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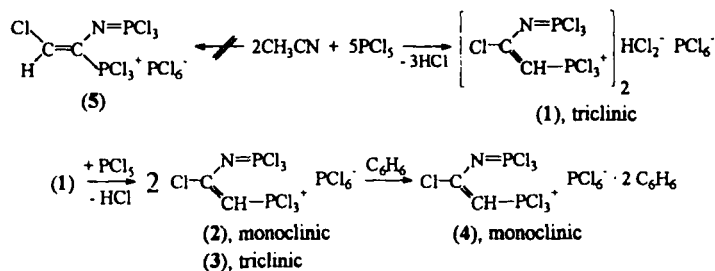
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Elucidation of the Reaction Products of Acetonitrile with Phosphorus Pentachloride

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The reaction of acetonitrile with PCl_5 results in the ionic compounds (1) to (4) containing the trichloro[2-chloro-2-[(trichlorophosphoranylidene)amino]ethenyl]phosphorus cations and not in the compounds $[\text{CH}_2=\text{C}=\text{N}(\text{PCl}_3)]\text{PCl}_6^{[1]}$ or trichloro[2-chloro-1-[(trichlorophosphoranylidene)amino]ethenyl]phosphorus hexachlorophosphate (5) as assumed from ^{31}P -NMR spectra $^{[2, 3]}$. The crystal structures of the compounds (1) to (4) were determined with X-rays at 95K. As observed for the $\text{Cl}-\text{C}(\text{N}(\text{PCl}_3)_2)^+$ cation $^{[4]}$, all the cations show *cis-trans* conformations with respect to their $\text{Cl}-\text{C}-\text{X}-\text{P}$ torsion angles. The $\text{N}(\text{PCl}_3)_2$ groups of the cations have two different orientations with one $\text{C}-\text{N}=\text{P}-\text{Cl}$ torsion angle of about 0° (*cis*) as in (1) or about 180° (*trans*) as in (3) and (4). In the salt (2) there are two formula units in the asymmetric unit with one cation showing the *cis* and the other showing the *trans* conformation.



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