Main-Group Mediated White Phosphorus Functionalization

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White phosphorus (P_4) serves as a central feedstock for the synthesis of organophosphorus compounds (OPCs). Consequently, the development of practical and efficient methods for the direct conversion of P_4 into OPCs is a long-standing objective in modern phosphorus chemistry. Despite notable recent advances, catalytic P_4 functionalization remains limited by long reaction times, difficulties in controlling selectivity, and modest product yields.[1]
This talk highlights the use of main-group reagents for P_4 functionalization toward polyphosphorus compounds or OPCs (Fig. 1). We demonstrate the application of silicon-based reagents for the deliberate stepwise synthesis of purely phosphorus-based transition-metal complexes, such as **1**.[2] Furthermore, we will present advances in photochemical and electrochemical P_4 functionalization enabled by main-group reagents. The use of main-group element hydrides has enabled efficient P_4 hydroelementation.[3] Building on these advances, we present our results on electrochemical P_4 functionalization using disulfide catalysts, demonstrating emerging strategies for the selective and sustainable transformation of P_4.[4]

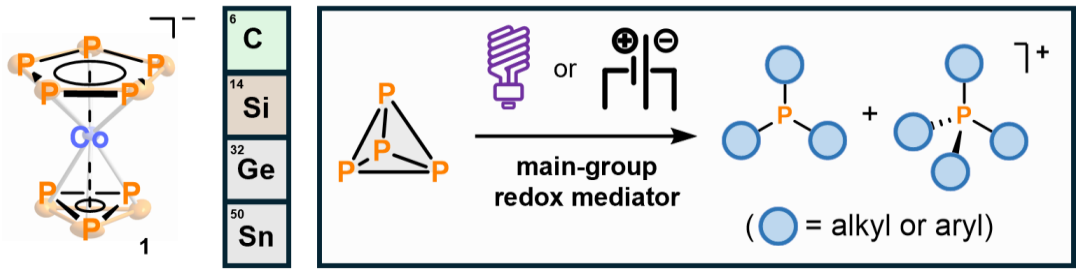


Fig. 1. Main-group element-mediated P_4 functionalization applied to the synthesis of the inorganic sandwich complex (**1**) and the synthesis of monophosphines and -phosphonium salts.

References:

[1] D. J. Scott, *Angew. Chem. Int. Ed.* **2022**, *61*, e202205019. [2] K. Trabitsch, C. G. P. Ziegler, L. Prock, G. Balázs, K. Schwedtmann, E. García-Padilla, F. Meurer, D. D. Snabilié, B. de Bruin, J. J. Weigand, R. Wolf, *J. Am. Chem. Soc.* **2026**, *148*, 11467–11472. [3] J. Cammarata, M. Schimpf, D. J. Scott, R. Wolf, *Inorg. Chem. Front.* **2025**, *12*, 5073–5079. [4] T. M. H. Downie, A. Velić, L. A. Coelho, R. Wolf, D. J. Scott, *ChemSusChem* **2025**, *18*, e202401895.