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

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