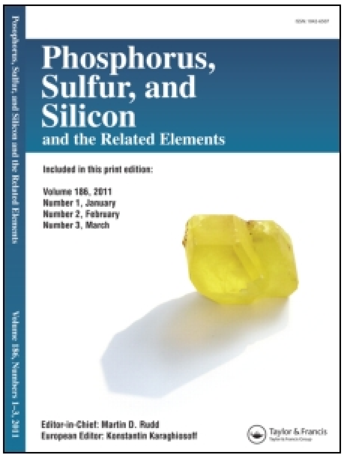

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Substitution Reactions of Hexachloro γ^5-diazadiphosphetidines - First Examples of Hexa(alkoxy)/(aryloxy) Derivatives, $[RNP(OR')_3]_2$

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SUBSTITUTION REACTIONS OF HEXACHLORO λ^5-DIAZADIPHOSPHETIDINES - FIRST EXAMPLES OF HEXA(ALKOXY)/(ARYLOXY) DERIVATIVES, $[RNP(OR')_3]_2$

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Abstract The reactions of the hexachloro λ^5-diazadiphosphetidine, $[(MeN)PCl_3]_2$ (I) with NaOR' (R = Ph or CH_2CF_3) lead to the isolation of the hitherto unprecedented hexa(alkoxy)/(aryloxy) derivatives, $[(MeN)P(OR')_3]_2$ (II) which have been characterized by mass spectrometry and NMR (^1H and ^{31}P) spectroscopy. The structure of the trifluoroethoxy derivative (II, R' = CH_2CF_3) has been confirmed by single crystal X-ray analysis. Analogous reactions of the N-phenyl derivative $[(PhN)PCl_3]_2$ afford only the monophosphazenes, $PhN{=}P(OR')_3$. Aniline reacts with I in a Kirsanov type of reaction accompanied by ring opening to give a bis(phosphineimino)diphosphazane derivative, (PhN=)(NHPh)(NHMe)PN(Me)-$P(NHPh)_2$(=NPh). The X-ray crystal structure of a related cyclic derivative trans-$[PhNP(NMe_2)(=NPh)]_2$ has been determined. The N_2P_2 ring and the aryl groups attached to the ring nitrogen atoms are coplanar; the exocyclic P=N bond (151.8 pm) is much shorter than the other P-N bonds (162.5, 169.8 pm).