

# Design and Synthesis of Phosphinidene Chalcogenides

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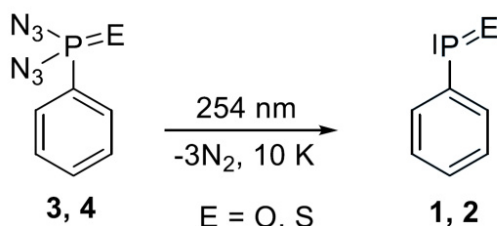
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## Introduction

Phosphinidene chalcogenides ( $\text{R-P=E}$ ; Ch = O, S, Se) are phosphorus analogues of organic nitroso compounds ( $\text{R-N=O}$ ). In contrast to the robust stability of  $\text{R-N=O}$ , 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  $\text{R-P=E}$  species can be achieved through coordination to metal centers (thermodynamic stability) or using bulky substituents (kinetic stability). Phenylphosphinidene oxide  $\text{Ph-P=O}$  (**1**) (the phosphorus analogue of nitrosobenzene) and phenylthiooxophosphine  $\text{Ph-P=S}$  (**2**), are hitherto unknown experimentally, although the structures and energies of  $\text{Ph-P=E}$  ( $\text{E} = \text{O, S}$ ) and their metal complexes have been computationally and experimentally studied.[6]

## Discussion

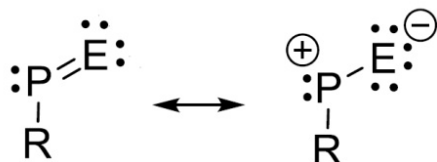
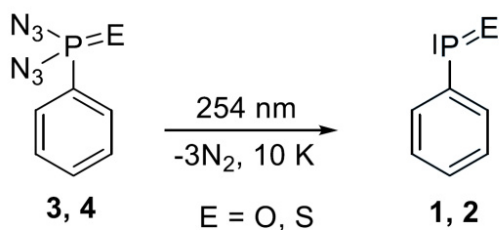
Herein, we aim at synthesizing and isolating yet unreported  $\text{Ph-P=O}$  and  $\text{Ph-P=S}$  through either flash vacuum pyrolysis or photolysis of their respective azide precursors  $\text{PhP(E)(N}_3)_2$  ( $\text{E} = \text{O, S}$ ), thus enabling further studies on their structures and reactivities as ligand-free species. We plan to extend our method to exploit mono-substituted azide precursors. Similar azide architectures have allowed a facile generation of transient nitrenes upon irradiation or thermolysis.[7]

## Outlook

We will study their chemical and physical properties 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 transition states for subsequent reactions.

## Figures



## Reference

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