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Alkoxyfluorophosphoranes. 3. Synthesis and Characterization of Some Di-, Tri-, and Tetraalkoxyfluorophosphoranes

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Several dialkoxyfluorophosphoranes $PhPF_2(OR)_2$ (R = CH_2CCl_3, CH_2CHCl_2, $CH(CH_3)(CN)$, CH_2CF_3) and $MePF_2(OCH_2CF_3)_2$ have been isolated and characterized by NMR, IR, and mass spectrometry and elemental analysis. Their formation can be facilitated by the disproportionation reaction $2R'PF_3(OR) \rightarrow R'PF_2(OR)_2 + R'PF_4$. These compounds are stable with respect to both further disproportionation and decomposition into phosphonates. The tetraalkoxyphosphorane $PhP(OCH_2CF_3)_4$ has also been isolated. Trialkoxyfluorophosphoranes $PhPF(OR)_3$ (R = CH_2CCl_3, CH_2CHCl_2, $CH(CH_3)(CN)$, CH_2CF_3) and $MePF(OCH_2CF_3)_3$ have been identified in mixtures but could not be separated from the other members of the $R'PF_{4-n}(OR)_n$ series.

Introduction

Phosphoranes containing simultaneously fluorine atoms and alkoxy groups were generally found to be unstable with respect to their decomposition into phosphoryl compounds according to[1,2]

$$R'PF_3(OR) \rightarrow R'P(O)F_2 + RF \tag{1}$$

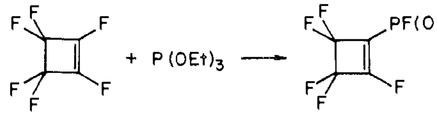
We have shown[3] that they could be stabilized by introducing electron-withdrawing substituents in the alkoxy moiety, and we have recently reported the preparation of a series of stable monoalkoxyfluorophosphoranes[4] through the general reaction[5]

$$R'PF_4 + (CH_3)_3SiOR \rightarrow R'PF_3(OR) + (CH_3)_3SiF \tag{2}$$

We now wish to report the preparation and isolation of several stable dialkoxydifluorophosphoranes of type $R'PF_2(OR)_2$ and of the tetraalkoxyphosphorane $PhP(OCH_2CF_3)_4$ as well as the identification of several trialkoxyfluorophosphoranes of type $R'PF(OR)_3$ which, although they could not be isolated in a pure form, were unambiguously characterized both by spectral determinations and by their transformation into the corresponding dialkoxydifluorophosphoranes.

Previous studies in the literature which produced nonionic multialkoxyfluorophosphoranes stable at room temperature appear to be limited to[6,7]

$$PF_3Cl_2 + 2\,t\text{-}C_4F_9OCl \longrightarrow (t\text{-}C_4F_9O)_2PF_3 + 2Cl_2$$



On the other hand, the related aryloxyfluorophosphoranes were found to be more stable than their alkoxy analogues.[8,9]

Experimental Section

All manipulations of fluorophosphoranes were carried out under a dry nitrogen atmosphere. Reactions involving CH_3PF_4 were carried

Table I. NMR Parameters for Di-, Tri-, and Tetraalkoxyphosphoranes of Types R′PF$_2$(OR)$_2$ (I), R′PF(OR)$_3$ (II), and R′P(OR)$_4$ (III)[a]

Type	R	R′	δ_{CH_3}[a]	δ_{CH_2}	δ_{CH}	$\delta_{F(P)}$	δ_P	$^3J_{HCCH}$	$^3J_{HCOP}$	$^3J_{HCCF}$	$^2J_{HCP}$	$^3J_{HCPF}$	$^1J_{FP}$
I	CH$_2$CCl$_3$	C$_6$H$_5$		4.62		38.0	59.1		7.5				824
I	CH$_2$CCl$_2$H	C$_6$H$_5$		4.34	5.78	41.9	58.0	5.4	10.5				822
I	CH(CH$_3$)(CN)	C$_6$H$_5$	1.95		5.55	39.8	58.8	7.0	7.0				826
I	CH$_2$CF$_3$	C$_6$H$_5$		4.27		43.2	58.5		10.3	8.3			808
II	CH$_2$CF$_3$	C$_6$H$_5$		4.19		40.5	57.2		8.4	8.3			820
III	CH$_2$CF$_3$	C$_6$H$_5$		4.01			58.7		5.0	8.3			
I	CH$_2$CF$_3$	CH$_3$	1.55	4.11		30.1[b]	45.4		10.5	7.9	21.2	12.7	819
II	CH$_2$CF$_3$	CH$_3$	1.52	4.00		34.0			8.3	7.9	19.5	14.2	813
III	CH$_2$CF$_3$	CH$_3$	1.47	3.96					5.6	7.9	17.1		

[a] ^{1}H, ^{19}F chemical shifts in ppm relative to internal Me$_4$Si and CFCl$_3$, ^{31}P relative to external H$_3$PO$_4$; coupling constants in Hz. [b] Chemical shift relative to external CFCl$_3$.

out using standard vacuum techniques in a system constructed with Pyrex glass with stopcocks lubricated with Apiezon N grease. C$_6$H$_5$PF$_4$, CH$_3$PF$_4$, and the alkoxysilyl ethers were prepared as previously reported.[4]

The ^{1}H and ^{19}F spectra were routinely recorded with a JEOL C-60 HL instrument of samples containing an approximate 10% solution of the compound in CDCl$_3$. The ^{31}P spectra were measured on neat liquids. Infrared spectra were recorded on films between KBr plates with a Perkin-Elmer 577 spectrometer. Mass spectra were measured with a CEC 21-130 instrument. The purity of all compounds has been checked by elemental analysis and by their spectrochemical properties which are given in Tables I and II.

Preparation of Bis(2,2-dichloroethoxy)difluorophenylphosphorane, C$_6$H$_5$PF$_2$(OCH$_2$CCl$_2$H)$_2$. (CH$_3$)$_3$SiOCH$_2$CCl$_2$H (4.29 g, 22.9 mmol) was added dropwise to C$_6$H$_5$PF$_4$ (2.07 g, 11.2 mmol) at −30 °C. The reaction mixture was allowed to warm slowly to room temperature and was then heated to 70 °C for 30 min. (CH$_3$)$_3$SiF (2.06 g, 21.6 mmol) was trapped at −75 °C. C$_6$H$_5$PF$_2$(OCH$_2$CCl$_2$H)$_2$ (3.61 g, 86%) was recovered as a colorless liquid by distillation (70 °C (10^{-2} mmHg)).

Anal. Calcd for C$_{10}$H$_{11}$Cl$_4$F$_2$O$_2$P: C, 32.11; H, 2.97; F, 10.16; Cl, 37.92; P, 8.28. Found: C, 32.15; H, 3.02; F, 10.42; Cl, 38.02; P, 8.23.

Under more drastic conditions (90 °C, 6 h) and with 3 equiv of the silyl ether, the formation of 80% C$_6$H$_5$PF(OCH$_2$CCl$_2$H)$_3$ (δ_F 36.1 ppm, J_{FP} = 821 Hz) was observed with 20% C$_6$H$_5$PF$_2$(OCH$_2$CCl$_2$H)$_2$.

Preparation of Bis(1-cyanoethoxy)difluorophenylphosphorane, C$_6$H$_5$PF$_2$[OCH(CH$_3$)(CN)]$_2$. (CH$_3$)$_3$SiOCH(CH$_3$)(CN) (3.07 g, 25.9 mmol) was added dropwise to C$_6$H$_5$PF$_4$ (2.29 g, 12.2 mmol) at −30 °C. The reaction mixture was allowed to warm slowly to room temperature and was then heated to 85 °C for 30 min. (CH$_3$)$_3$SiF (2.13 g, 23.3 mmol) was trapped at −75 °C. C$_6$H$_5$PF$_2$[OCH(CH$_3$)(CN)]$_2$ (3.18 g, 91%) was recovered from the reaction vessel as a yellow viscous nonvolatile liquid.

Anal. Calcd for C$_{12}$H$_{13}$F$_2$N$_2$O$_2$P: C, 50.35; H, 4.58; F, 13.28; N, 9.79; P, 10.82. Found: C, 50.74; H, 4.58; F, 13.01; N, 9.91; P, 10.77.

Under more drastic reaction conditions (100 °C, 1 h) the formation of ca. 5% C$_6$H$_5$PF[OCH(CH$_3$)(CN)]$_3$ (δ_F 34.8 ppm, J_{FP} = 824 Hz) was observed together with 95% C$_6$H$_5$PF$_2$[OCH(CH$_3$)(CN)]$_2$.

Preparation of Bis(2,2,2-trifluoroethoxy)difluorophenylphosphorane, C$_6$H$_5$PF$_2$(OCH$_2$CF$_3$)$_2$. (CH$_3$)$_3$SiOCH$_2$CF$_3$ (2.08 g, 12.1 mmol) was added dropwise to C$_6$H$_5$PF$_4$ (1.07 g, 5.82 mmol) at 0 °C. The reaction mixture was allowed to warm slowly to room temperature and to react for 30 h at this temperature. The (CH$_3$)$_3$SiF produced was allowed to escape from the reaction and was not collected. C$_6$H$_5$PF$_2$(OCH$_2$CF$_3$)$_2$ (1.81 g, 90%), a colorless liquid, was purified by removing the last traces of (CH$_3$)$_3$SiF and (CH$_3$)$_3$SiOCH$_2$CF$_3$ under vacuum 5 × 10^{-4}mm (20 °C).

Anal. Calcd for C$_{10}$H$_9$F$_8$O$_2$P: C, 34.90; H, 2.63; F, 44.17; P, 9.00. Found: C, 35.03; H, 2.61; F, 43.25; P, 9.16.

Preparation of Bis(2,2,2-trifluoroethoxy)difluoromethylphosphorane, CH$_3$PF$_2$(OCH$_2$CF$_3$)$_2$. (CH$_3$)$_3$SiOCH$_2$CF$_3$ (4.46 g, 25.9 mmol) and CH$_3$PF$_4$ (1.57 g, 13.0 mmol) were allowed to react in a sealed tube at 45 °C for 65 h. Vacuum fractionation afforded CH$_3$PF$_2$(OCH$_2$CF$_3$)$_2$ (2.81 g, 77%), as a stable colorless liquid collected at −45 °C, and (CH$_3$)$_3$SiF (2.66 g) which was trapped at −116 °C. A small amount of nonvolatile and as yet unidentified white solid (0.18 g) remained in the reaction tube.

Anal. Calcd for C$_5$H$_7$F$_8$O$_2$P: C, 21.29; H, 2.50; F, 53.88; P, 10.98. Found: C, 21.55; H, 2.51; F, 52.62; P, 10.99.

Preparation of Tetrakis(2,2,2-trifluoroethoxy)phenylphosphorane, C$_6$H$_5$P(OCH$_2$CF$_3$)$_4$. (CH$_3$)$_3$SiOCH$_2$CF$_3$ (26.8 g, 156 mmol) was added dropwise to C$_6$H$_5$PF$_4$ (2.13 g, 11.6 mmol) and the mixture was allowed to react at 70 °C for 63 h. The (CH$_3$)$_3$SiF produced was distilled out of the reaction system but not collected. The unreacted (CH$_3$)$_3$SiOCH$_2$CF$_3$ was pumped away (5 × 10^{-4} mmHg (22 °C)) and C$_6$H$_5$P(OCH$_2$CF$_3$)$_4$ (3.19 g, 54%) was collected and purified by distillation (64 °C, 5 × 10^{-4} mmHg). The compound is a white solid at room temperature (mp 62 °C).

Anal. Calcd for C$_{14}$H$_{13}$F$_{12}$O$_4$P: C, 33.35; H, 2.60; F, 45.22; P, 6.14. Found: C, 33.55; H, 2.53; F, 44.07; P, 6.33.

Preparation of Bis(2,2,2-trichloroethoxy)difluorophenylphosphorane, C$_6$H$_5$PF$_2$(OCH$_2$CCl$_3$)$_2$. (CH$_3$)$_3$SiOCH$_2$CCl$_3$ (3.97 g, 17.9 mmol) was allowed to react with C$_6$H$_5$PF$_4$ (0.77 g, 4.2 mmol) in a sealed tube (~25 cm^3) for 40 h at 100 °C. Vacuum fractionation of the volatile products afforded (CH$_3$)$_3$SiOCH$_2$CCl$_3$ (2.81 g, 12.7 mmol) which was collected at −45 °C and (CH$_3$)$_3$SiF (0.51 g, 5.5 mmol) which was trapped at −116 °C. Thus only 1.2 equiv of silyl ether had been consumed; previous work[4] has shown that the monoalkoxy compound is formed under these conditions. In a second step, the colorless nonvolatile liquid which remained in the reaction tube and consisted mainly of C$_6$H$_5$PF$_3$(OCH$_2$CCl$_3$) was pumped in for 12 h at 60 °C and C$_6$H$_5$PF$_4$ (0.28 g, 1.5 mmol) was recovered as the volatile product. C$_6$H$_5$PF$_2$(OCH$_2$CCl$_3$)$_2$ (1.01 g, 93%) was isolated from the reaction flask as a colorless liquid.

Anal. Calcd for C$_{10}$H$_9$Cl$_6$F$_2$O$_2$P: C, 27.12; H, 2.03; Cl, 48.04; P, 6.99. Found: C, 27.24; H, 2.13; Cl, 48.23; P, 7.08.

Under more drastic reaction conditions (150 °C, 40 h) the formation of 5% C$_6$H$_5$PF(OCH$_2$CCl$_3$)$_3$ (δ_F 33.5, J_{PF} = 806 Hz) was observed along with 95% C$_6$H$_5$PF$_2$(OCH$_2$CCl$_3$)$_2$.

Preparation of Mixtures of the Tri- and Tetraalkoxyphosphoranes CH$_3$PF(OCH$_3$CF$_3$)$_3$ and CH$_3$P(OCH$_2$CF$_3$)$_4$. Attempts to prepare CH$_3$PF(OCH$_2$CF$_3$)$_3$and CH$_3$P(OCH$_2$CF$_3$)$_4$ always resulted in mixtures of the two products. A typical example using a 6:1 molar ratio of (CH$_3$)$_3$SiOCH$_2$CF$_3$ and CH$_3$PF$_4$ afforded, after 75 h at 75 °C, a mixture containing ca. 90% CH$_3$PF(OCH$_2$CF$_3$)$_3$ and 10% CH$_3$P(OCH$_2$CF$_3$)$_4$ (by NMR; no dialkoxydifluorophosphorane detected). An 8:1 molar ratio of the reagents resulted, after 154 h at 100 °C, in a ca. 1:1 mixture of the tri- and tetrasubstituted products.

Results and Discussion

Dialkoxydifluorophosphoranes of type R′PF$_2$(OR)$_2$ (I) (R′ = Ph or Me, R = CH$_2$CCl$_3$, CH$_2$CHCl$_2$, CH(CH$_3$)(CN), CH$_2$CF$_3$) were isolated in good yields through reaction 2 and their thermal stability was found to be good (no changes were observed in any of these compounds after 6 months at room temperature, and they could be heated for 2 h at 100 °C without noticeable change). This further illustrates the stabilizing effect of electron-attracting substituents in the alkoxy groups which thus opposes the tendency of compounds of type I to decompose into phosphonates, according to eq 1.

These dialkoxydifluorophosphoranes were also found to be stable with respect to their disproportionation according to

$$2R'PF_2(OR)_2 \rightleftarrows R'PF_3(OR) + R'PF(OR)_3 \qquad (3)$$

i.e., eq 3 lies to the left and the mono- and trialkoxy compounds were not detectable by NMR. This contrasts with the behaviour of the monoalkoxyfluorophosphoranes, which were found to undergo such reactions easily[2,4]

$$2R'PF_3(OR) \rightleftarrows R'PF_2(OR)_2 + R'PF_4 \qquad (4)$$

Table II. Mass Spectra of Di- and Tetraalkoxyphosphoranes [*m*/*e*, assignments (relative intensity)]

$PhPF_2(OCH_2CCl_3)_2$	$PhPF_2(OCH_2CHCl_2)_2$	$PhPF_2[OCH(CH_3)(CN)]_2$	$PhPF_2(OCH_2CF_3)_2$	$MePF_2(OCH_2CF_3)_2$	$PhP(OCH_2CF_3)_4$
440 $C_{10}H_9Cl_6F_2O_2P$ (1)	353 $C_{10}H_{11}FCl_4O_2P$ (3)	286 $C_{12}H_{13}F_2N_2O_2P$ (2)	344 $C_{10}H_9F_8O_2P$ (7)	267 $C_4H_4F_8O_2P$ (3)	406 $C_{12}H_{12}F_9O_3P$ (15)
421 $C_{10}H_9Cl_6FO_2P$ (1)	315 $C_{10}H_8FCl_3O_2P$ (2)	267 $C_{12}H_{13}FN_2O_2P$ (2)	325 $C_{10}H_9F_7O_2P$ (20)	263 $C_5H_7F_7O_2P$ (70)	405 $C_{12}H_{11}F_9O_3P$ (100)
405 $C_{10}H_9Cl_5F_2O_2P$ (1)	276 $C_4H_6FCl_4O_2P$ (7)	216 $C_9H_9F_2NOP$ (60)	267 $C_4H_4F_8O_2P$ (33)	239 $C_5H_2F_6O_2P$ (1)	385 $C_{12}H_{10}F_8O_3P$ (3)
293 $C_8H_7Cl_3F_2OP$ (21)	259 $C_8H_8F_2Cl_2OP$ (38)	165 C_8H_8NOP (38)	246 $C_8H_8F_5OP$ (9)	183 $C_3H_5F_5OP$ (100)	325 $C_{10}H_9F_7O_2P$ (17)
274 $C_8H_7Cl_3FOP$ (1)	161 $C_2H_4Cl_2O_2P$ (100)	163 C_8H_6NOP (96)	245 $C_8H_7F_5OP$ (100)	181 $C_3H_3F_5OP$ (2)	322 $C_{10}H_9F_6O_3P$ (9)
163 $C_6H_6F_2OP$ (100)	160 $C_6H_6FO_2P$ (32)	162 $C_5H_6FNO_2P$ (28)	185 $C_2H_3F_5O_2P$ (16)	161 $C_3H_2F_4OP$ (3)	301 $C_7H_7F_5O_3P$ (7)
161 $C_6H_4F_2OP$ (12)	143 C_2HOCl_2P (24)	158 C_7H_8FOP (11)	165 $C_2H_2F_4O_2P$ (10)	101 F_2O_2P (81)	224 $C_8H_8F_3O_2P$ (6)
131 $C_2H_2Cl_3$ (9)	105 $H_2F_2Cl_2P$ (25)	103 C_4H_4NOP (15)	163 $C_6H_6F_2OP$ (20)	99 $C_2H_2F_3O$ (1)	223 $C_8H_7F_3O_2P$ (24)
103 $H_2F_2O_2P$ (17)	97 $C_2H_3Cl_2$ (21)	96 C_4H_5NO (58)	162 $C_6H_5F_2OP$ (13)	83 CH_2F_2P (43)	176 $C_7H_7F_2OP$ (12)
96 $C_2H_2Cl_2$ (18)	96 $C_2H_2Cl_2$ (32)	94 CHF_2NP (18)	143 C_6H_5FOP (7)	81 C_2F_3 (2)	143 C_6H_5FOP (28)
77 C_6H_5 (30)	94 C_2Cl_2 (15)	78 C_3H_5OP (17)	96 CH_2FO_2P (50)	69 CF_3 (3)	141 $C_6H_6O_2P$ (26)
61 C_2H_2Cl (6)	77 C_6H_5 (34)	77 C_6H_5 (82)	83 CH_5FOP (24)	64 CH_2FP (2)	133 $C_2H_5F_3OP$ (27)
51 HFP (11)	61 CH_2OP (15)	76 CH_2FNP (16)	77 C_6H_5 (42)	61 CH_2OP (2)	83 CH_5FOP (16)
50 FP (6)	51 HFP (23)	56 C_2H_2ON (28)	69 CF_3 (12)	51 HFP (1)	77 C_6H_5 (62)
	50 FP (12)	54 C_3H_4N (100)	61 CH_2OP (18)		69 CF_3, PF_2 (16)
		51 HFP (50)	51 HFP (31)		51 HPF, CF_2H (36)
		50 FP (24)			

There, the use of the electron-attracting substituents allows the retention of the five-coordinate character of the phosphorus atom, i.e., their decomposition into phosphonates can be avoided, but does not oppose the scrambling reaction 4. That such a phenomenon is not observed for the dialkoxyfluorophosphoranes, I, can be attributed to the reluctance of the alkoxy group to assume an apical position and reflects the difference in apicophilicity between fluorine atoms and alkoxy groups.

Profit can even be gained from reaction 4 in the preparation of the dialkoxyfluorophosphoranes, I. Thus a sample of pure $PhPF_2(OCH_2CCl_3)_2$ was obtained by first preparing the monoalkoxyfluorophosphorane and then shifting equilibrium 4 to the left by continuously pumping off the more volatile $PhPF_4$.

When the substitution series $R'PF_{4-n}(OR)_n$ is examined, one observes a marked increase in the difficulty of the substitution between $n = 2$ and $n = 3$; i.e., the reaction conditions have to become much more drastic if one wants to add an alkoxy group in the apical position. Thus, for example, the dialkoxy compound $PhPF_2(OCH_2CCl_2H)_2$ was formed quantitatively from a 2:1 molar ratio of reactants after 30 min at 70 °C while the trialkoxy compound $PhPF(OCH_2CCl_2)_3$ was formed only in 20% yield from a 3:1 ratio after 10 h at 75 °C. The dialkoxy compound $MePF_2(OCH_2CF_3)_2$ was obtained in 90% yield from a 2:1 molar ratio of reactants after 47 h at room temperature while the trialkoxy compound $MePF(OCH_2CF_3)_3$ was obtained in 50% yield after heating a 6:1 molar ratio of the reactants for 72 h at 74 °C. Similarly the dialkoxy compound $PhPF_2(OCH_2CF_3)_2$ was formed in a 90% yield from a 2:1 molar ratio of reactants after 48 h at room temperature while it took 40 days at the same temperature to obtain a 33% yield of the trialkoxy compound from a 3:1 molar ratio of the reactants.

It appears difficult to stop the substitution process at the trialkoxy compounds, $R'PF(OR)_3$, II, the conditions for tetra substitution being too similar. We were thus unable to obtain them in a pure form, but only in mixtures with the tetraalkoxy derivatives, although these mixtures were free of phosphonates. They were characterized by NMR and, in the case of $PhPF(OCH_2CF_3)_3$, by the addition to the mixture of the amount of $R'PF_4$ which is needed to convert all the constituents of the mixture into the dialkoxydifluoro compound according to

$$\{x\mathrm{PhPF(OCH_2CF_3)_3} + y\mathrm{PhP(OCH_2CF_3)_4}\} + (x/2 + y)\mathrm{PhPF_4} \rightarrow \mathrm{PhPF_2(OCH_2CF_3)_2} \qquad (5)$$

The completely substituted tetraalkoxy derivative $R'P(OCH_2CF_3)_4$ was identified in a mixture (with the trialkoxy compound), for R′ = Me, and isolated in the case of R′ = Ph.

No evidence for the formation of ionic species either directly or upon aging was encountered in these series. All the compounds were soluble in pentane, benzene, $CHCl_3$, CH_2Cl_2, and CH_3CN.

The NMR parameters are reported in Table I. The ^{19}F and ^{31}P chemical shifts and J_{PF} coupling constants are in agreement with those found previously for monoalkoxyfluorophosphoranes.[4] It is noteworthy that although J_{HCOP} is quite large (5–10 Hz) further J_{HCOPF} coupling is not resolved. For the trifluoroethoxyphosphoranes, for which we now have two complete substitution series $R'PF_n(OCH_2CH_3)_{4-n}$ (R′ = Ph and Me; n = 0–3), one observes a systematic increase in J_{HCOP} with n and at the same time a gradual downfield shift for the methylene proton signals. The four alkoxy groups of $PhP(OCH_2CF_3)_4$ remain equivalent in the ^1H NMR and give a well-resolved doublet of quadruplets down to −50 °C; these lines coalesce in one broad symmetric hump at ca. −70 °C suggesting that the alkoxy groups become nonequivalent at lower temperatures and that their exchange between the apical and equatorial sites of a trigonal bipyramid is rapid above this temperature.

The mass spectra (Table II) show a weak or nondetectable molecular ion. The fragments corresponding to the loss of F and OR are important. It is noteworthy that the loss of OR is generally extensive, while the loss of R is not detected; this is the opposite to what has been observed previously in the case of the analogous monoalkoxyfluorophenyl(or methyl)-phosphoranes, for which the breaking of the OR bond was an important feature.[4]

The infrared spectra show the expected ν_{as}(P–F) bands in the range of 920–800 cm^{-1}. These relatively low values are consistent with apical fluorines in a trigonal-bipyramidal structure[10] and comparable to those found in series of compounds R_3PF_2 having strongly electroattracting R groups.[11] The P–O–C linkage gives rise to three absorption bands near 1130, 1020, and 780 cm^{-1} [12]. The Ph–P linkage produces a characteristic vibration near 1450 cm^{-1}.[12] No vibrations assignable to ν(P═O) stretching vibrations were detected.

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Registry No. $C_6H_5PF_2(OCH_2CCl_3)_2$, 43227-68-5; $C_6H_5PF_2(OCH_2CCl_2H)_2$, 63325-03-1; $C_6H_5PF_2(OCH(CH_3)(CN))_2$, 55509-54-1; $C_6H_5PF_2(OCH_2CF_3)_2$, 63325-04-2; $C_6H_5PF(OCH_2CF_3)_3$, 63325-05-3; $C_6H_5P(OCH_2CF_3)_4$, 63325-06-4; $CH_3PF_2(OCH_2CF_3)_2$, 63325-07-5; $CH_3PF(OCH_2CF_3)_3$, 63325-08-6; $CH_3P(OCH_2CF_3)_4$, 63325-09-7; $(CH_3)_3SiOCH_2CCl_2H$, 51209-79-1; $(CH_3)_3SiOCH(CH_3)(CN)$, 41309-99-3; $(CH_3)_3SiOCH_2CF_3$, 56859-55-3; $(CH_3)_3SiOCH_2CCl_3$, 41262-38-8; $C_6H_5PF_4$, 666-23-9.

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Silicon–Transition Metal Chemistry. 9.[1] Synthesis, Properties, and Structure of the Rhenium Acylsilane Complex *fac*-$Re(CO)_3(diphos)[C(O)SiPh_3]$

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The reaction of $[Re(CO)_4(diphos)]ClO_4$ with Ph_3SiLi yields the acylsilane complex *fac*-$Re(CO)_3(diphos)[C(O)SiPh_3]$ (**1**). A stereospecific synthesis of the ^{13}CO-enriched precursor [*fac*-$Re(CO)_3(^{13}CO)(diphos)]ClO_4$ is given. When **1** is prepared from this material, the majority of the enrichment remains mutually cis to phosphorus, although there is some scambling to positions trans to phosphorus. Treatment of **1** and the unisolated $SiMePh_2$ analogue with Et_3OPF_6 yields the cationic carbene species [*fac*-$Re(CO)_3(diphos)\{C(OEt)SiPh_3\}]^+$ and [*fac*-$Re(CO)_3(diphos)\{C(OEt)SiMePh_2\}]^+$, respectively. The thermal decarbonylation of **1** yields *mer*-$Re(CO)_3(diphos)SiPh_3$, with loss of CO mutually cis to phosphorus. The crystal and molecular structure of **1** has been determined from three-dimensional x-ray data collected by counter techniques. The material crystallizes in the space group $P2_1/n$ of the monoclinic system with $a = 20.675$ (4) Å, $b = 11.372$ (2) Å, $c = 18.271$ (2) Å, and $\beta = 108.04$ (9)°. The observed density 1.54 (1) g cm^{-3} may be compared with 1.554 g cm^{-3} calculated for $Z = 4$. The structure was refined by a full-matrix least-squares procedure to an R value of 0.0401 for 3604 observations having $I/\sigma(I) > 3.0$. The structure consists of discrete monomers of slightly distorted octahedral geometry having facial substitution. The $Ph_3SiC(O)$ ligand is bonded to rhenium through the acyl carbon and contains a planar SiC(O)Re group. This plane roughly bisects the P–Re–P angle and is such that the $SiPh_3$ group is remote from the diphos ligand. Bond distances in the acyl group are Si–C = 1.969 (10) Å, Re–C = 2.199 (9) Å, and O–C = 1.23 (1) Å. Bond angles are Re–C–Si = 127.9 (5)°, Re–C–O = 124.4 (6)°, and Si–C–O = 107.7 (6)°.

Introduction

Transition metal–acyl complexes are important organometallic intermediates that have deservedly received much study.[2,3] Related carbamoyl,[4] alkoxycarbonyl,[4] and formyl[5] complexes are also known, in which the metal-bonded carbonyl carbon is attached not to carbon but to N, O, or H, respectively. However, little attention has apparently been directed toward the study of transition metal–acyl derivatives of the heavier group 4 elements, although acylsilanes, acylgermanes, and acylstannanes are well-known.[6]

Transition metal–acyl complexes are most commonly prepared as shown in eq 1 and 2; however, it has not been

$$L_nM(CO)(R) + L' \rightarrow L_nL'M[C(O)R] \quad (1)$$

$$L_nM(CO)_m^- + RC(O)X \rightarrow L_nM(CO)_m[C(O)R] + X^- \quad (2)$$

feasible to extend these routes to the synthesis of acyl complexes of the heavier group 4 elements. The carbonyl insertion reaction (eq 1) has not been observed to occur in bonds between metals and heavier group 4 elements. The appropriate acyl halides and anhydrides for eq 2 are unknown for heavier group 4 elements, and our attempts to prepare such materials have proved unsuccessful.

Accordingly, we adopted the route (eq 3) where a transition

$$[L_nM(CO)_m]X + R_3M'Li \rightarrow L_nM(CO)_{m-1}[C(O)M'R_3] + LiX \quad (3)$$

metal–carbonyl cation is treated with the appropriate lithium reagent, $R_3M'Li$. We reported recently the synthesis of *fac*-$Re(CO)_3(diphos)[C(O)SiPh_3]$ (**1**) by this route and noted its remarkable spectroscopic properties.[7] The cation $[Re(CO)_4(diphos)]^+$ had been chosen for this work because (i) rhenium acyls are known to have good thermal and photolytic stability,[3] (ii) the related cation [*trans*-$Re(CO)_4(PPh_3)_2]^+$ is