Design and Synthesis of Phosphinidene Chalcogenides

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Clusters
Skylla Cluster Gießen, Goethe-HLR Frankfurt

Additional Software
Linux, Windows

Institute
Institute of Organic Chemistry

University
Justus Liebig University Giessen

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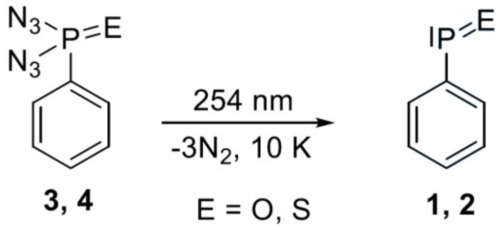


Introduction

Phosphinidene chalcogenides (R–P=E; Ch = O, S, Se) are phosphorus analogues of organic nitroso compounds (R–N=O). In contrast to the robust stability of R–N=O, phosphinidene chalcogenides have been considered extremely reactive species.[1-2] These transient species are very reactive toward organic molecules and have been thus used as efficient synthons for new organophosphorus derivatives.[3-5]

Stabilization of R–P=E species can be achieved through coordination to metal centers (thermodynamic stability) or using bulky substituents (kinetic stability). Phenylphosphinidene oxide Ph–P=O (**1**) (the phosphorus analogue of nitrosobenzene) and phenylthiooxophosphine Ph–P=S (**2**), are hitherto unknown experimentally, although the structures and energies of Ph–P=E (E = O, S) and their metal complexes have been computationally and experimentally studied.[6]

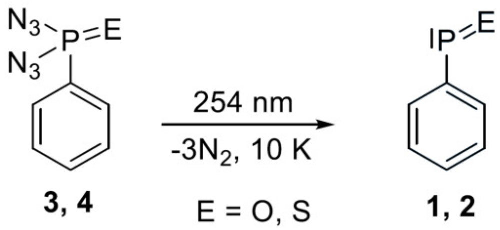
Discussion

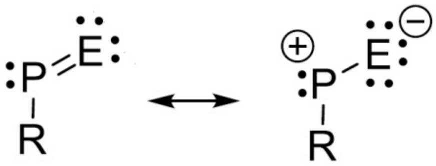
Herein, we aim at synthesizing and isolating yet unreported Ph–P=O and Ph–P=S through either flash vacuum pyrolysis or photolysis of their respective azide precursors PhP(E)(N3)2 (E = O, S), thus enabling further studies on their structures and reactivities as ligand-free species. We plan to extend our method to exploit mono-substituted azide precursors. Similar azide architectures have allowed a facilegeneration of transient nitrenes upon irradiation or themolysis.[7]

Outlook

We will study their chemical and physicalproperties using both experimental and computational methods. Density functional theory (DFT) and *ab initio* computations will be used to determine the substituent effects on the vibrational as well as optical spectra, photochemistry, geometries, and transitions states for subsequent reactions.

Figures





Reference

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