highest energy A′ mode in *cis*-$Mn(^{12}CO)_4(^{13}CO)(SO_2CH_3)$ and the shoulder at *ca.* 1995 cm^{-1} (g in Figure 2) to the ^{13}CO stretch in *trans*-$Mn(^{12}CO)_4(^{13}CO)(SO_2CH_3)$. The relative intensities of these absorptions indicate that a substantial amount of *trans*-$Mn(^{12}CO)_4(^{13}CO)(SO_2CH_3)$ is present in addition to the cis isomer. The Nujol mull spectrum of $Mn(^{12}CO)_4(^{13}CO)(SO_2CH_3)$ is qualitatively similar to that recorded for the CCl_4 solution.

Again the observation of isotopic scrambling does not permit differentiation between a nonstereospecific mechanism for the insertion, on one hand, and a rapid isomerization following the initial stereospecific sulfonylation, on the other. An attempted exchange between the CO's in $Mn(CO_5)(SO_2CH_3)$ and ^{13}CO in CH_3OH at 27° revealed no detectable incorporation of labeled CO in 24 hr.

The above result stands in sharp contrast to that on the carbonylation of $Mn(CO_5)CH_3$ using ^{13}CO. Only *cis*-$Mn(^{12}CO)_4(^{13}CO)(^{12}COCH_3)$ is obtained in the latter insertion.[6] Also pertinent is the finding[12] that the reaction of SO_2 with optically active π-$C_5H_5Fe(CO)_2$-$^*CH(CH_3)C_6H_5$ proceeds with substantial stereospecificity as concerns the asymmetric carbon.

In conclusion, we infer from these observations that synthesis of stereospecifically labeled complexes of the type $Mn(CO)_5X$ (and perhaps also those of other, related systems)[12a] will present a very formidable and, in some cases, an impossible task. Whether the difficulty is inherent in a structural nonrigidity (in the context of experimental isolation) of at least some of these compounds, cannot be ascertained at present. A recent study on $HMn(CO)_5$ shows[13] that any rearrangement which possibly leads to equivalence of the cis and trans CO groups with respect to isotopic exchange must be a slow process on the nmr time scale. However, the ranges in time scales for nmr spectroscopy and experimental isolation of isomeric species[14] render this finding of limited applicability to preparative studies.

Acknowledgment.—Support of this work through grants from the National Science Foundation (GP-8135 and GP-22544) is gratefully acknowledged.

[12] J. J. Alexander and A. Wojcicki in "Progress in Coordination Chemistry," M. Cais, Ed., Elsevier, New York, N. Y., 1968, pp 383–384.

[12a] NOTE ADDED IN PROOF.—$Mo(^{12}CO)_4(^{13}CO)NHC_5H_{10}$ preferentially labeled in the equatorial positions has been prepared by ultraviolet irradiation of $Mo(^{12}CO)_5NHC_5H_{10}$ and ^{13}CO in THF solution. See D. J. Darensbourg, M. Y. Darensbourg, and R. J. Dennenberg, *J. Amer. Chem. Soc.*, **93**, 2807 (1971).

[13] G. M. Whitesides and G. Maglio, *ibid.*, **91**, 4980 (1969).

[14] See, for example, E. L. Muetterties, *Inorg. Chem.*, **4**, 769 (1965).

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Synthesis of Trifluorophosphazodifluorophosphine from Aminodifluorophosphine

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Aminodifluorophosphine, PF_2NH_2, has recently been prepared from the reaction of ammonia with difluorohalophosphines.[1] Also, microwave spectral data indicated that the hydrogen atoms attached to the nitrogen exchanged rapidly with deuterium atoms of deuterium oxide to form PF_2ND_2.[1] It has now been found that both hydrogen atoms of the amino group can also be removed when dichlorotrifluorophosphorane, PF_3Cl_2, is used as a substrate and trifluorophosphazodifluorophosphine, $F_3P{=}NPF_2$, chlorodifluorophosphine, and ammonium chloride are the products

$$2PF_2NH_2 + PF_3Cl_2 \longrightarrow F_3P{=}NPF_2 + PF_2Cl + NH_4Cl \tag{1}$$

If, instead, hydrogen chloride or hydrogen difluorodithiophosphate are employed, scission of the P–N bond occurs to yield the amino and difluorophosphine groups

$$PF_2NH_2 + 2HX \longrightarrow PF_2X + NH_4X \tag{2}$$

where X = Cl or $SP(S)F_2$.

Experimental Section

Reagents.—Aminodifluorophosphine[1] and hydrogen difluorodithiophosphate[2] were prepared by the literature methods. Phosphorus trifluoride and chlorine, in lecture bottles, were obtained from the Ozark-Mahoning Co. and the Matheson Co., respectively. The PF_3Cl_2 was prepared by direct combination of Cl_2 with a slight excess of PF_3, was purified by trap-to-trap distillation, and was retained at −126°. Lecture bottles of dimethylamine and hydrogen chloride were procured from the J. T. Baker Co.

Technique and Instrumentation.—All volatile substances were handled within a standard Pyrex-glass vacuum system. The reactor in all syntheses was a 100-ml Pyrex-glass bulb with a stopcock attached. Infrared spectra were obtained with a Perkin-Elmer Model 621 grating spectrometer. A 10-cm path length cell with sodium chloride windows was used for gaseous samples. The spectra of solids were obtained as Nujol mulls between sodium chloride plates. The ^{19}F and ^{31}P nmr spectra were obtained with a Varian Model HA-100 spectrometer, operating at 94.1 and 40.5 HMz, respectively. Fluorotrichloromethane (internal) and 85% orthophosphoric acid (external) were used as standards. Samples were measured in 5-mm o.d. tubes at ambient temperature. A Varian CH-7 mass spectrometer operating at 70 eV was used to obtain the mass spectrum.

Synthesis of $F_3P{=}NPF_2$.—This reaction took place after combining PF_2NH_2 (0.72 mmol) and PF_3Cl_2 (0.40 mmol) at −196° and allowing the reactor to warm slowly and stand 15 min at room temperature. The products were slowly passed through cold traps at −95, −126, and −196°. The −126° trap held the $PF_3{=}NPF_2$ (0.35 mmol, 97% yield based on eq 1) and the −196° trap contained the PF_2Cl, along with trace quantities of POF_3 and PF_3 (0.37 mmol total). Hydrogen chloride also in a small quantity is sometimes observed as a product held in the latter trap. The white solid remaining in the reactor was identified as ammonium chloride by its infrared spectrum.

Properties of $F_3P{=}NPF_2$.—Trifluorophosphazodifluorophosphine is a white solid, mp $-87.2 \pm 0.7°$, and colorless liquid, bp 12.5° (extrapolated). The temperature dependence of the vapor pressure follows the equation $\log P_{mm} = 8.114 - (1494/T)$, determined by least squares, having a "goodness of fit" correlation coefficient equal to 0.998 and the standard error equal to 0.0146. Some measured vapor pressures at specified temperatures are as follows: 8.7 mm, −62°; 22.0 mm, −52.3°; 55.1 mm, −38.0°; 97.2 mm, −28.6°. The latent heat of vaporization is 6837 cal mol^{-1} and entropy of vaporization is 23.9 eu. The equation and thermodynamic constants are valid between −19.7 and −52.3°. Its molecular weight by the method of Regnault using a 208.2-ml bulb was measured to be 170.5 (calcd 170.9).

The following are the mass numbers (species) and relative abundances of the ions in the mass spectrum of $F_3P{=}NPF_2$: 171 ($PF_3NPF_2^+$), 38.7; 152 ($P_2F_4N^+$), 25.8; 102 (F_3PN^+), 54.8; 88 (PF_3^+), trace; 83 (F_2PN^+), 12.9; 69 (PF_2^+), 100; 64 (FPN^+),

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[1] J. E. Smith and K. Cohn, *J. Amer. Chem. Soc.*, **92**, 6185 (1970).

[2] R. W. Mitchell, M. Lustig, F. A. Hartman, J. H. Ruff, and J. A. Merritt, *ibid.*, **90**, 6329 (1968).

3.2; 50 (PF^+), 21.0; 45 (PN^+), 8.1; 31 (P^+), 3.2. The infrared and nmr spectra are considered in the Results and Discussion.

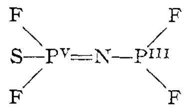
The compound was hydrolyzed by distilling 0.1731 g, 1.012 mmol, into a bulb with a Fischer-Porter valve containing excess 2 *N* NaOH. The solution was heated at 60° for 2 days. To analyze for nitrogen the ammonia produced was very carefully and slowly distilled out of the aqueous alkali and then redistilled twice through cold traps at −80 and −160°; the last held the ammonia. Both the pressure–volume–temperature relationship and the weight indicated 0.997 mmol of it corresponding to 98.5% recovery. The infrared spectrum of this ammonia at 50 mm indicated no impurities. The fluoride present in the hydrolysis solution was analyzed as triphenyltin fluoride.[3] The phosphorus was oxidized with concentrated nitric acid and measured by the titrimetric ammonium phosphomolybdate procedure.[4] The results are summarized. *Anal.* Calcd for F_5NP_2: F, 55.57; N, 8.24; P, 36.24. Found: F, 55.5; N, 8.12; P, 37.18.

Synthesis of PF_2Cl and $F_2P(S)SPF_2$.—Into the reactor were distilled PF_2NH_2 (0.365 mmol) and HCl (0.730 mmol). It was then allowed to warm to room temperature and its volatile contents distilled through traps cooled to −160 and −196°. That at −160° held the PF_2Cl (0.314 mmol, 83.2% yield based on eq 2) and the latter trap contained a small quantity of PF_3 and a trace of HCl. To prepare $F_2P(S)SPF_2$, PF_2NH_2 (0.608 mmol) and HPS_2F_2 (0.730 mmol) were condensed into the reactor and the reaction was allowed to progress in the same way indicated above. The volatile products were passed through traps maintained at −80 and −196°. The one at −80° retained the $PF_2SP(S)F_2$ (0.338 mmol, 92.2% yield) and the excess PF_2NH_2, and small quantities of PF_3 and an unidentified substance(s) were found in the −196° trap. The solids in the reactors were identified as the ammonium salts of the chloride and $PS_2F_2^-$ ions by their infrared spectra.

Results and Discussion

Fluorophosphorus compounds containing phosphorus in mixed valence states are rare. The only known examples were recently prepared by Cavell and coworkers[5,6] and DesMarteau,[7] and these are $F_2P(S)SPF_2$ and $F_2P(O)OPF_2$. Trifluoromethyl groups may be substituted for the fluorine atoms.[8] Also, the existence of F_3PPF has been speculated.[8] Trifluorophosphazodifluorophosphine, $F_3P{=}NPF_2$, is another example. However, in this case a nitrogen atom rather than an oxygen or sulfur atom separates the phosphorus atoms. The reaction between PF_2NH_2 and PF_3Cl_2 leads not only to $F_3P{=}NPF_2$ but also to PF_2Cl. These products may be explained by an initial reaction to give the phosphazo compound and hydrogen chloride. The hydrogen chloride would then react with PF_2NH_2 to give PF_2Cl according to eq 2. This second step must be rapid compared to the initial because HCl is rarely observed as a product. Equation 2 also provides a method for the synthesis of $F_2P(S)SPF_2$, recently prepared by a similar procedure employing a dialkylamidodifluorophosphine and HPS_2F_2.[6]

Spectroscopic analysis corroborates the proposed structural formulation given below for $F_3P{=}NPF_2$. The infrared spectrum of the compound has a complex, broad band having maxima at 1532 (m), 1460 (s), and 1416 cm^{-1} (ms) assigned to the P=N stretching frequency. The spectra of other trifluorophosphazo compounds also exhibit strong, broad, and complex absorptions in the same region.[9] A very strong-intensity absorption at 980 cm^{-1} having a shoulder at 964 cm^{-1} is associated with the PF_3 group P–F stretching vibration[9] while a broad peak at 816 cm^{-1} (m) is due to the PF_2 group stretching motion. Other PF_2-containing compounds display strong-intensity absorptions in this region, *e.g.*, PF_2Cl at 864 and 853, PF_2NH_2 at 875 and 804, and P_2F_4 at 842, 830, and 820 cm^{-1}.[10] Another unassigned band is centered at 675 cm^{-1} (wm). Further confirmation is obtained from the nmr spectra. The ^{19}F spectrum appears as a pair



of doublets of quadruplets centered at ϕ 45.72 ppm due to the PF_2 group and a doublet of triplets at ϕ 82.76 ppm for the PF_3 group fluorine atoms. The coupling constants are J_{P^V-F} = 1031 Hz, $J_{P^{III}-F'}$ = 1279 Hz, $J_{F-F'}$ = 7 Hz, and $J_{P^V-F'}$ = 24.1 Hz. No coupling is observed between P^{III} and F. The ^{31}P spectrum shows a triplet at low field, −129 ppm (J = 1290 Hz), and a quadruplet at high field, 43.6 ppm (J = 1027 Hz). Both the chemical shift and the coupling constants of the $F_3P{=}N-$ moiety in the ^{19}F spectra of other trifluorophosphazo compounds are close to the values reported above, *viz.*, ϕ 86.7 ppm (J = 1090 Hz) in the spectrum of $F_3P{=}NSO_2F$ and ϕ 85.2 ppm (J = 1045 Hz) in that of $F_3P{=}NP(S)F_2$,[9] and the chemical shift and P—F coupling constant of the PF_2 group fluorine nuclei are in the expected range.[6,11]

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Mass Spectrometric Evidence of Dimers in Bismuth Pentafluoride and Antimony Pentafluoride

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The group V pentafluorides show a wide range in physical and chemical properties.[1] While PF_5 (bp −84.5°) and AsF_5 (bp −52.6°) are gases, SbF_5 (bp 149°) is a viscous liquid, and BiF_5 (mp 151°) is a sublimable solid. The BiF_5 is the strongest oxidative fluorinating agent,[2,3] but the irregular order of strengths

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