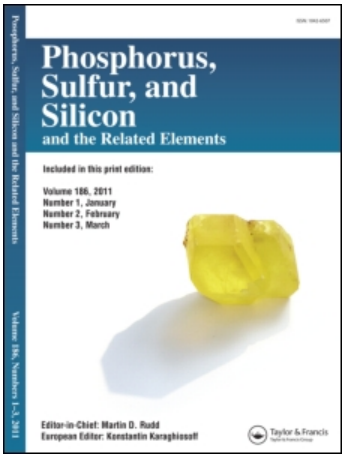

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Synthetic and Structural Studies of Cyclophosphathiazenes and their Adducts with Lewis Acids

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Synthetic and Structural Studies of Cyclophosphathiazenes and their Adducts with Lewis Acids

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The reactions of $(Me_3SiNR)PPh_2(NSiMe_3)$ (R = H, $SiMe_3$) with $(NSCl)_3$ or S_xCl_2 (x = 1, 2) provide improved preparative routes to mixed phosphazene-thiazene ring systems, e.g. $(Ph_2PN)(SN)_2$, 1,3- and 1,5-$(Ph_2PN)_2(SN)_2$. The interaction of these heterocycles with protonic and Lewis acids, e.g. HBF_4, BCl_3, $MeSO_3CF_3$, has been investigated in order to determine the site of attack and the effect of adduct formation on the molecular and electronic structures of these ring systems. These reactions have been monitored by UV-visible and ^{31}P NMR spectroscopies and the structures of crystalline adducts have been determined by X-ray crystallography. For example, the interaction of 1,3-$(Ph_2PN)_2(SN)_2$ with $MeSO_3CF_3$ gives a product in which the methyl group is attached to a nitrogen atom between phosphorus and sulfur. The resulting structural distortion in this and related adducts will be analyzed in the context of the electronic structures of mixed phosphazene-thiazene systems and their adducts with Lewis acids.