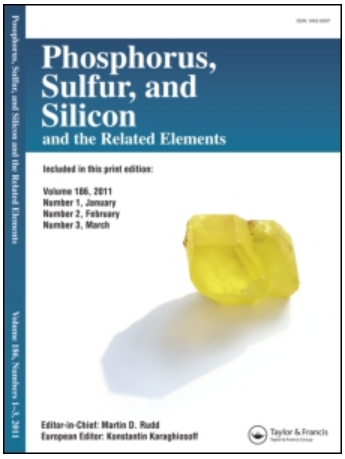

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Structural Investigations of the Reaction Products of Nitriles with PCl 5

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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 C_6H_5—CN the unsymmetrical compound C_6H_5P—C(Cl)=N—C(C_6H_5)=N—$PCl_3^+PCl_6^-$ (Figure 1) is obtained instead of the reported salt containing the symmetrical cation $Cl_2P(N{=}C(Cl){-}C_6H_5)_2^+$.[2]

The reaction of $CH_2(CN)_2$ with PCl_5 gave the [1,3,2]diazaphosphinines R—C[C(Cl)N]$_2PCl_2$ (R = H, Cl) (Figures 2 and 3)[3] and the hitherto unknown salts R—C[C(Cl)NPCl_3]$_2^+PCl_6^-$ (R = H, Cl) (Figures 4 and 5). The cations in the latter compounds show remarkable all-*cis* conformations in their N—C—C—C—N chains. In the cation of the salt with

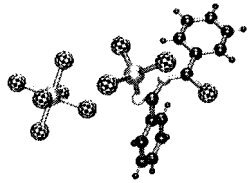

FIGURE 1 Structure of C_6H_5P–C(Cl)=N–C(C_6H_5)=N—$PCl_3^+PCl_6^-$.

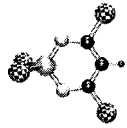

FIGURE 2 Structure of H–C[C(Cl)N]$_2PCl_2$.

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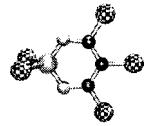

FIGURE 3 Structure of Cl–C[C(Cl)N]$_2$PCl$_2$.

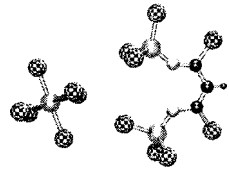

FIGURE 4 Structure of H–C[C(Cl)NPCl$_3$]2$^+$PCl$_6$.

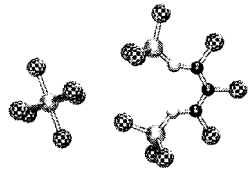

FIGURE 5 Structure of Cl–C[C(Cl)NPCl$_3$]2$^+$PCl$_6$.

R = H the distance between N1 and N3 of only 2.673(14)Å is 0.43Å 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)Å [comp. 2.674(3)Å in Cl–C[C(Cl)N]2PCl$_2$].

REFERENCES

[1] F. Belaj, *Phosphorus, Sulfur, and Silicon*, **147,** 27 (1999).
[2] E. Fluck and F. Horn, *Phosphorus*, **3,** 59–64 (1973).
[3] O. V. Kirsanov, M. D. Bodnarchuk, and V. I. Shevchenko, *Dopividi Akad. Nauk Ukr.*, *RSR*, 221 (1963).