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# *Design and Synthesis of Arylphosphinidenes and Phosphirenes*


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## Introduction

It is well-known that the irradiation of aromatic azides, including phenyl azide, in solution and at cryogenic temperatures results in photodenitrogenation to give singlet nitrenes ($^1$**2**), which then undergo intersystem crossing to triplet nitrenes ($^3$**2**) and ring expansion to ketenimines with azirines as intermediates.[1] Reports on the observation of benzazirines in matrices at cryogenic temperatures have been rather limited. In many studies on the photodecomposition of phenyl azide and its derivatives, only triplet nitrenes and ketenimines were observed.[1]

Replacing the nitrogen atom of benzazirine with phosphorus yields a phenylphosphirene that has **never been directly observed experimentally (I).** Why were these species not already known? A thorough search of the chemical literature for clues or precedents reveals several noteworthy reports of analogous syntheses of phosphirenes.[2-4]

## Results

The key question therefore is whether it would be possible to generate the first substituted phosphorus analogue of benzazirine. Our experience shows that careful control of the reaction conditions and of the nature of the substituents is crucial and therefore studying these factors in depth is important.[5-7] In phosphinidenes (phosphirenes), electronic effects play an important role.  Thus, computations predict that




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phosphinidenes are generally stable towards rearrangement to the isomeric phosphirenes. In order to prepare arylphosphirenes, they should be stabilized. How can this be achieved? To expedite the experimental efforts we will study computationally for a variety of substituents R (R = $NH_2$, $OCH_3$, $SCH_3$, etc.), the thermodynamic stability (i.e., energy differences) and the kinetic stability (i.e., energy barriers) of phosphinidenes towards rearrangement to the corresponding phosphirenes, respectively, in order to predict prior to conducting the experiments which phosphirenes can be isolated and which phosphinidenes would rearrange to the phosphirenes, which, however, are interesting species in their own right.

## Discussion

We believe that the delicate control of all these factors will enable the synthesis of the long-sought arylphosphirenes allowing to finally isolate and then to study their structures, properties, and reactivities. 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 transitions states for subsequent reactions.

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