Catalytic Functionalization of White Phosphorus

R. Wolf

Institute of Inorganic Chemistry, University of Regensburg, Germany

E-Mail: robert.wolf@ur.de

Organophosphorus compounds are an important class of molecules with numerous industrial uses, e.g. as pharmaceuticals, flame retardants, chemical reagents and catalysts.[1] Nearly all of these valuable compounds are presently synthesized via an atom-inefficient multi-step procedure involving the oxidation of white phosphorus (P_4) with chlorine gas. Catalysis offers the possibility for more atom-efficient transformations. However, catalytic P_4 functionalization still is in early stages of development.[2]

This lecture will describe our endeavours in catalytic P_4 functionalization. First, we will highlight the utility of photoredox catalysis for transforming P_4 into useful monophosphorus compounds. The photocatalytic arylation of P_4 using aryl iodides, bromides and chlorides will be described (Figure 1).[3,4] Mechanistic (^{31}P NMR) investigations revealed major reaction pathways and inspired the development of PH_3 arylation.[5] Furthermore, photocatalytic P_4 stannylation was found to be a useful method for preparing alkylphosphines and alkylphosphonium salts.[6] Finally, we will describe our ongoing studies into main-group-catalyzed P_4 functionalization, including our first results electrocatalytic P_4 functionalization using disulfide catalysts.[7]

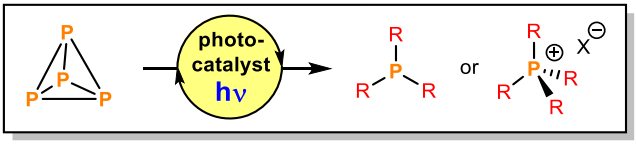

Figure 1: Photocatalytic organofunctionalization of white phosphorus.

[1] D. E. C. Corbridge, *Phosphorus 2000. Chemistry, Biochemistry and Technology*, Elsevier: Amsterdam, 2000. [2] Review: D. J. Scott, *Angew. Chem. Int. Ed* 2022, *61*, e202205019. [3] a) U. Lennert, P. B. Arockiam, V. Streitferdt, D. J. Scott, C. Rödl, R. M. Gschwind, R. Wolf, *Nat. Catal.* **2019**, *2*, 1101–1106; b) P. B. Arockiam, U. Lennert, C. Graf, R. Rothfelder, D. J. Scott, T. G. Fischer, K. Zeitler, R. Wolf, *Chem. Eur. J.* **2020**, *26*, 16374–16382. [4] R. Rothfelder, V. Streitferdt, U. Lennert, J. Cammarata, D. J. Scott, K. Zeitler, R. M. Gschwind, R. Wolf, *Angew. Chem. Int. Ed.* **2021**, *60*, 24650–24658. [5] M. Till, J. Cammarata, R. Wolf, D. J. Scott, *Chem. Commun.* **2022**, *58*, 8986–8989. [6] M. Till, V. Streitferdt, D. J. Scott, M. Mende, R. M. Gschwind, R. Wolf, *Chem. Commun.* **2022**, *58*, 1100–1103. [7] T. M. Horsley Downie, A. Velić, L. A. Coelho, R. Wolf, D. J. Scott, under review.