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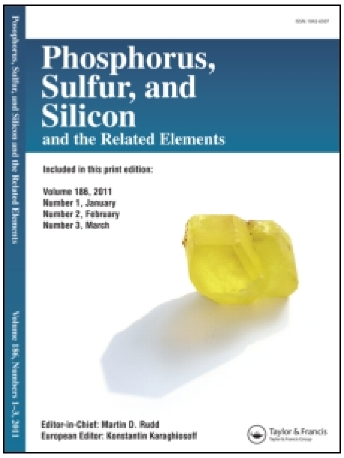

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FLUORINATED MONO AND SPIROCYCLIC $\lambda^5\sigma^5P$ AND $\lambda^5\sigma^6P$ DERIVATIVES OF $(HO)_{3-n}H_nPO$ (n= 0-3)

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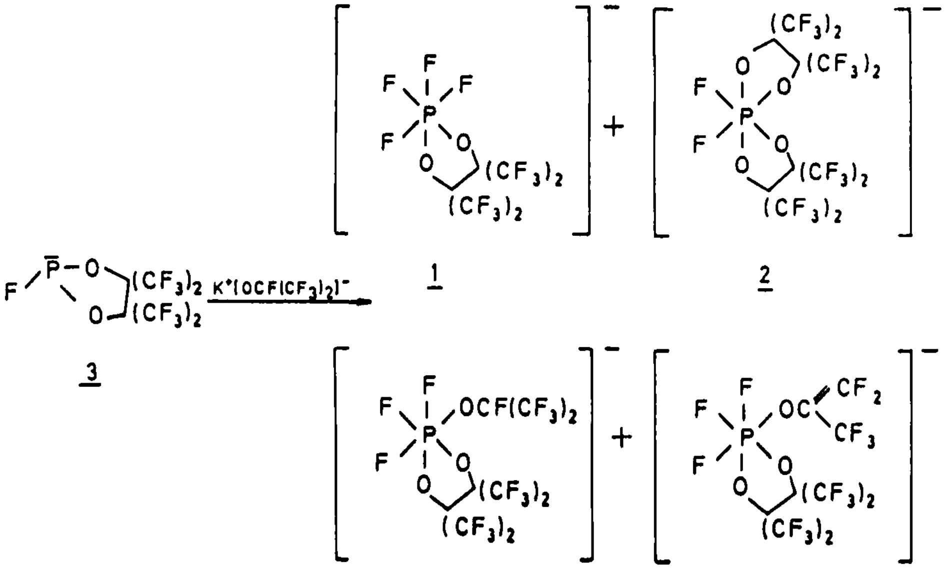
The properties of PF_5, HPF_4, H_2PF_3, and H_3PF_2 ($\lambda^5\sigma^5P$ derivatives of $(HO)_3PO$, $(HO)_2HPO$, $(HO)H_2PO$, and of the hypothetic H_3PO) and the formation of the related $\lambda^5\sigma^6P$ anions PF_6^-, HPF_5^-, and trans-$H_2PF_4^-$ have been studied some years ago[1-4]. The mono and spirocyclic dioxa and tetraoxa analogues, 1 and 2 available from the corresponding precursor phosphoranes by fluoride addition could be found also as products in the reaction of phosphite 3[5] and $K^+(CF_3)_2CFO^-$ together with two other phosphates, 4 and 5. A ^{19}F-^{19}F homocorrelated 2 D NMR spectrum of 2 indicated coupling of the P-F fluorine nuclei with two CF_3 groups by a non bond mechanism.



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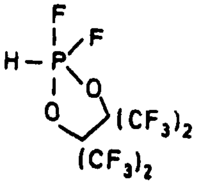
The monocyclic trifluorophosphorane[5] $F_3P\ OC(CF_3)_2C(CF_3)_2O$ was hydrogenated using Me_3SiH to yield hydrophosphorane 6. The spirocyclic tetraoxa(hydro)phosphoranes, 7, 8, and 9 were obtained when $NH_4^+\ HOC(CF_3)_2C(CF_3)_2O^-$ was made to react with various cyclic chlorophosphites, e. g. $ClP\ OC(CF_3)_2C(CF_3)_2O$ [6], $ClP(OCH_2CH_2O)$, and $ClP(OCH_2CH_2CH_2O)$. Compound 9 is the first stable five-six membered spiro(hydro)phosphorane.



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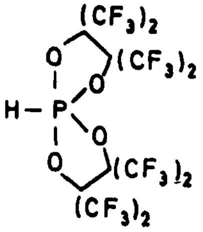

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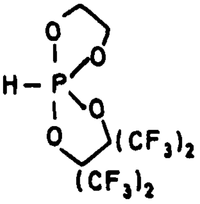

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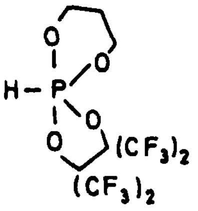

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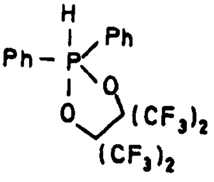
In the case of hydrophosphorane 10, formed from Ph_2PCl and $Et_3NH^+\ HOC(CF_3)_2C(CF_3)_2O^-$ hydrogen positioned axial in a trigonal bipyramide could be established by x-ray structure determination. Trimethylamine converted 6 into 3 and anion 11. Compound 12 was obtained from fluoride addition to hydrophosphorane 7 in a mixture with 11 and phosphoranide 13, which shows a considerable large difference in the two $P\text{-}O_{ax}$ bond lengths in the solid state.



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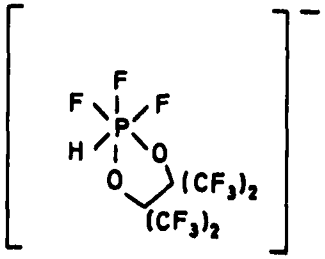

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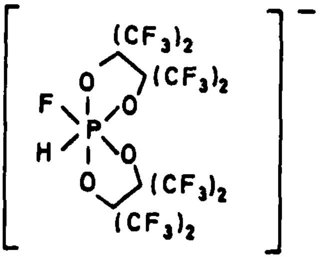

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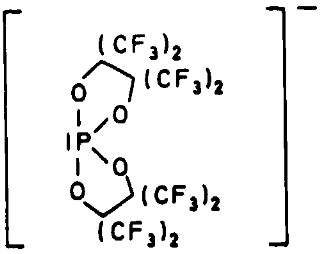
Compound 13 is a good nucleophile, e. g. sulfur reacted to give a phosphorane sulfide precursor for the corresponding acid 14 and the chlorosulfide 15.



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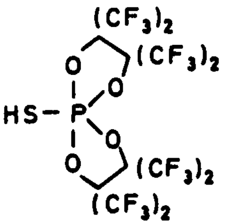

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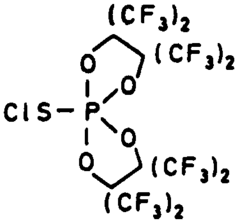

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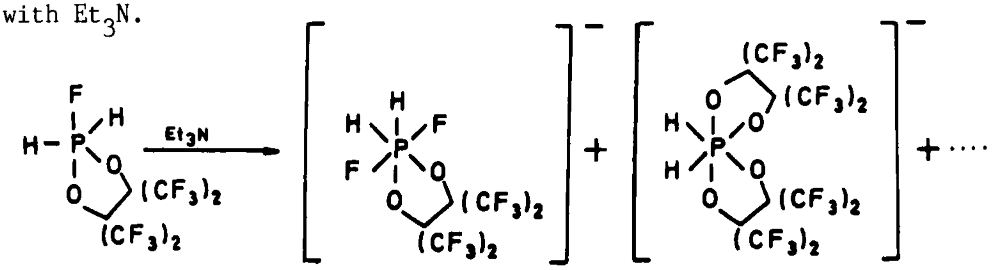
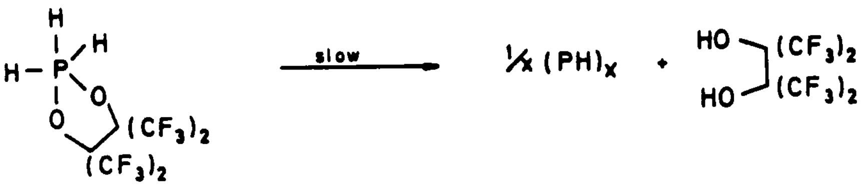
Dihydrophosphorane 16 product of the hydrogenation of 6 with Me_3SnH gave the phosphates 17, 18 and other species upon treating with Et_3N.



16 17 18

Trihydrophosphorane 19 was generated in solution from 16 and Me_3SnH. A slow decomposition into $(PH)_x$ and perfluoropinacol was observed.



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The hydrophosphoranes 6, 16, and 19 exhibited a remarkable thermal stability with the acyclic species HPF_4, H_2PF_3, and H_3PF_2. They can be considered hydrogen transfer reagents. The mechanism for the formation of $\lambda^5\sigma^6P$ phosphates will be discussed as well as possible geometrical isomers. The direct P-H coupling constants give insight into the degree of s-bond charcter of the bond in question.

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