Synthesis and Applications of β-Vinylated Tri(1-adamantyl)phosphine

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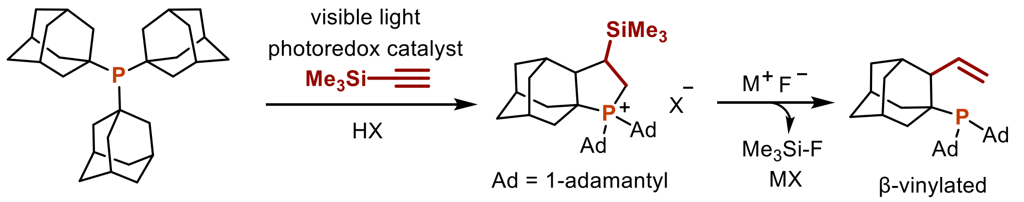
Keywords: phosphine, photocatalyst, C-H activation, phosphonium salt, phosphine ligand

Tertiary phosphines are a class of organic compounds used in a variety of applications. Among them, tri(*tert*-alkyl)phosphines, in which all three *P*-substituents are tertiary alkyl groups, are particularly useful as ligands for transition metal catalysts and frustrated Lewis pairs,[1] owing to their steric hindrance and electron-rich character. However, synthetic methods for tri(*tert*-alkyl)phosphines are limited, with only a few examples available, such as tri(*tert*-butyl)phosphine and tri(1-adamantyl)phosphine (**1**).[2] To date, no bifunctional variants of tri(*tert*-alkyl)phosphines have been reported.

Our group previously reported the synthesis of cyclic phosphonium salt **2** through the photocatalytic cycloaddition of tri(1-adamantyl)phosphine (**1**) with an alkyne.[3] Building on this finding, we attempted the synthesis of tri(1-adamantyl)phosphine featuring a vinyl group substituted at the β-position relative to the phosphorus atom by converting the phosphonium salt **2**. Specifically, cyclic phosphonium salt **2** was treated with a fluoride anion source. This reaction resulted in the elimination of fluorosilane, accompanied by the ring-opening of **2**, yielding β-vinylated tri(1-adamantyl)phosphine (**3**). The chemical structure of phosphine **3** was unambiguously confirmed by X-ray diffraction analysis of the corresponding phosphine sulfide. Various derivatives were synthesized by modifying either the phosphorus center or the vinyl group. The application of β-vinylated tri(1-adamantyl)phosphine as a ligand for transition metal complexes was also attempted.



tri(1-adamantyl)phosphine (**1**) **2** tri(1-adamantyl)phosphine (**3**)

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