Acknowledgment. These investigations were supported in part by Grant GP-27984X between the National Science Foundation and the University of Southern California.

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Fluorophosphine Ligands. IX. Reactions of Difluorophosphine with Alcohols

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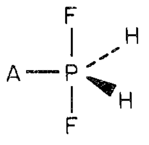
Received December 19, 1972

The controlled interaction of alcohols and primary or secondary amines with halophosphines is known to proceed in accordance with the general equation

$$PR_yX_{3-y} + AH \rightarrow HX + PR_yX_{2-y}A$$

where AH equals amine or alcohol, X equals halogen, and R signifies any other group.[2] Removal of HX through interactions with a suitable base will drive the reaction to completion. Yields are generally good with few side products. One of the most logical mechanisms for this process involves a pentacoordinate phosphorus intermediate.[3] The pentacoordinate complexes of general compositions $HF_2P{\cdot}HOR$ and $HF_2P{\cdot}HSR$ have now been isolated at low temperatures. The adducts have been unequivocally characterized as five-coordinate species by spectroscopic techniques. The data support the expected trigonal-bipyramidal structure with the fluorines in the apical positions



where A is OR or SR

Although several alkoxyfluorophosphoranes have been isolated,[4-6] the adducts reported herein are the first reported cases of a dihydridoalkoxyfluorophosphorane.[7,8]

Experimental Section

Materials and General Techniques. The F_2PH was prepared by literature methods.[9] Thioethanol was obtained from Eastman Organic Chemicals and used without purification. High-vacuum techniques were used throughout. Infrared spectra were recorded on a Beckman IR-20 using a gas cell with KBr windows. Nmr spectra for ^{19}F and ^{1}H were recorded on a Varian HR 56/60 spectrometer operating at 56 Hz for ^{19}F and 60 Hz for ^{1}H at −60°. Chemical shifts for fluorine are referred to $CFCl_3$ by tube interchange; for protons tetramethylsilane was used as an internal standard. Spectra for ^{31}P were obtained on a Varian HA-100 spectrometer operating at 40.4 Hz at −60°. Chemical shifts are referred to H_3PO_4 as external standard (tube interchange).

Synthesis of H_2F_2POR. Equimolar samples of HPF_2 and ROH ($R = CH_3, C_2H_5$) were condensed at −196° into a 75-cm^3 reaction bulb. The mixture was allowed to warm slowly to 0°. The sample was condensed rapidly into an nmr tube at −196° after which the tube was sealed. Decomposition in the gaseous state at room temperature occurred in less than 1 min. For this reason temperatures were held below 0°.

Nmr and Ir Spectra for $F_2H_2POCH_3$. The ^{19}F spectrum consists of a doublet (δ 40 ppm, $J_{FP} = 713$ Hz) each member of which is split into a triplet ($J_{FPH} = 104$ Hz). The ^{31}P spectrum is a triplet (δ 39.8 ppm, $J_{PH} = 805$ Hz) each member of which is split into a triplet ($J_{PF} = 704$ Hz). No further splitting was observed. The proton spectrum is a doublet (δ_{HP} −6.6 ppm, $J_{HP} = 813$ Hz) each member of which is split into a triplet ($J_{HPF} = 103$ Hz). The methyl protons appeared as a doublet (δ_{H_3C} −3.4 ppm, $J_{HCOP} = 11$ Hz). Infrared spectra in the P–H stretching region showed (gas phase) ν_s 2450 cm^{-1} and ν_{as} 2530 cm^{-1}. The data confirm the structure written.

Nmr and Ir Spectra for $F_2H_2POC_2H_5$. The ^{19}F spectrum is a doublet (δ_F 38.5 ppm, $J_{FP} = 711$ Hz) with each member split into a triplet ($J_{FPH} = 102$ Hz). The ^{31}P spectrum is a triplet (δ_P 38.2 ppm, $J_{PH} = 811$ Hz) with each member split into a triplet ($J_{PF} = 703$ Hz). The ^{1}H spectrum is a doublet (δ_{HP} −6.8 ppm, $J_{HP} = 804$ Hz) with each member split first into a triplet ($J_{HPF} = 102$ Hz). The methyl protons appear as a triplet (δ_{H_3C} −1.2 ppm, $J_{HCCH} = 11$ Hz) and the methylene protons appear as a quintet (δ_{H_2C} −3.9 ppm, $J_{HCCH} = 11$, $J_{HCOP} = 11$ Hz). Infrared spectra in the P–H stretching region show (gas phase) ν_s 2450 cm^{-1} and ν_{as} 2530 cm^{-1}.

Synthesis of $C_2H_5SPF_2H_2$. Equimolar samples of C_2H_5SH and PF_2H were condensed at −196° into a 75-cm^3 reaction vessel. On warming to 0°, a reaction occurred, but it was accompanied by extensive product decomposition. The impure product was held at −78° while the PH_3 and PF_3 were pumped off. The purified sample was then warmed to 0° and condensed into an nmr tube. A nonvolatile oil remained in the reaction vessel.

Nmr and Ir Spectra for $C_2H_5SPF_2H_2$. The ^{19}F pattern was identical in form with that observed for PF_2H_2OR (δ_F 28.9 ppm, $J_{FP} = 824$ Hz, $J_{FPH} = 109$ Hz); the ^{31}P pattern was a quintet resulting from the overlap of two triplets of triplets (δ_P 13.5 ppm, $J_{PH} = 840$ Hz, $J_{PF} = 840$ Hz). The infrared P–H stretching frequencies in the gas phase appear as ν_s 2475 cm^{-1} and ν_{as} 2540 cm^{-1}.

Results and Discussion

The nmr data at low temperature (−60°) support the expected trigonal-bipyramidal structure with the two fluorine atoms in the axial position. The PF coupling constant for $PF_2H_2OCH_3$ ($J_{PF} = 713$ Hz) and the comparatively low fluorine chemical shift (δ 40 ppm) are characteristic of axial fluorine atoms in difluorophosphoranes.[10] Further proof for the axial assignments is seen when comparing $CH_3OPF_2H_2$ with $C_6H_5PF_3OR$.[11] In $C_6H_5PF_3OR$ the axial fluorine appears as a doublet at 41 ppm ($CFCl_3$) with a J_{PF} of 830 Hz. The equatorial fluorine in $C_6H_5PF_3OR$ appears at 66 ppm ($CFCl_3$) with a J_{PF} of 975 Hz. The fluorine atoms in $H_2PF_2OCH_3$ appear at 40 ppm and show a J_{PF} of 713 Hz. Thus at the lowest temperature of the instrument the nmr offers direct evidence for the axial assignments for the fluorine and suggest no pseudorotation. At higher temperatures a broadening of the peaks occurs suggesting an exchange process (pseudorotation, dissociation of the adduct, etc.).

Registry No. $H_2F_2POCH_3$, 39023-06-8; $H_2F_2POC_2H_5$, 39023-07-9; $C_2H_5SPF_2H_2$, 39023-08-0.

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Acknowledgment. The support of this work through NSF Grant GP-32079 is gratefully acknowledged.

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Partial Hydrolysis of Rhenium and Osmium Hexafluorides. An Improved Synthesis and Characterization of Rhenium Oxide Tetrafluoride

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Received August 30, 1972

Simple transition metal oxide tetrafluoride compounds, MOF_4, have been known for some time. A convenient, general synthesis for the compounds, however, has not been described. In particular, rhenium oxide tetrafluoride was reported by Hargreaves and Peacock[2] as an unexpected but major product of the reaction between ReF_6 and metal carbonyls, *e.g.*, $W(CO)_6$. In our laboratory only small amounts of $ReOF_4$ have been isolated from this reaction. This observation is in agreement with a recent study by O'Donnell and Phillips[3] which indicated that under rigorously dry conditions a rhenium carbonyl fluoride, $Re(CO)_3F_3$, is the major product of the above reaction. Osmium oxide tetrafluoride was recently reported by Falconer and coworkers[4] to be a product of the reduction of $OsOF_5$ by a hot tungsten filament.

In the light of these studies, a general, improved synthesis for MOF_4 compounds was desired. We report here on a simple, high-yield synthesis of $ReOF_4$ from the partial hydrolysis of ReF_6. The initial hydrolysis chemistry of ReF_6 and OsF_6 also is qualitatively compared.

Experimental Section

The manipulation of the volatile compounds was accomplished in a Monel vacuum line[5,6] fitted with Pyrex glass reaction vessels and auxiliary Kel-F U traps. The metal vacuum line and Kel-F U traps were conditioned with fluorine and ClF_3. The glass reaction vessels were flamed and/or evacuated as described below but were not chemically conditioned. The ReF_6 and OsF_6 were prepared by known methods.[7,8] The metal hexafluorides were freed of trace amounts of HF by pumping on the samples held at −78°. Conductivity grade anhydrous HF was provided by L. A. Quarterman, Argonne National Laboratory.[9]

The mass spectra were recorded with a modified Bendix Model 12 time-of-flight mass spectrometer. The vapors above the solids (25°) were sampled directly into the ion source region. Thin-film infrared spectra were recorded on a Beckman IR-9 spectrophotometer (4000–400 cm^{-1}); the low-temperature cell will be described elsewhere.[10] The Raman spectra were recorded on the instrument described by Claassen and coworkers.[11] The 4880-Å Ar^+ laser excitation line was used, and the $ReOF_4$–HF (conductivity grade) solution was contained in a $^1/_4$-in. o.d. Kel-F sample tube. The conductivity of $ReOF_4$–HF solutions was measured as described by Frlec and Hyman.[12] The cell constant was 0.04214 cm^{-1} and all measurements were recorded at 0°.

Hydrolysis of ReF_6. A new 250-ml Pyrex flask was thoroughly evacuated and flamed until a good vacuum was obtained (*ca.* 10^{-6} Torr).[13] A 2.0-mmol sample of ReF_6 was condensed into the flask; the flask was closed with a high-pressure valve and warmed to 25°. After 2 weeks no reaction was detected, and the ReF_6 was quantitatively recovered.

In a second procedure a new 250-ml Pyrex flask was pumped for 1 hr to *ca.* 10^{-4} Torr without flaming. A 4.0-mmol sample of ReF_6 was condensed into the flask and then held at 25° for 2 weeks. The volatile products were vacuum distilled and retained as follows: HF, BF_3, SiF_4 (−196°), ReF_6 (−78°). About 80% of the ReF_6 was recovered. A small amount of blue crystalline material was sublimed at 60° from the glass reactor. When an identical reaction was run at 70°, conversion of the ReF_6 went noticeably faster and blue crystals sublimed out of the heated zone onto cooler surfaces of the flask. The volatile products were vacuum distilled as outlined above and about 40% of the ReF_6 was recovered unreacted. Higher reaction temperatures generally led to significant decomposition of the blue solid.

In a third system a new 250-ml Pyrex flask was loosely packed with Pyrex wool and the flask pumped for 30 min to *ca.* 10^{-4} Torr. A 5.0–7.0-mmol sample of ReF_6 was condensed into the flask; the flask was closed with a high-pressure valve and warmed to 25°. The glass wool was slowly coated with a gray-brown deposit and tiny blue crystals. After 7–10 days, the volatile reaction products were distilled as described above. About 30% of the ReF_6 was recovered unreacted and about 1 g of blue solid was collected (*ca.* 60% yield $ReOF_4$). Similar reactions run at higher temperatures (50–70°) resulted in a faster reaction, but more gray deposits and less blue solid were produced. The blue solid was characterized as outlined below and found to be $ReOF_4$.

The 1:1 reaction of water and ReF_6 also was investigated. In all experiments less than 10% $ReOF_4$ was obtained, and considerable quantities of black nonvolatile solids were formed.

Hydrolysis of OsF_6. A 5.0-mmol sample of OsF_6 was condensed into a thoroughly flamed and evacuated (*ca.* 10^{-6} Torr[13]) Pyrex reaction vessel. The flask was held at 25° for 5 days with no apparent reaction. In a second procedure, a 3.2-mmol sample of OsF_6 was condensed into a new 250-ml Pyrex flask which had been pumped for 1 hr to *ca.* 10^{-4} Torr. The flask was held at 25° for 5 days with no apparent reaction. In a third procedure, a new 250-ml Pyrex flask loosely packed with Pyrex wool was pumped for 30 min to *ca.* 10^{-4} Torr without flaming. A 4.0-mmol sample of OsF_6 was condensed into the flask. The flask was held at 25° for 2 weeks with no apparent reaction. Similar reactions run at higher temperatures (70–80°) produced small yields (*ca.* 20% OsF_6 consumed) of a slightly volatile yellow solid. The yellow solid sublimed with decomposition at 90°.

Characterization of Products. The blue, moisture-sensitive, crystalline solid obtained from the hydrolysis of ReF_6 was found to sublime at *ca.* 60° and melt at *ca.* 109°. The mass spectrum of the vapors above the solid at 25° was recorded and the principal ions are listed here [*m/e* (assignment) relative intensity]: 279 ($^{187}ReOF_4^+$) 16, 277 ($^{185}ReOF_4^+$) 9, 263 ($^{187}ReF_4^+$) 3, 261 ($^{185}ReF_4^+$) 2, 260 ($^{187}ReOF_3^+$) 100, 258 ($^{185}ReOF_3^+$) 53, 257 ($^{187}ReO_2F_2^+$) 3, 255 ($^{185}ReO_2F_2^+$) 2, 244 ($^{187}ReF_3^+$) 5, 242 ($^{185}ReF_3^+$) 3, 241 ($^{187}ReOF_2^+$) 10, 239 ($^{185}ReOF_2^+$) 7, 225 ($^{187}ReF_2^+$) 8, 223 ($^{185}ReF_2^+$) 4, 222 ($^{187}ReOF^+$) 6, 220 ($^{185}ReOF^+$) 4, 206 ($^{187}ReF^+$) 7, 204 ($^{185}ReF^+$) 4, 203 ($^{187}ReO^+$) 3, 201 ($^{185}ReO^+$) 2, 187 ($^{187}Re^+$) 2, 187 ($^{187}Re^+$) 10, 185 ($^{185}Re^+$) 6. The infrared spectrum of a cold (−196°), sublimed thin-film sample was recorded and the absorptions (cm^{-1}) are as follows: 1075 (s), 710 (sh, m), 655 (s), 605 (sh, m), 555 (m). The Raman spectrum of a 3.8 *m* solution of $ReOF_4$ in HF was recorded at 25°. The bands (cm^{-1}) are 1072 (vs, pol), 667 (w), 303 (m), 256 (m), 245 (m), 168 (w, br). The solution was dark blue. The specific conductance of anhydrous HF at 0° was $\kappa_{solv} = 2.593 \times 10^{-5}$ ohm^{-1} cm^{-1}. The specific conductance at 0° of a 0.1004 *M* HF solution of $ReOF_4$ was $\kappa_{soln} = 35.8 \times 10^{-5}$ ohm^{-1} cm^{-1} which results in $\kappa_{soln}{}^{cor} = 33.2 \times 10^{-5}$ ohm^{-1} cm^{-1}. The equivalent conductance

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