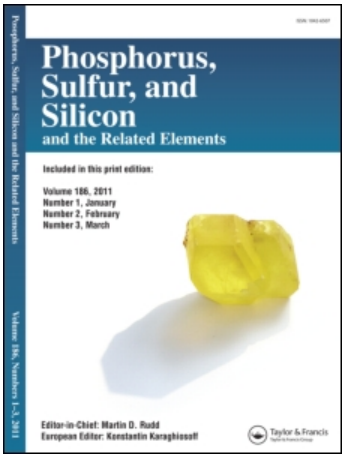

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Reaction of Hexafluoroacetone with Aminophosphites Containing the 2,2,2-Trifluoro-1-(trifluoromethyl)ethyl Grouping

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Reaction of Hexafluoroacetone with Aminophosphites Containing the 2,2,2-Trifluoro-1-(trifluoromethyl)ethyl Grouping

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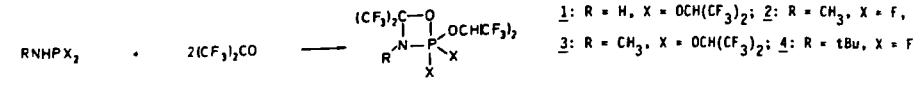
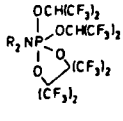
The reactions of dihaloaminophosphines $RNHPF_2$ (R=H, Me, tBu) and R_2NPCl_2 (R=Me, Et, $SiMe_3$; $R_2=CH_2(CH_2CMe_2)_2$ with $LiOCH(CF_3)_2$ yield the corresponding aminophosphites $R_2NP[OCH(CF_3)_2]_2$. Hexafluoroacetone reacts with $RNH[OCH(CF_3)_2]_2$ as well as $MeNHPF_2$ and $tBuNHPF_2$ in good yields to the 1,3,5λ^5-oxazaphosphetanes 1 - 4, which show rapid pseudorotation at room temperature.



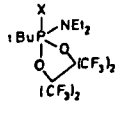
1: R = H, X = $OCH(CF_3)_2$; 2: R = CH_3, X = F,
3: R = CH_3, X = $OCH(CF_3)_2$; 4: R = tBu, X = F

The X-ray structure of 1 exhibits a distorted trigonal bipyramid.

With dialkylaminophosphites hexafluoroacetone gives the monocyclic phosphoranes 5 and 6, whereas with aminophosphites containing bulky alkylgroups no reaction occurs. A replacement of the $(CF_3)_2CHO$-groups by smaller substituents results in easier addition of hexafluoroacetone. Therefore the aminophosphines $tBuP(X)NEt_2$ (X=F, Cl, $OCH(CF_3)_2$) react with hexafluoroacetone in high yields to the 1,3,2λ^5-dioxaphospholanes 7 - 9. The phosphoranes 5 - 9 show no ligand exchange process at room temperature.



5: R = Me
6: R = Et



7: X = F, 8: X = Cl,
9: X = $OCH(CF_3)_2$