present in the form of a $C_{10}H_8$ ligand in the dimer (structure II). This structure would be perfectly in accord with the occurrence of the ion $C_{10}H_8^+$ in the mass spectra of both the hydride and the chloride, and of the ion M − C_5H_5TiCl in the spectrum of the chloride. Since there is little hope of distinguishing structures I and II by ir, nmr, or other spectral techniques, this particular problem might have to be settled by a crystal structure determination of the dimer.

An interesting question is whether the species $(h^5\text{-}C_5H_5)_2Ti$ can be regenerated from $(C_{10}H_9TiH)_2$. It has been observed that $(h^5\text{-}C_5H_5)_2Ti(CO)_2$ can be obtained, although inefficiently, from titanocene and CO.[20] This would indicate that—given a sufficient driving force and the absence of efficient competing reactions—regeneration of $(h^5\text{-}C_5H_5)_2Ti$ as a transient species is a marginal possibility. We plan to investigate further into the characteristics and possible modes of stabilization of the hypothetical reaction intermediate $(h^5\text{-}C_5H_5)_2Ti$ and of related compounds.

Experimental Section

Procedures for the handling of the air-sensitive materials and gases used were as outlined in an earlier publication.[13] Mass spectra were obtained on an AEI SP902 mass spectrometer with direct inlet system.

Preparation of $(C_{10}H_9TiCl)_2$. $(C_{10}H_9TiH)_2$ (538 mg, 1.51 mmol), obtained according to ref 3, is suspended in 15 ml of ether in a reaction vessel attached to a vacuum assembly. HCl gas (5 mmol) is condensed into the reaction vessel at liquid nitrogen temperatures. After warming to room temperature and stirring for about 1 hr, the initially green material is completely converted to a purple slurry and the initially vigorous hydrogen evolution ceases. The reaction mixture is then freed from H_2 gas and filtered on the vacuum line. The precipitate is washed with a little ether and dried *in vacuo*. The purple product, which is obtained in essentially quantitative yields—520 mg after purification—is moderately air-sensitive, especially in the presence of solvents; it can be stored indefinitely under Ar. The compound thus obtained has the correct elemental composition and spectral properties identical with those described by Salzmann and Mosimann.[3] On the other hand, differences are to be noted between this preparation and titanocene samples described by Watt, Baye, and Drummond.[2] In particular, Dr. Watt has drawn our attention to the observation that his samples are much more reactive toward air than ours, and to noticeable differences in the ir spectrum, such as a substantially lower intensity of the band at 1230 mμ, in his preparations. The causes for these differences are not clear at present.

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Synthesis and Characterization of Aminodifluorophosphine

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Abstract: The reaction of NH_3 and PF_2Cl or PF_2Br results in the formation of aminodifluorophosphine, H_2NPF_2. The deuterium derivative D_2NPF_2 was prepared by an analogous reaction between ND_3 and PF_2Cl. A similar reaction between CH_3NH_2 and PF_2Cl yields methylaminodifluorophosphine, $(CH_3NH)PF_2$. These compounds were characterized by mass, infrared, and nmr spectral studies.

Although aminophosphine dihalides of the type R_2NPX_2 (where X = F, Cl, Br, or I, and R is an alkyl or aryl group) have been known for almost 100 years, the fundamental member of the series, H_2NPX_2, has never been prepared. We wish to report the synthesis and characterization of H_2NPF_2, which is obtained from the reaction of NH_3 with difluorohalophosphines. A similar reaction occurs with CH_3NH_2. Specifically, when PF_2Br or PF_2Cl is allowed to interact with NH_3 or CH_3NH_2 at 23° the reaction proceeds according to

$$2RNH_2 + PF_2X \longrightarrow RHNPF_2 + NH_3RBr \tag{1}$$

where X = Cl or Br and R = H or CH_3.

The reaction of NH_3 and PF_2Br to give H_2NPF_2 may be contrasted with the reaction of PH_3 and PF_2I. The latter reaction has been shown to yield only PF_2I and PF_2H as products, although it was postulated that the initial product was H_2PPF_2.[1] The interactions of PF_2X and NH_3 or RNH_2 are analogous to both the reaction between bis(trifluoromethyl)chlorophosphine and ammonia[2] and the reaction between trichloromethyldifluorophosphine and methylamine.[3]

Experimental Section

Synthesis. The work was carried out in Pyrex systems by using standard vacuum techniques. All gaseous reactants and products were measured by means of a calibrated volume. Spectral data were obtained as previously described.[4]

Chlorodifluorophosphine and bromodifluorophosphine were prepared by using previously described procedures.[5] Ammonia was dried over sodium before use. Methylamine (Matheson) was used as obtained.

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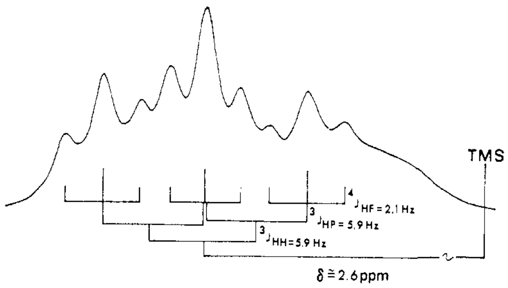

Figure 1. ^{1}H nmr spectrum of CH_3NHPF_2.

The Reaction of Difluorochlorophosphine with Ammonia. In a typical reaction a 11.8-mmol sample of PF_2Cl was condensed at −196° into a previously dried 500-ml round-bottom flask equipped with a high-vacuum stopcock. A 23.6-mmol sample of NH_3 was condensed on top of the sample of PF_2Cl. The reaction mixture was allowed to warm to 23° over a period of about 5 min. An immediate reaction was indicated by formation of a white cloud. The volatile products were separated by codistillation.[6] A 0.9-mmol sample of PF_3 and a 3.4-mmol sample of PF_2Cl were recovered. These were identified by their gas-phase ir spectra. In addition, a 2.4-mmol sample of H_2NPF_2 was recovered. Characterization of this product is presented in a subsequent portion of this paper. Ammonium chloride, NH_4Cl, was obtained as a product in the reaction bulb. It was identified by its X-ray diffraction powder pattern which was identical with that of an authentic sample of NH_4Cl. Other unidentified white solids are deposited on the walls of the vacuum line when H_2NPF_2 is allowed to stand in the liquid phase at 23° for more than a few minutes. The production of these solids may account for the rather lower yield of H_2NPF_2. The deuterium analog of H_2NPF_2 was obtained in a fashion almost identical with that described for the preparation of H_2NPF_2. Although detailed data were not obtained on the course of the reaction, H_2NPF_2 can also be obtained by the interaction of PF_2Br with NH_3.

Reaction of Difluorochlorophosphine with Methylamine. The reaction was carried out in a manner almost identical with that described for H_2NPF_2. Methylaminodifluorophosphine, CH_3NHPF_2, was characterized by its ir and ^{19}F nmr spectra, which were identical with previously reported spectra.[3] The proton spectrum, reported to be a broad unresolvable band,[3] is presented in Figure 1. It consists of two doublets which overlap to give a triplet ($^3J_{PH} = {}^3J_{HH} \cong 5.9$ Hz). Each member of the triplet is further split into a triplet by the two equivalent fluorines ($^4J_{FH} = 2.1$ Hz, lit.[3] $^4J_{FH} = 2.0$ Hz). The broad high-field band in Figure 1 may be assigned to protons directly attached to nitrogen.

Discussion

Unequivocal characterization of aminodifluorophosphine, H_2NPF_2, was obtained from the ^{1}H (60 MHz), ^{19}F (56.4 MHz), and ^{31}P (40.4 MHz) nmr spectra. The proton spectrum at −80° shows a broad absorption. The broadening arises from the spin–lattice relaxation of the proton resonances by the quadrupole moment of the nitrogen. The fluorine spectrum of H_2NPF_2 (−80°) consists of a doublet ($J_{PF} = 1188$ Hz) centered at +18.3 ppm from a F_2PBr internal standard. Each member of the doublet is further split into a 1:2:1 triplet ($J_{HF} = 12.6$ Hz). The fluorine spectrum of D_2NPF_2 consists of a doublet ($J_{PF} = 1184$ Hz). The phosphorus spectrum of H_2NPF_2 (−70°) consists of a broad (quadrupole relaxation) 1:2:1 triplet ($J_{PF} = 1190$ Hz) centered at +5.1 ppm from a F_2PBr[7] internal standard. The coupling constants for H_2NPF_2 are independent of the spectrum from which they were obtained, as expected. Both the coupling constants and chemical shifts are consistent with the proposed formulation and are similar to values previously reported for alkylaminodifluorophosphines.[8]

The compound H_2NPF_2 exhibits gas-phase ir absorptions at 3520 (w), 3400 (w), 1546 (m), 972 (w), 960 (w), 953 (m), 945 (m), 940 (m), 932 (m), 884 (s, sh), 875 (s), 862 (s), and 804 (vs) cm^{-1}. We have assigned the absorptions 3519 and 3401 cm^{-1} to the asymmetric and symmetric N–H stretches, respectively. The band at 1547 cm^{-1} is assigned to the HNH bending mode. Upon deuteration these absorptions are shifted to 2640 (w), 2505 (w), and 1185 (m) cm^{-1} (theoretical: 2680, 2590, and 1178 cm^{-1}), which confirms the assignments. The absorptions at 875 and 804 cm^{-1} are assigned to the symmetric and asymmetric PF stretching modes. We are in the process of obtaining ir and Raman spectral data and will present a complete spectral analyses in a future publication.

The mass spectrum of H_2NPF_2 obtained at 74 V is consistent with the proposed formulation. It consisted of the following peaks (listed as the *m/e* ratio, relative intensity, and tentative assignments): 88, 5.8, PF_3^+; 86, 2.9, ?; 85, 100, $PF_2NH_2^+$; 84, 3.8, PF_2NH^+; 83, 1.0, PF_2N^+; 82, 1.9, ?; 81, 1.9, ?; 69, 61.5, PF_2^+; 66, 21.2, $PFNH_2^+$; 65, 3.8, $PFNH^+$; 64, 1.0, PFN^+; 50, 7.7, PF^+; 47, 1.9, PNH_2^+; 46, 34.8, PNH^+; 45, 2.9, PN^+; 31, 1.0, P^+. Peaks which we assign to fragments which contain H are shifted to higher mass numbers consistent with our assignments in the mass spectrum of D_2NPF_2. Molecular weight vapor density measurements gave values of 84.7, 87.9, and 89.9 g/mol which correspond well with the theoretical value for H_2NPF_2 of 85.0.

Preliminary microwave spectral data clearly show that a sample of H_2NPF_2 obtained as indicated in eq 1 and purified by codistillation does not contain any NH_3 as a contaminant, but does contain PF_3. This suggests the decomposition of H_2NPF_2 proceeds as follows

$$2H_2NPF_2 \longrightarrow (H_2N)_2PF + PF_3 \qquad (2)$$

We are investigating this possibility. Microwave spectral data also show that the hydrogen atom attached to nitrogen exchanges rapidly with deuterium atoms attached to water.

$$H_2NPF_2 + D_2O \rightleftarrows D_2NPF_2 + H_2O \qquad (3)$$

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