

REACTION OF $\text{PF}_5 \cdot \text{CH}_3\text{CN}$ WITH SULFIDE

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Nitriles react with PF_5 and also with AsF_5 , SbF_5 forming 1:1-adducts. Using $\text{C}_2\text{Cl}_3\text{F}_3$ as a solvent is of advantage for this reaction. $\text{PF}_5 \cdot \text{CH}_3\text{CN}$ and $[\text{N}(\text{C}_2\text{H}_5)_4]\text{SH}$ give $[\text{N}(\text{C}_2\text{H}_5)_4][\text{P}_2\text{S}_2\text{F}_8]$ with a sulfur double bridge and hexafluorophosphate in acetonitrile [1]. In case of $\text{AsF}_5 \cdot \text{CH}_3\text{CN}$ a salt with the anion $[\text{AsF}_5\text{-NH-CS-CH}_3]^-$ has been isolated [2]. Following products have been confirmed in a reaction mixture of $\text{PF}_5 \cdot \text{CH}_3\text{CN}$ and SH^- in acetonitrile by NMR (^{31}P and ^{19}F): $[\text{PF}_6]^-$, $[\text{F}_5\text{P-S-PF}_5]^{2-}$, $[\text{F}_4\text{P} \begin{smallmatrix} \text{S} \\ \text{S} \end{smallmatrix} \text{PF}_4]^{2-}$, F_4PSH , F_3PS , HPS_2F_2 , $[\text{PS}_2\text{F}_2]^-$, $[\text{F}_5\text{P-N=C(SH)-CH}_3]^-$, $[\text{F}_5\text{P-NH-CS-CH}_3]^-$, $[\text{F}_5\text{PSH}]^-$. With a ratio $\text{PF}_5 \cdot \text{CH}_3\text{CN} : \text{SH}^- = 2:1$ the S-bridge-complexes are preferred whereas in case of a ratio 1:1 the non-bridged P-complexes are the main products.

1 L.Kolditz, U.Calov a. Chr.Bechstein, Z.Chem.,20, 303 (1980)

2 L.Kolditz a. I.Beierlein, Z.Chem. 18, 452 (1978)