were measured relative to sodium 3-(trimethylsilyl)-1-propanesulfonate (DSS) as internal standard for all solutions except the strongly basic ones, in which it was insoluble. For these solutions, DSS was used as an external standard.

Buffer solutions were prepared to approximate pH values and known, high ionic strengths. Appropriate amounts were taken to ensure total ionic strengths of 1.0 in the solutions studied. Both J_{PH} and pH were measured values for the same solution.

CONTRIBUTION FROM ROHM AND HAAS COMPANY,
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Nucleophilic Displacement of Bromide from Phosphorus with Some 2-Substituted Perfluoroisopropoxide Anions. Formation of μ-Oxo-difluorophosphine, μ-Oxo-difluorophosphoryl, and μ-Oxo-difluorothiophosphoryl Compounds

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A series of new μ-oxo-fluorophosphorus compounds—2-cyano-2-(μ-oxo-difluorophosphine)hexafluoropropane, 2-cyano-2-(μ-oxo-difluorophosphoryl)hexafluoropropane, 2-cyano-2-(μ-oxo-difluorothiophosphoryl)hexafluoropropane, 2-azido-2-(μ-oxo-difluorophosphoryl)hexafluoropropane, 2-isothiocyanto-2-(μ-oxo-difluorophosphoryl)hexafluoropropane, 2-thiocyanato-2-(μ-oxo-difluorophosphoryl)hexafluoropropane, and 2,4-bis(trifluoromethyl)-4-(μ-oxo-difluorophosphine)-3-azapentene-2—has been synthesized. These compounds were prepared by the reaction of the corresponding 2-halogenoidoperfluoroisopropoxide anion with the appropriate phosphorus(III) bromide difluoride or phosphorus(V) oxide bromide difluoride. The synthetic methods and some physical properties of these compounds are recorded and discussed.

Several μ-oxo-fluorophosphate(III) esters of the type $(CF_3)_2C(X)OPF_2$, where X = Br, I, or H, have been prepared by the addition of phosphorus bromide difluoride, PF_2Br, or phosphorus iodide difluoride, PF_2I, to hexafluoroacetone, HFA, and by the reaction of the PF_2I–HFA addition compound with hydrogen iodide in the presence of mercury.[2] However, these methods for the synthesis of μ-oxo-difluorophosphorus compounds have limited application.[2] A more general approach has been found which involves reactions employing halogenoidohydrin salts.

Halogenated ketones are known to form stable addition compounds with sodium cyanide[3] and the resulting cyanohydrin salts have been shown[3b] to undergo esterification in the presence of an acyl, sulfur, or phosphorus chloride or an anhydride. We have used this approach to include the reactions of phosphoryl and thiophosphoryl bromide difluoride and phosphorus bromide difluoride with sodium 2-cyanoperfluoroisopropoxide, $Na^+(CF_3)_2C(CN)O^-$, to prepare the corresponding μ-oxo esters. This general method has been extended to include other halogenoidohydrin salts, derived from the ligands N_3^- and SCN^-. The latter were prepared *in situ* as the precursors to the fluorophosphate esters. When the OCN^- ion was allowed to react with HFA, carbon dioxide was evolved, and the resulting solid reacted with PF_2Br to yield the interesting new azapentene, $(CF_3)_2C{=}NC(OPF_2)(CF_3)_2$, containing the μ-oxo-difluorophosphine group.

Experimental Section

Reagents.—The PF_2Br,[2] POF_2Br,[2,4,5] PSF_2Br,[4,5] and $Na^+(CF_3)_2C(CN)O^-$ [3a] were synthesized and purified by known methods. The NaCN, NaN_3 NaOCN, NaSCN, and the HFA were obtained from the General Chemical Division of the Allied Chemical Corp. The salts were dried by pumping *in vacuo* at 100° and were used without further purification. The nitrobenzene, which was stored over 5A molecular sieves, was procured from the Eastman Kodak Co. Spectroquality acetonitrile was obtained from Matheson Coleman and Bell, Division of the Matheson Co.

Apparatus and General Procedure.—A standard Pyrex vacuum apparatus was used for transfer and purification of volatile materials. Mercury manometers were covered with Kel-F No. 10 oil. The μ-oxo phosphorus derivatives were prepared in 50-ml Pyrex bulbs each fitted with a Fischer-Porter Teflon valve. Gaseous mixtures were characterized by pressure-volume-temperature (*PVT*) measurements and analyzed mass spectrometrically. Solids and liquids of low volatility were handled within a nitrogen drybox.

$(CF_3)_2C(CN)OPF_2$.—In a typical experiment 4.06 mmol each of $Na^+(CF_3)_2C(CN)O^-$ and PF_2Br were added together to the reactor at $-196°$. The bulb was allowed to warm to room temperature over a 15-min period and was allowed to stand an additional 15 min. The volatile products were then passed through a set of traps at -95, -126, and $-196°$. The $-95°$ trap caught pure $(CF_3)_2C(CN)OPF_2$ (3.05 mol, 75.1% yield), the $-126°$ trap caught a small amount of an unidentified material as well as a trace of the μ-oxo derivative, and the last trap held PF_3 (0.25 mmol), PF_2OPF_2 (0.27 mmol), and traces of CO_2 and POF_3. *Anal.* Calcd for C_4F_8NOP: C, 18.40; F, 58.23; N, 5.37; P, 11.86. Found: C, 18.37; F, 58.0; N, 5.48; P, 11.4.

$(CF_3)_2C(CN)OP({=}O)F_2$.—A mixture of the sodium cyanohydrin salt and POF_2Br (5.60 mmol each) was treated as above. The $(CF_3)_2C(CN)OP({=}O)F_2$ (4.88 mmol, 87.1% yield) was caught in the $-95°$ trap. *Anal.* Calcd for $C_4F_8NO_2P$: C,

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TABLE I

INFRARED SPECTRA FREQUENCIES (cm^{-1})

$(CF_3)_2C(CN)$-OPF_2	$(CF_3)_2C(CN)OP$-$(=O)F_2$	$(CF_3)_2C(CN)OP$-$(=S)F_2$	$(CF_3)_2C(N_3)OP(=O)F_2$	$(CF_3)_2C(NCS)OP(=O)F_2$ and $(CF_3)_2C(SCN)OP(=O)F_2$[a]	$(CF_3)_2C=$$NC(OPF_2)(CF_3)_2$
2272 w, sp	2283 w, sp	2272 w, sp	2298 vs	2183	1739 mw
1360 vs	1408 vs	1342 sh	2267 w	2088[b]	1326 s
1250 vs	1316 vs	1312 vs	2160 s	2040 sh	1295 s
1220 m	1258 vs, complex	1266 vs, complex	1389 s	2012 vs	~1260 vs, complex
1190 m	1227 sh	1226 m	1333 w	1399	1215 vs
1150 s	1199 m	1198 mw	1267 vs, complex	1297	1179 ms
1130 ms	1162 vs	1163 s	1190 w	1258 vs, complex	1169 sh
1070 s	1136 sh	1138 m	1076 s	1188	1125 s
976 s	1074 vs	1083 s	1038 ms	1136 vs	1085 ms
891 s	980 vs	978 vs, complex	1012 s	1094[b]	982 s
862 s	950 vs	939 s	970 s, complex	980 vs	884 ms
847 s	868 ms	909 s	868 m	955 vs	861 ms
833 s	725 s	764 w	765 w	926	850 vs
720 s	640 m	730 ms	614 m, complex	893[b]	753 mw
653 m	565 w	717 s	537 w	862	724 s
500 w, sh	538 w	598 wm	498 s	749	610 m
485 m, sp	500 s	540 vs	473 ms	717	581 mw
473 ms, sp	472 ms	475 ms	~460 sh	658	550 vs
460 s, sh	448 m	438 ms	~450 sh	600	532 w
440 w, sh	380 w	410 w	400 w	581[b]	505 mw
380 w				553	410 vs
				497	
				470	
				444	
				401	
				397 sh	

[a] Intensities are given only for those bands of very strong intensity due to the presence of an isomeric mixture and the probable overlapping of some bands. [b] Bands tentatively assigned to thiocyanate isomer.

17.34; F, 54.87; P, 11.18. Found: C, 17.50; F, 54.4; P, 11.6.

$(CF_3)_2C(CN)OP(=S)F_2$.—Sodium 2-cyanohexafluoroisopropoxide (4.35 mmol) and PSF_2Br (3.42 mmol) were combined at −196°. The mixture was heated at 45° for 10 hr; then the product was purified as above. The $(CF_3)_2C(CN)OP(=S)F_2$ (2.08 mmol, 60.8% yield) was caught at −95°, the PSF_2Br (trace) at −126°, and the PSF_3 (0.85 mmol) at −196°. *Anal.* Calcd for C_4F_8NOPS: C, 16.30; F, 51.85; N, 4.78. Found: C, 16.50; F, 51.8; N, 5.01.

$(CF_3)_2C(N_3)_2OP(=O)F_2$.—To NaN_3 (10.89 mmol) in nitrobenzene (1.5 ml) HFA (8.71 mmol) was added and the mixture was stirred at room temperature for 25 hr at which time *PVT* measurements indicated that 6.6 mmol of HFA had been consumed. POF_2Br (7.31 mmol) was added to this mixture at −196° and the mixture was brought slowly to room temperature and stirred for 20 min. Separation of the volatiles was achieved with distillation traps at −45, −95, and −196°. The first trap caught the nitrobenzene, the −95° trap the $(CF_3)_2C(N_3)OP(=O)F_2$ (4.72 mmol, 64.6% yield), and the last trap the POF_3 (0.35 mmol) and HFA. *Anal.* Calcd for $C_3F_8N_3O_2P$: C, 12.30; F, 51.87; N, 14.34; P, 10.57. Found: C, 12.22; F, 50.8; N, 14.48; P, 10.3.

$(CF_3)_2C(NCS)OP(=O)F_2$ and $(CF_3)_2C(SCN)OP(=O)F_2$.—The reactants, NaSCN and HFA (7.32 mmol each), were stirred in 1.5 ml of nitrobenzene for 24 hr at room temperature. Although there was no absorption, 7.13 mmol of POF_2Br was added. After stirring for 30 min the gaseous products were passed through traps at −45, −95, and −196°. The −196° trap contained traces of POF_3 and HFA. The −95° trap contained the thiocyanate and isothiocyanate mixture, present in a 1.0:4.5 molar ratio, respectively, according to the ^{19}F spectrum. Nitrobenzene was retained in the −45° trap.

The isomers were refractionated by their very slow distillation through a trap set at −64° and into another at −95° (4.53 mmol, 63.5% yield). During this fractionation the contents of both traps were periodically monitored by infrared spectral analysis. Accordingly, the thiocyanato isomer appears to be the more volatile as the infrared spectrum of the sample which first passed through the trap at −64° showed a small relative intensity increase of the bands at 2088, 1094, 893, and 581 cm^{-1}, tentatively assigned to this isomer (see Table I). The isothiocyanato compound constituted the major fraction of this sample. Further purification was not achieved because the mixture did not survive passage through the gas chromatographic columns of perfluorotri-*t*-butylamine, Kel-F No. 10 oil, and diisodecyl phthalate, each on each on Chromosorb P.

Because of the presence of minor, unidentified impurities, no chemical analyses, molecular weight determinations, or vapor pressure measurements were obtained. Therefore, these compounds are considered to be only partially characterized, although the spectra properties provide adequate structural information. The spectral absorptions assumed to be due to the impurities are not reported. According to ^{19}F nmr measurements, there is no change in relative abundance of these isomers on allowing the mixture to stand 14 days in a sealed tube.

$(CF_3)_2C=NC(OPF_2)(CF_3)_2$.—NaOCN and HFA (13.0 mmol each) were stirred for 30 min in nitrobenzene (5 ml). During this interval, the solid appeared to dissolve partially and then to settle out. Approximately 6.5 mmol of CO_2 was then pumped away and 5.2 mmol of PF_2Br was added. After stirring for 1 hr more, the volatile products were passed through traps at −45, −95, and −196°. The −196° trap retained 0.7 mmol of an approximately equimolar mixture of HFA and PF_3. The trap at −45° held nitrobenzene and the trap at −95° contained the aza compound (2.37 mmol, 45.4% yield). Further purification was accomplished by passing the azapentene through a chromatograph equipped with a 10-ft column consisting of Kel-F No. 10 oil, 20% by weight, on Chromosorb P, regular 80–100 mesh. The helium flow rate was 60 ml/min and the retention time was 7.1 min at 10.0°. *Anal.* Calcd for $C_6H_{14}NOP$: C, 18.06; F, 66.66; N, 3.51. Found: C, 18.07; F, 66.0; N, 3.78.

Reaction of $Cs^+(CF_3)_2CFO^-$ with PF_2Br.—Cesium heptafluoroisopropoxide was prepared by the reaction of 5.39 mmol of CsF and a slight excess of HFA in 2 ml of CH_3CN. After stirring for 24 hr the excess HFA was vented and 5.33 mmol of PF_2Br was added. The resulting mixture was stirred for 30 min. The volatile phase was passed through traps at −126 and −196°. The latter contained a nearly quantitative yield of almost equal quantities of PF_3 and HFA.

Analyses.—Carbon and nitrogen analyses were performed by conventional combustion. To determine phosphorus, samples were burned in an oxygen flask, and the products were absorbed in 6 *N* nitric acid. The resulting phosphate was measured by the phosphovanadomolybdate spectrophotometric method. Fluorine was analyzed by reduction of the compounds with lithium in *n*-propylamine followed by distillation of the fluoride as H_2SiF_6 and titration with thorium nitrate. The results have been given above.

Physical Properties. A. Infrared Spectra.—The spectra in the 4000–250-cm^{-1} region were taken with a Perkin-Elmer 521 spectrophotometer using a 10-cm path length gas cell with CsBr windows at sample pressures <15 mm. See Table I for the data.

B. Mass Spectra.—A Consolidated Engineering Corp. Model 61-620 spectrometer with a heated inlet system and operating at an ionization potential of 100 eV was used. The results are summarized in Table II.

C. Nmr Spectra.—The ^{19}F and ^{31}P nmr spectra were taken with a Varian Model V4310 spectrometer operating at 40 and 12.8 Mc, respectively. Samples were measured at ambient temperature in 5-mm o.d. Pyrex tubes using CCl_3F as an internal fluorine standard and H_3PO_4 as an external phosphorus standard. The fluorine spectra are given in Table III, and the ^{31}P data are given in the Discussion.

D. Ultraviolet Spectrum.—The spectra were obtained with a Beckmann Model DK-1 recording spectrometer. An *n*-hexane solution of $(CF_3)_2C(NCS)OP({=}O)F_2$, present as an isomeric mixture, shows λ_{max} at 294 mμ and $\epsilon_{max} \simeq 621$. The extinction coefficient has been calculated from the experimentally determined value after measuring the relative concentration of each isomer in a solution of known concentration by ^{19}F nmr spectroscopy.

E. Vapor Pressures.—Vapor pressure measurements were made by the method of Foord.[6] Tables IV and V give the vapor pressure and the thermodynamic data. Cathetometers were employed for measuring the pressure indicated by a mercury manometer and the null point of the spoon gauge. All the vapor pressures listed are precise to within 0.2 mm.

F. Melting Points.—Melting points were observed visually. Samples containing 5-mm o.d. Pyrex tubes were immersed in an alcohol cold bath held in a dewar flask with an unsilvered strip. The bath warmed at ~0.25°/min. See Table IV. All temperatures were measured with a potentiometer using a copper–constantan thermocouple. The accuracy of the measurements are within 0.1°. It is assumed that the sample and bath temperatures deviate less than the temperature measurement error.

G. Molecular Weights.—Molecular weights were obtained from vapor density measurements assuming ideal gas behavior. A 208.2-ml Pyrex bulb was used and pressure measurements, accurate to ±0.2 mm, were made using a mercury manometer read with the aid of a cathetometer. Molecular weights: $(CF_3)_2C(CN)OPF_2$, 261.0 (calcd, 261.0); $(CF_3)_2C(CN)OP({=}O)F_2$, 278.6 (calcd, 277.9); $(CF_3)_2C(CN)OP({=}S)F_2$, 294.0 (calcd, 293.1); $(CF_3)_2C(N_3)OP({=}O)F_2$, 292.3 (calcd, 293.0); and $(CF_3)_2C{=}NC(OPF_2)(CF_3)_2$, 395.3 (calcd, 399.1).

Results and Discussion

The substitution of the bromine atom on phosphorus with fluoroorganoisopropoxide anions provides a simple, high-yield method of preparing μ-oxo derivatives. The effectiveness of the method depends upon the nature of the halogenoid ligand, L^-, upon which also depends the stability of the halogenoidoisopropoxide ion. When $L^- = CN^-$, the cyanohydrin salt is stable and can be isolated. It may be used with the desired phosphorus bromide and the phosphate esters may be prepared this way in the absence of a solvent, whereas previous workers have used CH_3CN[3a] or ethers[3b] as

Table II

Mass Spectra[a]

Mass number (species) relative abundance

$(CF_3)_2C(CN)OPF_2$: 12 (C^+) 0.5, 14 (N^+) 0.1, 25 (CF_2^{2+}, PF^{2+}) 0.9, 26 (CN^+) 0.4, 28 (CO^+) 1.3, 31 (CF, P^+) 5.9, 38 (C_2N^+) 0.6, 47 (COF^+, PO^+) 1.6, 50 (CF_2^+, PF^+) 3.6, 54 ($COCN^+$) 5.2, 57 ($CFCN^+$) 0.4, 66 (CF_2O^+, POF^+) 0.5, 69 (CF_3^+, PF_2^+) 100.0, 70 (i[b]) 1.0, 76 (CF_2CN^+) 1.0, 78 ($C_2F_2O^+$, $COPF^+$) 1.0, 85 (C_2FOCN^+, POF_2^+) 4.1, 88 (PF_3^+) 5.0, 95 (CF_3CN^+, PF_2CN^+) 1.0, 97 ($C_2F_3O^+$, $COPF_2^+$ (2.5, 104 ($C_2F_2OCN^+$, $COPFCN^+$, POF_3^+) 4.4, 107 ($C_2F_3CN^+$) 0.6, 119 ($C_2F_5^+$) 0.5, 128 ($C_3F_4O^+$) 0.5, 128 ($C_3F_4O^+$, $C_2F_3O^+$) 1.9, 147 ($C_3F_5O^+$, $C_2F_4OP^+$) 0.2, 150 ($C_3F_6^+$) 2.2, 154 ($C_2F_3OPCN^+$) 2.5, 192 ($C_3F_6OCN^+$, $C_2F_3OPF_2CN^+$) 1.6, 242 ($C_3F_7OPCN^+$) 1.4, 261 ($C_3F_8OPCN^+$) 1.3.

$(CF_3)_2C(CN)OP({=}O)F_2$: 12 (C^+) 0.4, 14 (N^+) 0.2, 25 (CF_2^{+2}, PF^{2+}) 0.1, 26 (CN^+) 0.2, 28 (CO^+) 0.8, 31 (CF^+, P^+) 5.3, 38 (C_2N^+) 0.5, 47 (COF^+, PO^+) 1.4, 50 (CF_2^+, PF^+) 1.7, 54 ($COCN^+$) 3.8, 57 ($CFCN^+$) 0.4, 66 (CF_2O^+, POF^+) 0.2, 69 (CF_3^+, PF_2^+) 100.0, 70 (i) 1.0, 76 (CF_2CN^+) 0.6, 78 ($C_2F_2O^+$) 0.4, 85 (C_2FOCN^+, $COPCN^+$, POF_2^-) 8.8, 88 (PF_3^+) 0.7, 97 ($C_2F_3O^+$, $COPF_2^+$), 1.1, 104 ($C_2F_2OCN^+$, $COPFCN^+$, POF_3^+) 3.1, 107 ($C_2F_3CN^+$) 0.2, 119 ($C_2F_5^+$) 0.3, 126 ($C_2F_4CN^+$) 0.2, 147 ($C_3F_5O^+$, $C_2F_4OP^+$) 0.4, 151 ($C_2F_2O_2PCN^+$) 0.7, 154 ($C_2F_3OPCN^+$) 0.4, 189 ($C_2F_4OPOCN^+$) 0.2, 192 ($C_3F_6OCN^+$, $C_2F_3OPF_2CN^+$) 0.1, 208 ($C_2F_3OPOF_2CN^+$) 0.3, 277 ($C_3F_6OPOF_2CN^+$) 0.3.

$(CF_3)_2C(CN)OP({=}S)F_2$: 12 (C^+) 0.5, 14 (N^+) 0.2, 26 (CN^+) 0.5, 28 (CO^+) 1.0, 31 (CF^+, P^+) 8.0, 32 (S^+) 6.2, 38 (C_2N^+) 0.7, 46 (SN^+) 0.3, 47 (COF^+, PO^+) 1.4, 50 (CF^+, PF^+) 3.1, 51 (SF^+) 3.8, 54 ($COCN^+$) 2.0, 57 ($CFCN^+$) 0.5, 63 (PS^+) 1.1, 66 (CF_2O, POF^+) 0.2, 69 (CF_3^+, PF_2^+) 100.0, 70 (i, SF_2^+) 2.4, 76 (CF_2CN^+) 1.5, 77 ($SFCN^+$) 1.3, 78 ($C_2F_2O^+$, $COPF^+$) 0.5, 81 ($C_2F_3^+$) 0.3, 82 (PSF^+) 1.1, 85 (C_2FOCN^+, $COPCN^+$, POF_2^+) 1.8, 97 ($C_2F_3O^+$, $COPF_2^+$) 1.4, 101 (PSF_2^+) 25.3, 103 (i) 2.1, 107 ($C_2F_3CN^+$) 0.4, 117 ($OPSF_2^+$) 17.8, 119 ($C_2F_5^+$, i) 1.6, 128 ($C_3F_4O^+$, $C_2F_3OP^+$) 5.9, 147 ($C_3F_5O^+$, $C_2F_4OP^+$) 0.1, 205 ($C_2F_4OPSCN^+$) 6.4, 274 ($C_3F_7OPSCN^+$) 1.1, 293 ($C_3F_6OPSF_2CN^+$) 13.7.

$(CF_3)_2C(N_3)OP({=}O)F_2$: 14 ($N^+$) 1.4, 25 ($CF_2^{2+}$, PF^{2+}) 0.2, 26 (CN^+) 0.3, 28 (CO^+, N_2^+) 38.6, 31 (CF^+, P^+) 6.7, 42 (N_3^+) 1.3, 47 (COF^+, PO^+) 4.8, 50 (CF_2^+, PF^+) 6.1, 66 (CF_2O^+, POF^+) 1.1, 69 (CF_3^+, PF_2^+) 100.0, 70 (i, CON_3^+) 1.4, 76 (CF_2CN^+) 0.8, 78 ($C_2F_2O^+$, $COPF^+$) 1.5, 85 (C_2FOCN, $COPCN^+$, POF_2^+) 14.5, 97 ($C_2F_3O^+$, $COPF_2^+$) 2.3, 104 ($C_2F_2OCN^+$, $COPFCN^+$, POF_3^+) 10.4, 119 ($C_2F_5^+$) 1.1, 147 ($C_3F_5O^+$, $C_2F_4OP^+$) 3.2, 151 ($C_2F_2O_2PN_3^+$) 0.6, 166 ($C_2F_3OPF_2^+$) 0.6, 205 ($C_2F_4OPON_3^+$) 0.3, 224 ($C_2F_3OPOF_2N_3$) 2.2, 251 ($C_3F_6OPOF_2^+$) 1.4.

$(CF_3)_2C{=}NC(OPF_2)(CF_3)_2$: 12 ($C^+$) 0.1, 25 ($CF_2^+$, PF^+) 0.2, 26 (CN^+), 0.1, 28 (CO^+) 0.7, 31 (CF^+, P^+) 4.5, 47 (COF^+, PO^+) 1.1, 59 (CF_2^+, PF^+) 3.2, 66 (CF_2O^+, POF^+) 0.2, 69 (CF_3^+, PF_2^+) 100.0, 70 (i) 0.9, 76 (CF_2CN^+) 1.6, 78 ($C_2F_2O^+$, $COPF^+$) 0.6, 85 (C_2FONC^+, $CNCOP^+$, POF_2^+) 0.8, 88 (PF_3^+) 0.9, 92 ($CNOPF^+$) 1.0, 97 ($C_2F_3O^+$, $COPF_2^+$) 5.0, 100 ($C_2F_4^+$) 0.4, 107 ($C_3F_6N^+$) 0.2, 112 ($C_3F_4^+$) 0.4, 119 ($C_2F_5^+$) 2.5, 126 ($C_3F_4N^+$) 0.5, 135 ($C_3F_2NOP^+$) 3.7, 145 ($C_3F_5N^+$) 0.2, 147 ($C_3F_5O^+$, $C_2F_4OP^+$) 7.4, 154 ($C_3F_3NOP^+$) 0.2, 164 ($C_3F_2N^+$) 3.5, 169 ($C_3F_7^+$) 2.5, 176 ($C_3F_6NC^+$) 0.5, 192 ($C_3F_5NOP^+$) 2.4, 211 ($C_3F_6NOP^+$) 1.2, 226 ($C_3F_8N^+$) 1.5, 245 ($C_5F_9N^+$) 0.5, 261 ($C_5H_9NO^+$) 4.8, 292 ($C_5F_9NOP^+$) 0.3, 314 ($C_6F_{12}N^+$) 5.4.

[a] The spectra of the isomers $(CF_3)_2C(NCS)OP({=}O)F_2$ and $(CF_3)_2C(SCN)OP({=}O)F_2$ are not included but some spectral data are presented in the text. [b] i refers to the ^{13}C or ^{34}S isotope.

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TABLE III

^{19}F NMR SPECTRA[a]

$(CF_3)_2C(CN)OPF_2$			
ϕ[b]	Area ratio[c]	Assignment	Splitting (*J*, cps)
45.0	1.0	PF_2	Doublet (1380) of septets (1.5)
75.7	3.2	CF_3	Doublet (6.0) of triplets (1.5)

$(CF_3)_2C(N_3)OP(=O)F_2$[d]		
ϕ	Assignment	Splitting (*J*, cps)[e]
79.0	PF_2	Doublet (1048) of multiplets
78.1	CF_3	Multiplet

$(CF_3)_2C(CN)OP(=O)F_2$			
ϕ	Area ratio[c]	Assignment	Splitting (*J*, cps)
78.9	1.0	PF_2	Doublet (1064) of septets (1.0)
75.0	2.6	CF_3	Triplets (1.0) of doublets (0.4)

$(CF_3)_2C(NCS)OP(=O)F_2$			
ϕ	Area ratio[f]	Assignment	Splitting (*J*, cps)
77.3	1.0	PF_2	Doublet (1056) of septets (1.2)
76.8	3.0	CF_3	Triplet (1.2) of doublets (0.3)

$(CF_3)_2C(CN)OP(=S)F_2$			
ϕ	Area ratio[c]	Assignment	Splitting (*J*, cps)
40.5	1.0	PF_2	Doublet (1176) of septets (1.5)
75.4	2.8	CF_3	Triplet (1.4) of doublets (0.4)

$(CF_3)_2C(SCN)OP(=O)F_2$[d]		
ϕ	Assignment	Splitting (*J*, cps)
78.4	PF_2	Doublet (1062) of triplets (1.2)
79.5	CF_3	Multiplet

$(CF_3)_2C=NC(OPF_2)(CF_3)_2$			
ϕ	Area ratio[f]	Assignment	Splitting (*J*, cps)
40.7	1.0	PF_2	Doublet (1396) of septets (8.3)
66.0 b	3.0	$CF_3—C=N—$	Unresolved multiplet
75.9 sp	3.1	$CF_3—C—N=$	Doublet (40) of triplets (8.5) of septets (1.8)

[a] See the Discussion for further details. [b] Position of multiplet center. [c] Area ratios measured by planimetry. [d] Area ratios not measured. [e] Further resolution not obtained. [f] Area ratios measured by current integration.

TABLE IV

PHYSICAL PROPERTIES

Compound	Mp, °C	Bp,[a] °C	Molar heat of vapn, kcal	Trouton const, eu	Log P_A = [($-A$ × 10^3)/*T*] + *B*	*B*
$(CF_3)_2C(CN)OPF_2$	-90.0 ± 1.0	51.7 ± 0.6	6.451	19.88	1.412	7.227
$(CF_3)_2C(CN)OP(=O)F_2$	-55.5 ± 0.8	73.6 ± 0.4	7.802	22.49	1.705	7.797
$(CF_3)_2C(CN)OP(=S)F_2$	-88.6 ± 0.3	74.6 ± 0.3	7.486	21.52	1.636	7.585
$(CF_3)_2C(N_3)OP(=O)F_2$	(Glass)	81.5 ± 0.6	7.303	20.55	1.596	7.392
$(CF_3)_2C=NC(OPF_2)(CF_3)_2$	-58.7 ± 1.3	84.7 ± 1.0	8.502	23.75	1.858	8.071

[a] Extrapolated.

TABLE V

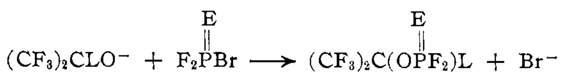
VAPOR PRESSURES

$(CF_3)_2C(CN)OPF_2$		$(CF_3)_2C(CN)OP(=O)F_2$		$(CF_3)_2C(CN)OP(=S)F_2$		$(CF_3)_2C(N_3)OP(=O)F_2$		$(CF_3)_2C=NC(OPF_2)(CF_3)_2$	
T, °C	*P*, mm	*T*, °C	*P*, mm	*T*, °C	*P*, mm	*T*, °C	*P*, mm	*T*, °C	*P*, mm
6.8	148.8	−3.1	30.7	−4.0	31.6	4.7	43.8	0.5	18.7
12.0	193.8	2.1	39.0	2.0	39.5	15.8	68.6	8.8	31.9
17.3	227.5	12.1	64.0	8.3	56.0	21.2	86.1	20.5	58.1
20.4	262.0	23.6	107.9	15.7	82.2	31.8	132.0	28.6	84.0
24.2	299.9	29.6	142.1	20.9	101.7	39.9	184.4	33.7	108.3
28.0	343.6	37.9	202.0	27.0	135.0	51.5	279.1	42.6	152.9
31.5	387.5	45.2	271.1	34.4	179.1	57.3	340.8	49.2	200.4
35.3	436.4	55.0	400.8	45.9	275.4	61.9	397.8	55.8	262.1
39.2	491.4	62.7	578.5			72.2	555.8	63.5	346.7
		71.1	690.9			80.7	742.9	67.3	395.7

solvents. The interaction of PSF_2Br with the cyano salt proceeds more slowly than PF_2Br and POF_2Br.

When $L^- = N_3^-$, there is evidence of interaction with HFA in nitrobenzene solution, but when $L^- = SCN^-$, there is no evidence of complex formation under the same conditions. For phosphate ester formation involving these ligands it is necessary to generate the isopropoxide salts *in situ* followed by reaction with the appropriate phosphorus bromide. Infrared and nmr spectra indicate that the reaction involving the SCN^- ion yields both the thio- and isothiocyanato isomers. These reactions may be represented by

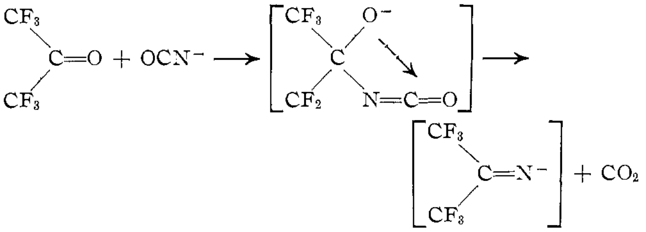
$$L^- + (CF_3)_2C{=}O \rightleftharpoons (CF_3)_2CLO^-$$



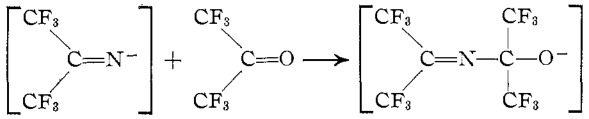
$$(CF_3)_2CLO^- + F_2\overset{\overset{\textstyle E}{\|}}{P}Br \longrightarrow (CF_3)_2C(O\overset{\overset{\textstyle E}{\|}}{P}F_2)L + Br^-$$

where $L^- = CN^-$, N_3^-, or SCN^- and E = O, S, or a nonbonding valence electron pair.

In experiments where OCN^- is employed, reaction with HFA produces CO_2 and a solid. Reaction of POF_2Br with the solid yields the azapentene $(CF_3)_2C{=}NC(OPF_2)(CF_3)_2$. A possible explanation can be provided by the formation of the intermediate isocyanate which then cyclizes to split off CO_2 and form an imine anion. A similar reaction



has been reported.[7] The imine anion is supposed to interact at once with another molecule of HFA to produce the aza salt, which with PF_2Br can produce



the observed μ-oxo-phosphate(III) ester. Similarly, the 2-hydridohexafluoroisopropoxide ion can react with HFA, and a complex involving further HFA addition is not observed.[8] A kinetic effect, presumably due to the high nucleophilicity of the imine ion, may explain the formation of an addition compound involving two molecules of HFA rather than one.[8] When $L^- = F^-$, the perfluoroisopropoxide ion either directly or indirectly, *via* F^- ion, reacts with PF_2Br, but no μ-oxo compound results. Instead, PF_3 and HFA are generated essentially quantitatively.

The characteristic infrared spectra of these compounds are complicated; hence, only some tentative frequency assignments are given. The spectra of the 2-cyano derivatives show weak but sharp bands between 2283 and 2272 cm^{-1} which are assigned to the $-C{\equiv}N$ group. The fluoroalkylnitriles absorb in the 2270-cm^{-1} region.[9] The 2-azido derivative shows strong absorption at 2160 cm^{-1} which is assigned to the N_3 asymmetric stretching vibration.[10] The frequency assigned to the asymmetric stretching vibration of the isothiocyanate group of $(CF_3)_2C(NCS)OP({=}O)F_2$ corresponds to a very strong absorption at 2012 cm^{-1} with a shoulder at 2040 cm^{-1} while the corresponding absorption associated with the thiocyanate linkage of the 2-thiocyanato isomer is believed to be that at 2088 cm^{-1}. Thiocyanate and isothiocyanate bands in these regions have been previously reported.[10,11] The $C{=}N$ group stretching frequency of the 3-azapentene is assigned as the medium-intensity band at 7139 cm^{-1}. A perfluoroazaalkene reported by Dresdner and Johar[12] exhibits a medium band at 1725 cm^{-1} assigned to this group.

All of the phosphoryl compounds have strong to very strong bands in the 1389–1408-cm^{-1} domain which are presumably associated with $P{=}O$ stretching motions. Müller, *et al.*,[13] have studied this region in the variety of spectra of phosphorus compounds and have shown the frequency to depend upon the electronegativities of the other atoms or groups bound to the phosphorus. The higher the sum of electronegativities, the higher the frequency at which the $P{=}O$ stretch was found, with the upper limit at 1415 cm^{-1} in the case of $POF_3(g)$. Since the 2-halogenoidoisopropoxy group is highly electronegative, the observed bands in the 1400-cm^{-1} region may be safely assigned as a $P{=}O$ frequency. The thiophosphoryl compound shows a strong band at 717 cm^{-1} that is believed to be the $P{=}S$ stretch.[13] All of the phosphorus(III) and -(V) esters show multiple absorptions in the region associated with C—F, C—O—P, and P—F stretching motions.[14]

The mass spectra cracking patterns are also complex (see Table II). All of the 2-halogenoido derivatives show a small relative intensity peak (0.2–0.5) for the halogenoid group with the exception of the isothiocyanato–thiocyanato isomeric mixture which has a medium-intensity peak. Peaks corresponding to the molecule ion, p^+, and the molecule ion less a fluorine, $(p - F)^+$, appear in the spectra of some of these compounds. The molecule ion is also observed in the spectrum of the thiocyanato–isothiocyanato mixture. The pattern of the thioester exhibits some ions presumably derived from rearrangements, *e.g.*, SN^+, SO^+, SF^+, SF_2^+, and $SFCN^+$.

The ^{19}F nmr spectra are diagnostic (Table III). The resonance positions,[2,15,16] area ratios, splitting values,[2,15,16] and patterns are consistent with the structural conclusions from the other observations. The ^{31}P resonance of the PF_2 group in the phosphorus(III) compounds lies at lower field (ϕ 40.7–45.0) than that of the same group in the phosphoryl compound which is located in the region ϕ 77.3–79.0. However the same group in the thiophosphoryl derivative absorbs at ϕ 40.5. It is observed that the ^{19}F nmr of the CF_3 groups bonded to the tertiary carbon atom in each of the phosphate(III) esters is split to a greater extent by the phosphorus nucleus than by the nuclei of the two fluorines bound to the phosphorus. The reverse is true in the case of the phosphate(V) esters.

Although the ^{19}F nmr spectrum of $(CF_3)_2C{=}NC(OPF_2)(CF_3)_2$ resembles those of the halogenoid relatives, the presence of the additional two equivalent CF_3 groups further complicates the spectrum. The resonance of the two CF_3 groups in the $(CF_3)_2C{-}N$ system, which is split into a doublet (at ϕ 75.4 and 76.4) of triplets of septets, can be converted to a doublet of triplets by irradiating the resonance at ϕ 66.0 arising from the two CF_3 groups in the $(CF_3)_2C{=}N$ system. Upon irradiation of the low-field member of the PF_2 group doublet (at ϕ 23.2), the corresponding low-field

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member of the two CF_3 groups doublet at ϕ 75.4 is reduced to a single septet while the higher field member is unaltered. Likewise, when the higher field member of the PF_2 group doublet (at ϕ 58.1) is irradiated, the resonance at ϕ 76.4 is converted to a septet leaving the resonance of lower field member unchanged.

The ^{31}P spectra of several of the compounds were measured. The resonances are divided into triplets with further small couplings. That of $(CF_3)_2C(N_3)OP(=O)F_2$ shows a resonance centered at 394 cps, that of $(CF_3)_2C(NCS)OP(=O)F_2$ at 451 cps, that of $(CF_3)_2C(CN)OP(=S)F_2$ at 414 cps, and that of $(CF_3)_2C(CN)OPF_2$ at -1505 cps. A compound, $(CF_3)_2C(I)OPF_2$, prepared previously[2] shows a resonance centered at -1728 cps. The trend in δ values is in the direction opposite to that expected from a change of oxidation state of the phosphorus atom. It is also observed that the ^{31}P resonance of the thiophosphate(V) ester is centered at lower field than those of the corresponding phosphate compounds.

The ultraviolet spectrum of $(CF_3)_2C(NCS)OP(=O)F_2$ is typical for an isothiocyanato derivative. Both λ_{max} (249 mμ) and ϵ_{max} (621) are consistent with other published results.[17]

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Olefin–Phosphine Complexes of Manganese(I) and Rhenium(I)

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Monoolefin complexes of manganese(I) and rhenium(I) have been prepared using the bidentate olefin phosphine ligands 2-*cis*-propenylphenyldiphenylphosphine (*cis*-PP), 2-allylphenyldiphenylphosphine (AP) and 2-styrylphenyldiphenylphosphine (SP). These include neutral $LM(CO)_3X$ species (where L = *cis*-PP, AP, or SP and X = halide) and also complexes containing $LM(CO)_4^+$ cations. Coordination of both the olefin and the phosphorus atom in these complexes is evidenced by infrared and nmr spectral data. The results of the infrared spectral measurements are discussed in terms of the bonding between olefin and metal.

Introduction

It has been shown that air-stable monoolefin complexes of the zerovalent group VI transition metals[2–5] as well as derivatives of Pt(II),[6,7] Pd(II),[7] Ag(I), and Cu(I)[8] can be prepared through the use of bidentate olefin–phosphine ligands. We now report the extension of this series of chelated monoolefin complexes to include derivatives of the type $LM(CO)_3X$ (L = olefin–phosphine ligand; M = Mn, Re; X = halogen) and $[LM(CO)_4{}^+]Y^-$ (Y^- = monovalent anion).

Although a wide variety of carbonyl-containing univalent group VII metal complexes are known,[9] very few of these contain coordinated monoolefins.[10,11] Indeed, the olefin–phosphine derivatives of Re(I) described herein apparently have been precedented only by the $[(C_2H_4)_2Re(CO)_4][AlCl_4]$ complex reported by Fischer and Oefele.[11] In addition to the interest in these complexes as further members of a new class of chelated olefin derivatives, their preparation offers an opportunity to study, in a more direct fashion than was previously possible, the effect of the charge on the metal upon the metal–olefin bond strength. In the case of the metal carbonyls it appears that a decrease in the electron density on the metal lowers the metal–carbon bond order, presumably owing to inhibition of π bonding between the metal and the CO groups.[12,13] This decrease in electron density may be accomplished either by attaching groups of increasing electronega-

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