



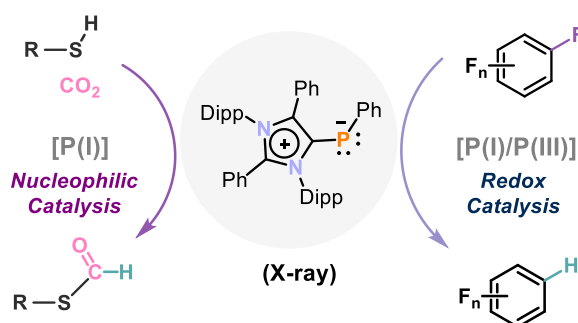
Dual Reactivity at a Low-Valent Phosphorus Center

Transition metals have long dominated catalysis due to their remarkable ability to switch between oxidation states, enabling complex redox transformations. In recent years, however, there has been growing interest in replacing these scarce and often toxic metals with sustainable main group element based catalysts. Among these, phosphorus has emerged as an exciting candidate because of its versatile bonding and redox behavior.

In our recent work, we designed and synthesized a low-valent phosphorus (I) compound stabilized by an abnormal N-heterocyclic carbene (aNHC), a mesoionic N-heterocyclic phosphinidene (mNHP). This unique system features two reactive lone pairs at the phosphorus center, which enable dual catalytic behavior. We demonstrated that one lone pair drives nucleophilic activation (as in reversible CO₂ binding and thiol formylation), while the other participates in P(I)/P(III) redox cycling, allowing C-F bond activation and hydrodefluorination reaction.

This discovery marks a major step toward achieving transition-metal-like reactivity using an entirely metal-free system. Through combined experimental, spectroscopic, and theoretical studies, we established that mNHP not only bridges nucleophilic and redox chemistry but also enables two distinct catalytic transformations under mild conditions, a rare feat for a main group element.

Our findings open new avenues in main group catalysis, highlighting how phosphorus-based low-valent systems can mimic, and even extend, the reactivity traditionally reserved for transition metals, paving the way for sustainable catalytic design.



Ref: **N. Gautam**, Sreejyothi P., K. Soni, S. Chakraborty, S. Maji, K. Bhattacharyya and **S. K. Mandal**, *J. Am. Chem. Soc.*, 2025, **147**, 23001-23013.