

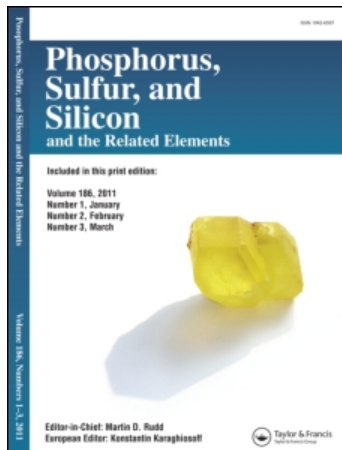
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Nucleophilic Substitution Reactions at the Dicoordinated Phosphorus Atom: Synthetic Aspects

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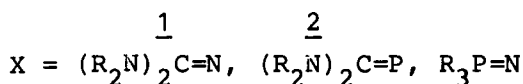
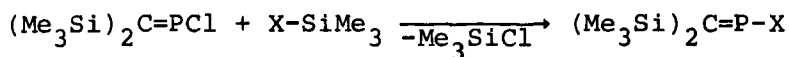
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NUCLEOPHILIC SUBSTITUTION REACTIONS AT THE DICOORDINATED PHOSPHORUS ATOM: SYNTHETIC ASPECTS

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The nucleophilic substitution reactions in the series (a) P-chloro-phosphaalkenes $\text{Cl-P}=\text{CR}^1\text{R}^2$; (b) P-aryloxy- λ^3 -imino-phosphines $\text{ArO-P}=\text{NMe}^*$; (c) P-halodiphosphenes $\text{Hlg-P}=\text{P-Me}^*$ were studied. Reactions of the phosphalkene 1 with N- and P-nucleophiles of type 2 represent a convenient route to obtain various phosphadienes 3.¹



In the case of P-aryloxyiminophosphines substitution of ArO-group of RO^- , RS^- , R_2P^- and R_2N^- anions can be easily realized. An interesting result was obtained in the reaction between $\text{PhO-P}=\text{NMe}^*$ and Me_2NLi . Although this reaction gives the product of normal nucleophilic substitution, it has unusual structure. This is the first cis-isomer, detected and identified structurally in the series of iminophosphines $\text{XP}=\text{NY}$.²

Diphosphene $\text{Me}^*\text{-P}=\text{P-NPr}_2$ (4), by action of HHlg , was transformed to the corresponding P-halodiphosphenes $\text{Me}^*\text{-P}=\text{P-Hlg}$ (5-7): 5, $\text{Hlg} = \text{Cl}$, $\delta_{\text{P}} 522.8, 473.4$, $^1\text{J}_{\text{PP}} 598 \text{ Hz}$; 6: $\text{Hlg} = \text{Br}$, $\delta_{\text{P}} 532.3, 458.3$, $^1\text{J}_{\text{PP}} 586 \text{ Hz}$; 7: $\text{Hlg} = \text{I}$, $\delta_{\text{P}} 560, 431$, $^1\text{J}_{\text{PP}} 574 \text{ Hz}$. Reactions of the diphosphene 5 with nucleophilic reagents XLi ($\text{X} = \text{RO}^-$, R_3Si^- , R_2N^- et al.) lead to the derivatized diphosphenes.

1. L.N. Markovsky, V.D. Romanenko, L.S. Kachkovskaya et al., Zh. Obshch. Khim. 57, 901 (1987).
2. V.D. Romanenko, A.V. Ruban, A.N. Chernega et al., Zh. Obshch. Khim. 58, 948 (1988).