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STRUCTURAL INVESTIGATIONS OF THE REACTION PRODUCTS OF NITRILES WITH PCl_5

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After the investigation of the reaction products of PCl_5 with acetonitrile,¹ the products with benzonitrile and malodinitrile were characterized by single-crystal x-ray structural analyses at 90K in an attempt to clarify the reaction of PCl_5 with nitriles: With $\text{C}_6\text{H}_5\text{—CN}$ the unsymmetrical compound $\text{C}_6\text{H}_5\text{P—C(Cl)=N—C(C}_6\text{H}_5\text{)=N—PCl}_3^+\text{PCl}_6^-$ (Figure 1) is obtained instead of the reported salt containing the symmetrical cation $\text{Cl}_2\text{P(N=C(Cl)—C}_6\text{H}_5\text{)}_2^+$.²

The reaction of $\text{CH}_2(\text{CN})_2$ with PCl_5 gave the [1,3,2]diazaphosphinines $\text{R—C[C(Cl)N]}_2\text{PCl}_2$ (R=H, Cl) (Figures 2 and 3)³ and the hitherto unknown salts $\text{R—C[C(Cl)NPCl}_3\text{]}_2^+\text{PCl}_6^-$ (R=H, Cl) (Figures 4 and 5). The cations in the latter compounds show remarkable all-*cis* conformations in their N—C—C—N chains. In the cation of the salt with

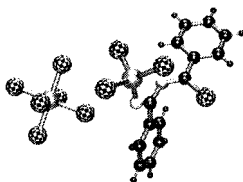


FIGURE 1 Structure of $\text{C}_6\text{H}_5\text{P—C(Cl)=N—C(C}_6\text{H}_5\text{)=N—PCl}_3^+\text{PCl}_6^-$.

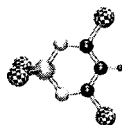


FIGURE 2 Structure of $\text{H—C[C(Cl)N]}_2\text{PCl}_2$.

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FIGURE 3 Structure of $\text{Cl}-\text{C}[\text{Cl}(\text{N})_2]\text{PCl}_2$.

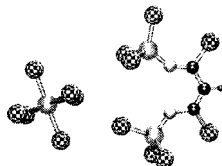


FIGURE 4 Structure of $\text{H}-\text{C}[\text{Cl}(\text{NPCl}_3)_2]^+\text{PCl}_6^-$.

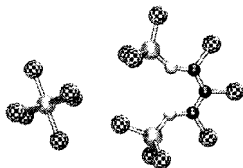


FIGURE 5 Structure of $\text{Cl}-\text{C}[\text{Cl}(\text{NPCl}_3)_2]^+\text{PCl}_6^-$.

$\text{R} = \text{H}$ the distance between N1 and N3 of only $2.673(14)\text{\AA}$ is 0.43\AA shorter than the sum of the van der Waals radii. Due to the substitution of the H atom by a Cl atom this distance is further diminished to only $2.637(4)\text{\AA}$ [comp. $2.674(3)\text{\AA}$ in $\text{Cl}-\text{C}[\text{Cl}(\text{N})_2]\text{PCl}_2$].

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