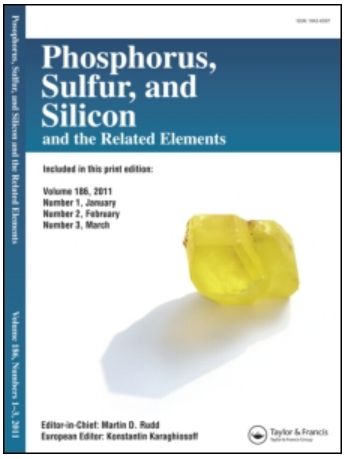

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The First Example of 1,1-σ-Complexes of Phosphorus Nucleophiles

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THE FIRST EXAMPLE OF 1,1-σ-COMPLEXES OF PHOSPHORUS NUCLEOPHILES.

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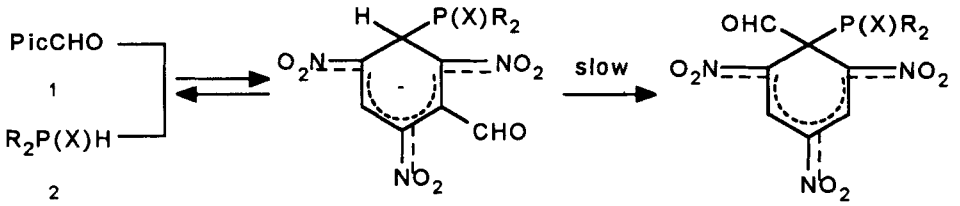
We report on the first phosphorus 1,1-σ-complexes, relatively stable in DMSO. Adducts of this type are important as possible intermediates in nucleophilic aromatic substitution reactions but for phosphorus nucleophiles 1,1-σ-complexes were never detected [1]. We have found that interaction of 1 with 2 in DMSO leads initially to 1,3-σ-complexes 3 which slowly rearrange to 1,1-σ-complexes 4.



R = Alk, Ph; X = O, S

The effect of R and X on the σ-complexation and mechanism of 1,3-phosphorotropic rearrangement 3→4 will be discussed. The results obtained show that nucleophilic phosphorylation of electron-deficient aromatics can, in principle, proceed by addition-elimination S_NAr mechanism. The capability of phosphorus atom to change its coordination number provides new pathways (in particular, those involving five-coordinated intermediates) of aromatic substitution for phosphorus nucleophiles.

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