

PHOSPHINES IN LEWIS BASE AND REDOX CATALYSIS

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INTRODUCTION

Phosphines are commonly recognized for their ability to serve as ligands to a wide variety of metals, as well as for being selective reducing agents. Furthermore, they are recognized for their ability to serve as powerful nucleophiles in both catalytic and stoichiometric processes.^[1] Electronic and steric properties of phosphines are easy to fine-tune, which expands their application in synthesis. Moreover, one can easily take advantage of either a stereogenic backbone or phosphorus atom, or a combination of both to achieve enantioselective processes, which opens great opportunities in development of catalytic systems.

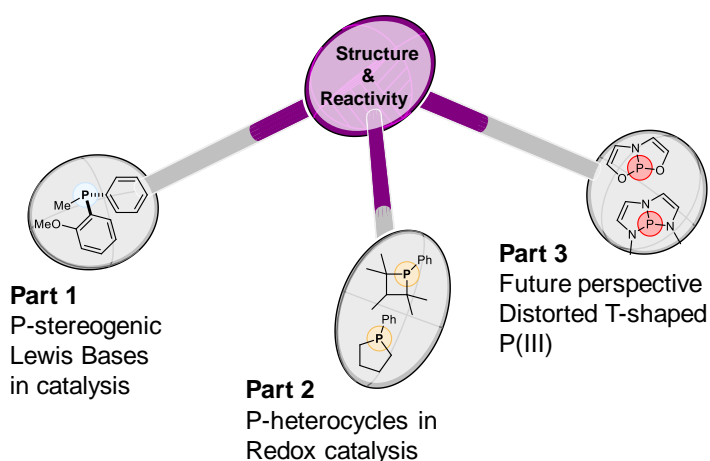


FIGURE 1. OUTLINE OF THE SEMINAR

For example, from a wide variety of phosphine-based organocatalysts, only a handful of them take advantage of seemingly the easiest structural modification: differential substitution that renders the phosphorus atom stereogenic (Figure 1).^[3] Other effects, including changes in valence angles, also remained unexplored until recently.^[4,5] Multiple groups have recognized that the constriction of angles in small P-heterocyclic phosphine oxides leads to enhanced rates of their reduction to corresponding phosphines. That led to realization of the first P^{III} / P^V redox cycles, that made some of the classic stoichiometric phosphorane chemistries (Wittig, Appel, Mitsunobu, Cadogan *etc.*) available in catalytic fashion.

P-STEREOGENIC PHOSPHINES IN LEWIS BASE CATALYSIS

Since the first isolation of enantioenriched P-chirogenic phosphines by Mislow,^[2a] they received significant attention in metal-catalyzed hydrogenation that ultimately resulted in the first enantioselective homogeneous catalysis done on industrial scale.^[2b] However, they remained underutilized in the field of organocatalysis. One of the first breakthroughs was achieved by the Vedejs group where

The main goal of this report is to summarize how *structural and geometrical features inherent to phosphines* can be utilized in catalysis. For decades, focus on phosphine development was mostly on the effects of the backbone, remaining largely underexplored with respect to modifications on the phosphorus atom itself. Even the effects of the most obvious structural modifications remain underexplored. For

phosphabicyclooctane system was optimized to provide high degree of enantioinduction in kinetic resolution and desymmetrization processes.^[3a,b] Another advancement in the field was realized by the Kwon group, devising another practical and selective catalyst, particularly suited for (3 + 2) cycloadditions.^[3c,d] These catalysts were commercialized and were shown to be applicable in the total synthesis.

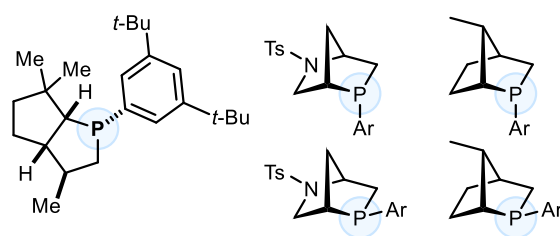
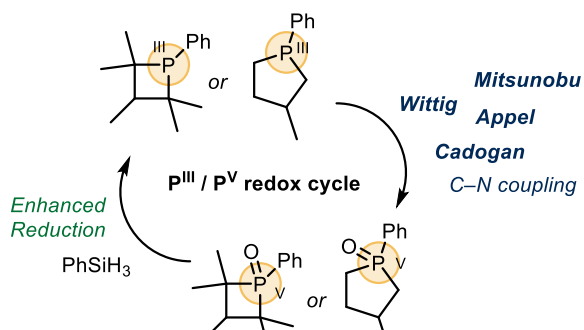


FIGURE 2. P-STEREOGENIC LEWIS BASE ORGANOCATALYSTS

PHOSPHINES IN REDOX CATALYSIS

First report of a Wittig reaction made catalytic in phosphine was by the O'Brien group in 2010 which led to the recognition of how a relatively small ring distortion incorporated in phospholane ring can result in significant improvements in the rates^[4b] of catalytic turnovers.^[4a] Even better increase of efficiency was observed in more strained phosphetanes as reported by the Radosevich group in several subsequent publications.^[4c-e]

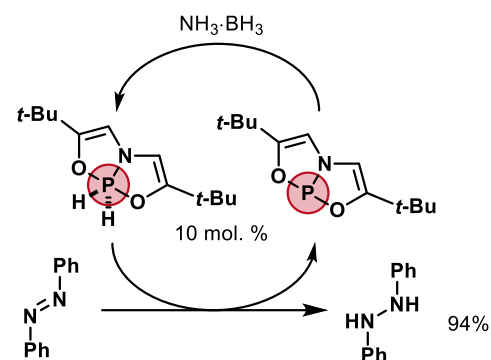


SCHEME 1. PHOSPHOLANES AND PHOSPHETANES IN REDOX CATALYSIS

Distorted T-shaped geometries can lead to even more drastic differences in reactivity.^[5] First reported by Arduengo,^[5a] and then studied extensively by the Radosevich group,^[5b,c] these complexes display the ability to undergo transformations that phosphorus is otherwise unknown to do. It should be noted, however, that the investigations are still underway and thus this area remains one of the exciting future perspectives in phosphorus redox catalysis development.

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SCHEME 3. 10-P-3 PHOSPHORAMIDITES IN REDOX CATALYSIS