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Three Different Fates for Phosphinidenes Generated by Photocleavage of Phospha-Wittig Reagents $\text{ArP}=\text{PMe}_3$

Shashin Shah, M. Cather Simpson,* Rhett C. Smith, and John D. Protasiewicz*

Department of Chemistry
Case Western Reserve University
Cleveland, Ohio 44106-7708

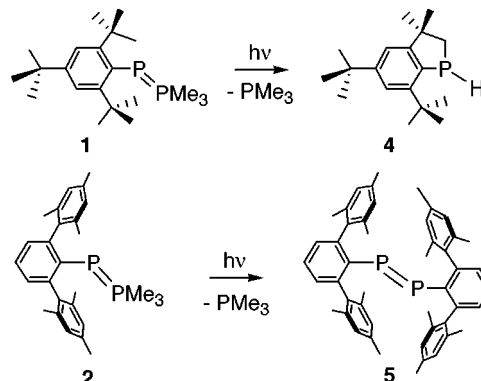
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A longstanding challenge in the chemistry of free phosphinidenes (RP) has been the obtainment of definitive evidence for their generation.¹ The chemistry of free phosphinidenes remains sparse, in contrast to free carbenes and other reactive intermediates, due in large part to the limited set of available precursors to these electron deficient species. Although alkali metal reduction of R_2PCl_2 readily leads to cyclopolyphosphines $(\text{RP})_n$ and, in select cases, diphosphenes $(\text{RP}=\text{PR})$, mechanisms involving metalloid or radical species are equally or more viable compared to mechanisms involving simple phosphinidene intermediates. Additionally, Mathey has stressed that identification of products formally derived from phosphinidenes does not constitute absolute proof, since alternative mechanisms can often be presented that do not postulate phosphinidene intermediates.² Photochemical methods for the generation of phosphinidenes have produced some of the best evidence for generation of these intermediates.^{3,4} In this report we describe evidence for the photochemical generation of free phosphinidenes from three closely related phosphanylidene- σ^4 -phosphoranes ($\text{ArP}=\text{PMe}_3$). Quite amazingly, each precursor spawns phosphinidenes that undergo *different* reaction paths that lead to products of intramolecular CH bond insertion, *net* dimerization to diphosphenes, or novel CC bond insertion.

We recently reported the synthesis and characterization of the stable phosphanylidene- σ^4 -phosphoranes $\text{Mes}^*\text{P}=\text{PMe}_3$ (**1**) and 2,6-Mes₂C₆H₃P= PMe_3 (**2**).⁵ These materials act as phospha-Wittig reagents upon reaction with aldehydes.⁶ Early studies of unstable $\text{CF}_3\text{P}=\text{PMe}_3$ led to a recognition of the potential of $\text{RP}=\text{PR}_3$ as precursors to free phosphinidenes.⁷ Theoretical work suggests that the LUMO in $\text{HP}=\text{PH}_3$ is σ^* in character,⁸ and thus we investigated the possibility that photochemical irradiation of $\text{ArP}=\text{PMe}_3$

PMe_3 may lead to photodissociation of PMe_3 to produce free phosphinidenes.

Pale yellow solutions of **1** in benzene-*d*₆ subjected to 355 nm laser irradiation quickly (15 min) fade in color.⁹ Analysis of such solutions by ³¹P and ¹H NMR spectroscopy reveal that PMe_3 and **4** (>95%), are produced in high yields (Scheme 1). Compound **4** is formally derived by insertion of the phosphinidene $\{\text{Mes}^*\text{P}\}$ into a vicinal CH bond of a methyl group.

Scheme 1. Photolyses of $\text{ArP}=\text{PMe}_3$ 

The same phosphaindan is formed by a number of other experiments that have been proposed to generate $\{\text{Mes}^*\text{P}\}$, such as photolysis of either $\text{Mes}^*\text{P}(\text{N}_3)_2$ ⁴ or the phosphirane $\text{Mes}^*\text{P}[\text{CH}_2]_2$.^{3a} In addition, the diphosphene $\text{Mes}^*\text{P}=\text{PMe}_3$,¹⁰ the possible product from dimerization of two $\{\text{Mes}^*\text{P}\}$ units, is itself photochemically active and will also produce **4** over time, quite possibly by initial cleavage to two $\{\text{Mes}^*\text{P}\}$.¹¹ This process is much slower than conversion of **1** to **4**, and no $\text{Mes}^*\text{P}=\text{PMe}_3$ is detected by ³¹P NMR spectroscopy during the photolysis of **1**.

The behavior of compound **2** bearing a *m*-terphenyl-protecting group is strikingly different. The products of photolysis are the diphosphene 2,6-Mes₂C₆H₃P=PC₆H₃-2,6-Mes₂ (**5**, 90–95%) and PMe_3 (Scheme 1). Diphosphene **5** is very stable to photolysis under the reaction conditions, even in the presence of added PMe_3 . The closely related diphosphene 2,6-Mes₂-4-MeC₆H₃P=PC₆H₃-4-Me-2,6-Mes₂ is also inert to photolysis.¹³

Recent work from Power's group suggested yet a new, third possible reaction channel for free phosphinidenes.¹⁴ During the reduction of 2,6-Trip₂C₆H₃PCl₂ with magnesium metal, a phosphafluorene (**6**, 68%), arising from formal intramolecular insertion of a putative phosphinidene into an Ar-^{*i*}Pr carbon–carbon bond, is obtained. The analogous reduction using potassium metal provides the diphosphene 2,6-Trip₂C₆H₃–P=P–C₆H₃-2,6-Trip as the main product, however. Although these reductions of ArPCl_2

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(2) More recently, ESR observation of a triplet phosphinidene produced by the photolysis of *trans*-2,3-dimethyl-1-mesitylphosphirane has been achieved. See: Li, X.; Weissman, S. I.; Lin, T.-S.; Gaspar, P. P.; Cowley, A. H.; Smirnov, A. I. *J. Am. Chem. Soc.* **1994**, 116, 7899–7900.

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(9) Samples (ca. 0.04 M) were photolyzed in quartz NMR tubes (Wilmad) in C₆D₆ using a nanosecond Nd:YAG laser (Continuum, Inc) at a wavelength of 355 nm and power of 200–220 mW and monitored by ¹H (yields are versus internal standard) and ³¹P NMR spectroscopy.

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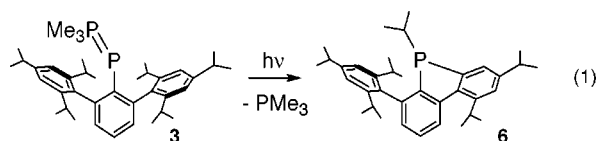
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may involve free phosphinidenes, pathways involving radicals or metalloid species such as $\text{RP}(\text{Cl})\text{MgCl}$ cannot be ruled out. Similar questions are unresolved in related insertions into C–C bonds of *m*-terphenyl ligands by reactive boron and silicon centers.¹⁵

To ascertain if a phosphinidene would insert into a carbon–carbon bond under a metal-free environment we prepared the phosphanylidene- σ^4 -phosphorane 2,6-Trip₂C₆H₃P=PMe₃ (**3**). Compound **3** was prepared in 70% yield in the same manner as **1** and **2**, that is, by the reduction of 2,6-Trip₂C₆H₃PCl₂ by zinc dust in the presence of PMe₃.¹⁶ Yellow crystalline **3** displays a pair of diagnostic doublets in the ³¹P NMR spectrum at –1.6 and –113.4 ppm (J_{PP} = 564 Hz).

As anticipated, photolysis of **3** does indeed give **6** in 90% yield (equation 1) in addition to minor amounts of the corresponding diphosphene. Our data thus support the proposition that



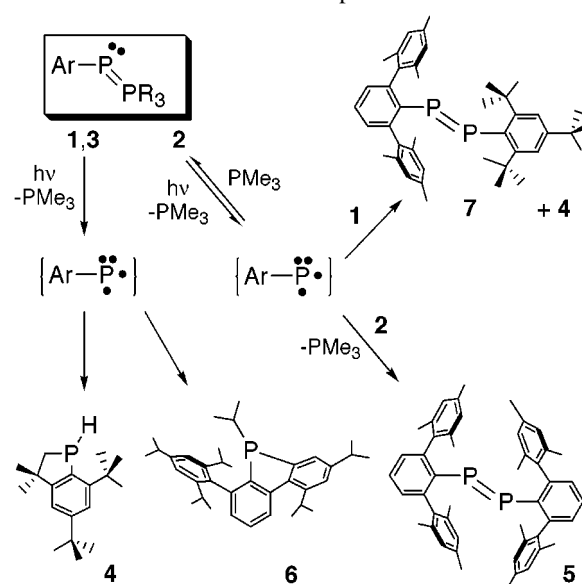
free phosphinidenes may be involved in the magnesium reduction of 2,6-Trip₂C₆H₃PCl₂.¹⁷

To assay the reversibility of the initial photocission of **1–3**, photolyses were conducted in the presence of excess PMe₃. For reactions of **1** and **3**, no significant impact on the rate of product formation was observed, suggesting that both CH and CC bond insertion processes of the phosphinidene are faster than trapping with phosphine to reform **1** or **3**. Interestingly, the presence of added PMe₃ during the photolysis of **2** considerably slows the formation of **5** (Supporting Information), indicating that in this case the phosphinidene can be trapped by added phosphine to reform **2**.

A deceptively simple explanation for formation of diphosphene **5** is the dimerization of two {ArP}. This hypothesis seems unlikely, given the high reactivity of {ArP} derived from **1** and **3**. A more likely scenario is that the electrophilic {ArP} derived from **2** reacts with nucleophilic **2**. An interesting consequence of this proposal is that photolysis of **2** in the presence of increasing amounts of **1** yields more asymmetric diphosphene Mes*P=PC₆H₃-2,6-Mes₂ (**7**, Scheme 2).

One possible explanation for the highly diverse array of products derived by photolysis of **1–3** is that the phosphinidenes thus generated are increasingly stabilized by varying the substituents on the phenyl ring.¹⁹ The phosphinidene {Mes*P}, being the least stable, and having vicinal CH bonds near the phosphorus center, undergoes rapid intramolecular CH bond insertion. The phosphinidene derived from **2** may have a longer lifetime, sufficient such that abstraction of phosphinidene unit from **2** can occur to afford diphosphene **5**. The stability of *m*-terphenyl containing systems having reactive multiple bonds, relative to systems bearing the somewhat comparably sized Mes* group, has

Scheme 2. Reactions of Free Phosphinidenes



been noted.²⁰ The phosphinidene derived from **3** could face a greater steric barrier to phosphinidene abstraction from **3**, thus allowing enough time for the CC bond-insertion reaction to occur. Alternatively, the various reactions may reflect the inherent differences in the chemical reactivity of the *meta* substituents.

The current work is paralleled by similar studies aimed at increasing the lifetimes of free carbenes by photochemical extrusion of dinitrogen from sterically congested azoalkanes. These carbenes can competitively dimerize to olefins or undergo formal intramolecular CH bond insertions.²¹

In conclusion, we have demonstrated remarkable reaction diversity for free phosphinidenes generated from phosphanylidene- σ^4 -phosphoranes that differ only slightly in the nature of the sterically demanding groups. It must also be noted that while photolysis of ArP=PMe₃ appears to be a general method, attempts to generate *m*-terphenyl phosphinidenes using other standard approaches are not viable. For example, extension of the photochemistry of Mes*P(N₃)₂ to other ArP(N₃)₃ produces not phosphinidenes but cyclic azido phosphazenes.²² Likewise, the phosphirane 2,6-Mes₂-4-MeC₆H₃P[CH₂]₂ has been shown to be relatively photochemically inert and thus not effective for the photoinduced retroaddition approach to phosphinidenes.^{3b} Further studies aimed at the ESR detection of these species, as well as other trapping experiments, are underway.

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Supporting Information Available: Synthesis and characterization of **3** and complete experimental details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(16) See Supporting Information for full details.

(17) Interestingly, compound **6** is photoreactive and slowly produces two new species. Efforts to identify these secondary photoproducts are underway.

(18) Compound **7** (³¹P{¹H} NMR (C₆D₆): δ 526.0 (d, J_{PP} = 571 Hz), 455.3 (d, J_{PP} = 571 Hz)) has been independently prepared and structurally characterized. Details to be published elsewhere.

(19) Compounds **1–3** are thermally stable under the reaction conditions.

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