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From Neutral to Cationic Adducts: Investigations on the System Halogeno (Imino) Phosphane (Bisiminophosphorane)/DMAP

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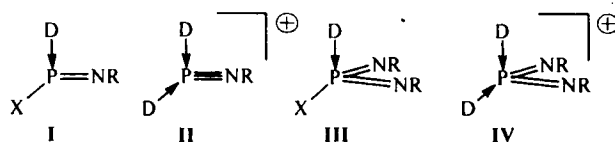
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From Neutral to Cationic Adducts: Investigations on the System Halogeno(Imino)Phosphane (Bisiminophosphorane)/DMAP

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Cations containing a unifold coordinated phosphorus center have been verified in the case of iminophosphenium salts^[1a], and their chemistry has been explored in some detail^[1b]. Herein we report on the Lewis-acid/base reactions between halogeno-(imino)phosphanes (X=Cl, Br, I) and the neutral amine-donor dimethylaminopyridine (DMAP).



The reaction results in the formation of the neutral adducts (I) as well as the iminophosphenium salts (II), the constitution of which was elucidated by means of NMR-investigations and X-ray crystal structure determinations. Based on a variety of crystal structures of I (X=Cl), which show different phases of the base approaching to the halogeno(imino)phosphane, a mechanism for the donor-acceptor reaction is proposed. Analogous treatment of halogeno-bis(imino)phosphoranes with DMAP leads to the formation of the adducts (III) and the bis(imino)phosphonium salts (IV) respectively. X-ray crystal structures of the bromo-bis(imino)phosphorane/base adduct (III) as well as of the bis(imino)phosphonium salt (IV) could be obtained.

References

- [1] a) E. Niecke, F. Reichert, M. Nieger, W.W. Schoeller, *Angew. Chem. Int. Ed. Engl.* **1988**, 27, 1715-1717, b) D. Gudat, *Coordination Chemistry Reviews* **1997**, 163, 71-106.