Synthesis of Chiral and Non-chiral Phosphites Containing the Hexafluoroisopropoxy Group

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A series of new phosphorus(III) compounds containing the hexafluoroisopropoxy group has been synthesised by reacting halophosphines with lithium hexafluoroisopropoxide. The phosphites BuPX[OCH(CF3)2] (where X = F, Cl), BuMeP[OCH(CF3)2] and C6H5PF[OCH(CF3)2] each contain a chiral center at phosphorus.

Continuing on from our previous investigations of phosphorus(III) and phosphorus(V) compounds [1, 2] containing the hexafluoroisopropoxy group, we now present a series of phosphites containing this substituent. A variety of other substituents (F, Cl, CH3, CF3, Bu, C6H5, C6F5) have been included to study the resultant electronic steric and chirality effects.

Results and Discussion

The hexafluoroisopropoxy group was linked to phosphorus by the reaction of the lithium salt Li[OCH(CF3)2]2 (1) with the appropriate halophosphine. Reaction of PbF3 with 1 gave only the phosphite P[OCH(CF3)2]2 (2) [1] even when up to a twentyfold excess of PbF3 was used. The analogous reactions using PF3 and PCl3 gave mixtures of all possible products (1).

\[
P[OCH(CF_3)2]_2 \quad \text{P}X_3 + 1 \xrightarrow{\text{LiX}} XP[OCH(CF_3)2]_2 \quad (1)
\]

\[
3: X = F \quad 4: X = Cl
\]

\[
5: X = F \quad 6: X = Cl
\]

\[\text{SiP} \text{NMR was used to identify the products which were separated using trap to trap condensation under high vacuum conditions. The mixtures contained approximately equimolar ratios of the products (1) as well as unreacted PX3. Compounds 2 and 5 have previously been reported [1, 3].}

Adding PCl3 or PF3 to 2 again yields a mixture of products as described by (1). Altering the ratio of PX3:1 between 1:1 and 20:1 causes no noticeable change in the ratio of the reaction products. Apparently a rapidly established equilibrium exists between all the products in (1). Such equilibria have been reported for similar systems [2, 4]. However, once each of the products has been isolated, no further ligand scrambling is observed.

Compounds 4 and 6 can be easily fluorinated with SbF5 to give 3 and 5, respectively. Again these compounds show no evidence for ligand scrambling once they have been isolated as pure substances. Compounds 3, 5, and 6 are air- and moisture-sensitive whereas 2 reacts only slowly with the atmosphere.

Bis-trifluoromethyl-[1,1,1,3,3,3-hexafluoroisopropyl]phosphine (7), phenyl-bis-(hexafluoroisopropyl)-phosphite (9) and pentafluorophenyl-bis-(hexafluoroisopropyl)phosphite (8) have also been prepared from bis-trifluoromethyl iodophosphine [5] or pentafluorophenyl dichlorophosphine [6] and phenyl dichlorophosphine, respectively. No compounds evident of ligand scrambling were obtained.

Surprisingly, reaction of tert-buty1 dichlorophosphine with 1 yields only tert-buty1-chloro-[hexafluoroisopropyl]phosphite (10). Even heating the reaction mixture at 100 °C for six hours did not produce significant amounts of tert-buty1-bis-[hexafluoroisopropyl]phosphite. Bis-tert-buty1 chlorophosphine does not react with 1 even when the reaction mixture is refluxed for six hours. On the other hand tert-buty1 methyl chlorophosphine [7] reacts readily with 1 to form tert-buty1-methyl-[hexafluoroisopropyl]phosphite (12) in good yield. These results suggest the operation of a combination of electronic and steric effects which hinder formation of tert-buty1-bis-[hexafluoroisopropyl]phosphite.

Compound 10 can be fluorinated using SbF5 to give a mixture containing tert-buty1-fluoro-[hexa-
fluoroisopropyl)phosphite (11) and tert-butyl-difluorophosphine. Alternatively, 11 can be prepared from the reaction of tert-butyl-difluorophosphine with 1. Phenyl difluorophosphine reacts readily with 1 to give phenyl-fluoro-(hexafluoroisopropyl)-phosphite (13) in good yield. Compounds 10–13 have chiral centers at non-inverting phosphorus [8].

\[ ^1H, ^19F, \text{and } ^{31}P \text{NMR data are listed in Tables I and II.} \]

All compounds show shift values and coupling constants characteristic of the \((\text{CF}_3)_2\text{CHO}\)-group. Within the series \(\text{F}_n\text{P}[\text{OCH(CF}_3)_2]_{3-n} (n=1, 2, 3)\) there is a noticeable decrease of \(\delta P\) and increase of \(\delta PF\) with increasing \(n\). The opposite effect is found for \(\delta P\) values for the series \(\text{Cl}_n\text{P}[\text{OCH(CF}_3)_2]_{3-n} (n=1, 2, 3)\). Shift values for \(\text{PCl}_3\) and \(\text{PF}_3\) have been included for comparison.

Two magnetically non-equivalent \(\text{CF}_3\)-groups are expected for compounds 10–13 due to the chiral center at phosphorus in these compounds. Compound 10 shows two \(\text{CF}_3\)-signals which are well separated from each other (\(\Delta \delta \text{CF}_3 0.6 \text{ppm}\)), each signal is split into a doublet of quartets (\(\text{A}_3\text{M}_3\) spectrum; \(\delta J_{PF} 8.0 \text{ Hz}, \delta J_{PF} 1.0 \text{ Hz}\)). The \(\text{^19F}\) spectrum of 11 also shows different \(\text{CF}_3\)-groups (\(\Delta \delta \text{CF}_3 0.1 \text{ppm}\)) but the fine structure could not

**Table I.** Ambient temperature \(^1\text{H}, ^{19}\text{F}, \text{and } ^{31}\text{P NMR data of halophosphines } X_n\text{P}[\text{OCH(CF}_3)_2]_{3-n} (X = \text{F, Cl}; n = 0, 1, 2, 3); (\delta \text{ in ppm, } J \text{ in Hz}).

<table>
<thead>
<tr>
<th>Compound</th>
<th>(^3J_{PH}) OCH</th>
<th>(^3J_{PH}) CF(_3)</th>
<th>(^{13}P)</th>
<th>(^{19}F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{F}_2\text{P})</td>
<td>5.4 (^c)</td>
<td>34.0 ((\delta J_{PF} 1440)) 97(^b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{F}_2\text{P}[\text{OCH(CF}_3)_2]_2) (5)</td>
<td>9.0</td>
<td>47.2 ((\delta J_{PF} 1370)) 105</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{FP}[\text{OCH(CF}_3)_2]_2) (3)</td>
<td>9.0</td>
<td>52.0 ((\delta J_{PF} 1270)) 126</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{P}[\text{OCH(CF}_3)_2]_3) (2)</td>
<td>9.7</td>
<td>-77.3</td>
<td>141</td>
<td></td>
</tr>
<tr>
<td>(\text{PCl}_3)</td>
<td>13.5</td>
<td>-78.5</td>
<td>189</td>
<td></td>
</tr>
<tr>
<td>(\text{CIP}[\text{OCH(CF}_3)_2]_2) (4)</td>
<td>5.3 (^d)</td>
<td>-77.8</td>
<td>170</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Highfield from TMS, \(\text{CFCl}_3\), 85% \(\text{H}_2\text{PO}_4\) are measured as negative; \(^b\) see reference [9]; \(^c\) values in parentheses from reference [3]; \(^d\) not resolved.

**Table II.** Ambient temperature \(^1\text{H}, ^{19}\text{F}, \text{and } ^{31}\text{P NMR data of compounds 7–13}; (\delta \text{ in ppm, } J \text{ in Hz}).

<table>
<thead>
<tr>
<th>Compound</th>
<th>(^3J_{PH}) OCH(CF(_3)) (_2)</th>
<th>(^3J_{PH}) CF(_3)</th>
<th>(^{13}P) OCH(CF(_3)) (_2)</th>
<th>(^{19}F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{CF}_3)_2\text{P}[\text{OCH(CF}_3)_2]_2) (7)</td>
<td>10.5</td>
<td>4.4</td>
<td>4.5</td>
<td>-78.8(^b) 107</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_5\text{P}[\text{OCH(CF}_3)_2]_2) (8)</td>
<td>6.5</td>
<td>4.8</td>
<td>4.5</td>
<td>-78.3(^d) 185</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_5\text{P}[\text{OCH(CF}_3)_2]_2) (9)</td>
<td>9.0</td>
<td>4.6 (^c)</td>
<td>5.0</td>
<td>-74.1 221</td>
</tr>
<tr>
<td>(\text{Bu}_{1}\text{PCI}[\text{OCH(CF}_3)_2]_2) (10)</td>
<td>9.6</td>
<td>4.7</td>
<td>5.7</td>
<td>-73.5(^e) 191</td>
</tr>
<tr>
<td>(\text{Bu}_{1}\text{PP}[\text{OCH(CF}_3)_2]_2) (11)</td>
<td>7.5</td>
<td>4.7 (^e)</td>
<td>5.7</td>
<td>-74.0(^f) 223</td>
</tr>
<tr>
<td>(\text{Bu}_{1}\text{MeP}[\text{OCH(CF}_3)_2]_2) (12)</td>
<td>8.1</td>
<td>4.5</td>
<td>5.7</td>
<td>-73.8 172</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_5\text{PF}[\text{OCH(CF}_3)_2]_2) (13)</td>
<td>9.0</td>
<td>4.5 (^d)</td>
<td>6.0</td>
<td>-74.8(^f) 229</td>
</tr>
</tbody>
</table>

\(^a\) Upfield from TMS, \(\text{CFCl}_3\), 85% \(\text{H}_2\text{PO}_4\) are measured as negative; \(^b\) \(\delta \text{FCF}_3\), 65.2; \(^c\) \(\delta \text{J}_{PF}, 100\); \(^d\) \(\delta \text{FCIP}\), complex signal between 7.2–7.3; \(^e\) \(\delta \text{FCF}_3\) —739 (\(\delta \text{F}\)); \(^f\) \(\delta \text{J}_{PF}\), complex signal between 7.1–7.6.
be further resolved. Compounds 12 and 13 have complex $^{19}$F spectra where $\Delta\delta$CF$_3$ is obviously small and the spectra are of the A$_2$B$_2$ type.

The $^1$H NMR spectra of 10, 11, 12, and 13 show a complex fine structure for the OCH protons (a doublet of overlapping septets). Phosphorus decoupling simplifies the spectra and reveals the expected septet. There is no measurable difference in the coupling constants $3J_{PH}$ and $3J_{FH}$ of the non-equivalent CF$_3$-groups.

**Experimental**

The normal precautions required in handling air and moisture sensitive compounds were observed. $^1$H, $^{19}$F and $^{31}$P NMR spectra were recorded on a Jeol JNM-C 60 HL instrument at 60.0, 56.4 and 24.3 MHz respectively. Reference compounds were TMS (internal), CCl$_4$ (internal) and 85% H$_2$PO$_4$ (external).

Whenever possible, compounds were condensed under a vacuum of greater than 10$^{-3}$ mm. The starting compounds, Li[OCH(CF$_3$)$_2$]$_2$ [12], C$_6$F$_5$PCl$_2$ [6], Bu'MePCl [7], and Bu'PCl [10], were prepared as described in the literature.

Mass spectra were recorded on an AEI MS9 instrument.

**Fluoro-bis-(1,1,1,3,3,3-hexafluoroisopropyl)phosphite** (3)

Chloro-bis-(1,1,1,3,3,3-hexafluoroisopropyl)phosphite (2.0 g; 5 mmol) was condensed into a glass tube, fitted with a teflon valve, at $-196^\circ$C and containing SbF$_5$ (0.55 g; 3 mmol). The tube was left to warm to room temperature and was then left for 2 h. The colourless liquid 3 was condensed into a trap at $-80^\circ$C. B.p. 43 °C. Yield 1.45 g (82% based on 4).

Found C 18.8 H 0.5 F 64.3.
Calcd C 18.9 H 0.6 F 64.1.

M.S. 384 (M$^+$, 3%), 43 (PC$^+$, 100%).

**Chloro-bis-(1,1,1,3,3,3-hexafluoroisopropyl)phosphite** (4)

Phosphorus trichloride (1.35 g; 10 mmol) was condensed into a glass tube at $-196^\circ$C containing 1 (3.5 g; 20 mmol). The tube was allowed to warm to room temperature over a period of two h and the volatiles were condensed into a second glass tube at $-196^\circ$C. An approximately equimolar mixture (identified by $^{31}$P NMR) of PCl$_3$, 2, 4, and 6 was obtained and was separated using trap to trap condensation with traps at 0 °C, $-40^\circ$C, and $-196^\circ$C. The trap at $-40^\circ$C contained the colourless liquid 4. A second fractional condensation was necessary to obtain pure 4. B.p. 85 °C. Yield 0.8 g (20%, based on PCl$_3$). C$_6$H$_2$F$_2$O$_2$PCl (400.47).

M.S. 400 ($^{35}$Cl) (M$^+$, 1%), 77 (H$_2$ClF$_2$+, 100%).

**Dichloro-(1,1,1,3,3,3-hexafluoroisopropyl)phosphate** (6)

PCl$_3$ (1.35 g; 10 mmol) was condensed into a glass tube at $-196^\circ$C containing 1 (1.75 g; 10 mmol). The tube was allowed to warm to room temperature over 2 h. Again a mixture of products was obtained and was separated using traps at $-40^\circ$C, $-80^\circ$C and $-196^\circ$C. The trap at $-80^\circ$C contained the colourless liquid 6.

B.p. 68 °C. Yield 0.65 g (24%, based on PCl$_3$). C$_6$HF$_5$OPCl$_3$ (268.93).

M.S. 269 ($^{35}$Cl) (M$^+$, 5%), 101 (HC$_6$F$_7$+ or F$_2$O$_2$P+, 100%).

**Difluoro-(1,1,1,3,3,3-hexafluoroisopropyl)phosphate** (5)

Dichloro-(1,1,1,3,3,3-hexafluoroisopropyl)phosphate (1.9 g; 7 mmol) was condensed into a tube at $-196^\circ$C containing SbF$_5$ (0.7 g; 4 mmol). The tube was allowed to warm to room temperature over 2 h and the colourless liquid product, 5, was condensed into another tube at $-196^\circ$C. Yield 1.4 g (80%, based on 6).

**Bis-trifluoromethyl-(1,1,1,3,3,3-hexafluoroisopropyl)phosphite** (7)

Bis-trifluoromethyl iodophosphine (3.0 g; 10 mmol) was condensed into a tube at $-196^\circ$C containing 1 (1.9 g; 11 mmol). The tube was allowed to warm to room temperature over 1 h and the colourless liquid product, 7, condensed into another tube at $-196^\circ$C.

B.p. 71 °C. Yield 2.8 g (85%, based on trifluoromethyl iodophosphine).

C$_6$HF$_3$OP (336.01).

Found C 17.5 H 0.3 F 67.3.
Calcd C 17.9 H 0.3 F 67.9.

M.S. 336 (M$^+$, 30%), 69 (CF$_2$+, 100%).

**Pentafluorophenyl-bis-(1,1,1,3,3,3-hexafluoroisopropyl)phosphite** (8)

Pentafluorophenyl dichlorophosphine (2.7 g; 10 mmol) was added through a syringe, under nitrogen, to a flask containing 1 (3.8 g; 22 mmol). The mixture was heated at 60 °C for 2 h; the colourless liquid, 8, was distilled at 48°/10$^{-3}$ mm. Yield 3.2 g (60%, based on pentafluorophenyl dichlorophosphine).

C$_{12}$H$_2$F$_7$O$_2$P (5332.09).

Found C 27.2 H 0.4 F 60.5.
Calcd C 27.1 H 0.4 F 60.7.

M.S. 535 (M$^+$, 100%).

**Phenyl-bis-(1,1,1,3,3,3-hexafluoroisopropyl)phosphite** (9)

Phenyl dichlorophosphine (3.6 g; 20 mmol) was added through a syringe, under nitrogen, to a flask...
containing 1 (7.6 g; 44 mmol). The mixture was heated to 60 °C for 2 h and the colourless liquid, 9, was distilled at 70 °C/0.1 mm.

Yield 5.9 g (67%, based on phenyl dichlorophosphine).

C₁₂H₇F₁₂O₂P (442.14)
Found H 1.6 F 51.3,
Caled H 1.6 F 51.6.
M.S. 442 (M⁺, 100%).

Tert-butyl-chloro-(1,1,1,3,3,3-hexafluoroisopropyl)-phosphite (10)

Tert-butyl-dichlorophosphine (1.6 g; 10 mmol) was condensed into a tube containing 1 (3.8 g; 22 mmol). The tube was allowed to warm to room temperature over 1 h and was then left a further 2 h. The colourless liquid, 10, was condensed into another tube at —196 °C.

B.p. 128 °C. Yield 2.3 g (80%, based on tert-butyl-dichlorophosphine).

C₇H₃F₇OPCl (290.57)
Found H 3.3 F 40.8,
Caled H 3.5 F 39.3.
M.S. 290 (M⁺, 2%), 57 (C₁H₉⁺, 100%).

Tert-butyl-fluoro-(1,1,1,3,3,3-hexafluoroisopropyl)-phosphine (11)

Tert-butyl-difluorophosphine [11] (0.6 g; 5 mmol) was condensed into a tube at —196 °C containing 1 (2.6 g; 15 mmol). The tube was allowed to warm to room temperature over 1 h and then left for a further two days. The volatiles were condensed into a second trap at —196 °C at —70 °C containing the colourless liquid, 11. The mixture was separated by trap to trap condensation using traps at —70 °C and —196 °C. The trap at —70 °C containing the colourless liquid product, 11.

B.p. 38–40 °C. Yield 0.8 g (60%, based on tert-butyl-difluorophosphine).

C₅H₁₅F₇OP (274.09)
Found C 32.6 H 1.6 F 51.6,
Caled C 32.4 H 1.6 F 51.3.
M.S. 274 (M⁺, 7%), 57 (C₁H₅⁺, 100%).

Tert-butyl-methyl-(1,1,1,3,3,3-hexafluoroisopropyl)-phosphine (12)

Tert-butyl-methyl-chlorophosphine (2.8 g; 20 mmol) was condensed into a tube at —196 °C containing 1 (3.8 g; 22 mmol). The tube was allowed to warm to room temperature over 1 h and then left for a further 2 h. The colourless liquid, 12, was condensed into another tube at —196 °C.

B.p. 132 °C. Yield 6.2 g (95%, based on tert-butyl-methyl-phosphine).

C₅H₁₃F₅OP (270.16)
Found C 35.2 H 4.7 F 42.3,
Caled C 35.5 H 4.8 F 42.3.
M.S. 270 (M⁺, 4%), 57 (C₁H₅⁺, 100%).

Phenyl-fluoro-(1,1,1,3,3,3-hexafluoroisopropyl)-phosphine (13)

Phenyl difluorophosphine (2.9 g; 20 mmol) was condensed into a tube at —196 °C containing 1 (3.8 g; 22 mmol). The tube was allowed to warm to room temperature and then warmed at 80 °C for 4 h. The colourless liquid, 13, was distilled at 40 °C/10⁻² mm. Yield 4.5 g (77%, based on phenyl difluorophosphine).

C₅H₄F₄OP (294.16)
Found C 36.5 H 2.0 F 45.2,
Caled C 36.7 H 2.0 F 45.2.
M.S. 294 (M⁺, 73%), 77 (C₁H₅⁺, 100%).

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