

## New applications of organometallic catalysts in organic chemistry\*

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*Abstract:* An overview is provided of our work on tin hydride-catalyzed processes, palladium-catalyzed coupling reactions, and asymmetric catalysis with “planar-chiral” heterocycles.

### INTRODUCTION

During the past seven years, we have been exploring catalysts based both on main-group metals (e.g., tin) and on transition metals (e.g., palladium, iron, and rhodium). Our goals have been two-fold—to discover new reactivity and to develop new stereoselective reactions.

### TIN HYDRIDE-CATALYZED PROCESSES

We have developed  $\text{Bu}_3\text{SnH}$ -catalyzed variants of an array of reactions that had previously employed stoichiometric quantities of  $\text{Bu}_3\text{SnH}$  [e.g., Barton–McCombie deoxygenation of alcohols (Fig. 1) and the reductive cyclization of enals]. These new catalytic processes exploit the sometimes unique reactivity of  $\text{Bu}_3\text{SnH}$  while decreasing the quantity of toxic organotin waste that is produced [1].

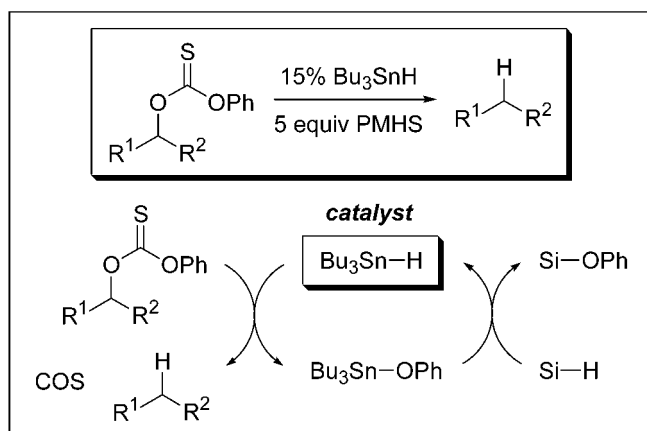


Fig. 1  $\text{Bu}_3\text{SnH}$ -catalyzed Barton–McCombie deoxygenation.

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## PALLADIUM-CATALYZED COUPLING REACTIONS

Whereas many procedures have been reported for palladium-catalyzed coupling reactions (e.g., Suzuki, Stille, Negishi, and Heck couplings) of aryl bromides, iodides, and triflates, until recently there were no general methods for effecting the corresponding reactions of aryl chlorides. Aryl chlorides are an especially important family of coupling partners because of their increased availability and decreased cost relative to other aryl halides.

During the past three years, we have demonstrated that the use of  $P(t\text{-Bu})_3$ , a particularly electron-rich and bulky phosphine, as a ligand leads to efficient palladium-catalyzed Suzuki, Stille, Negishi, and Heck couplings of a wide array of aryl chlorides (Fig. 2). We have also established that  $\text{Pd}/P(t\text{-Bu})_3$  serves as an unusually mild (room-temperature) and versatile catalyst for coupling reactions of aryl bromides [2].

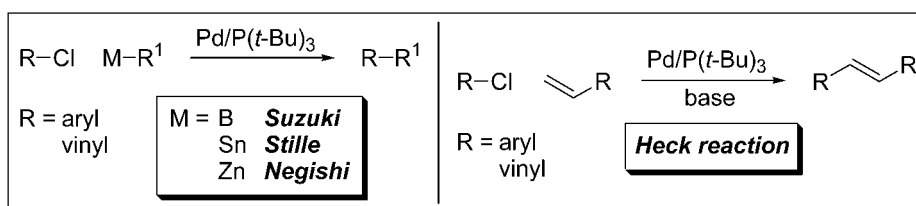


Fig. 2 Coupling reactions of aryl and vinyl chlorides catalyzed by  $\text{Pd}/P(t\text{-Bu})_3$ .

## ASYMMETRIC CATALYSIS WITH “PLANAR-CHIRAL” HETEROCYCLES

Lewis acid catalysis is a widely used strategy for accelerating chemical reactions. Lewis base (nucleophilic) catalysis, on the other hand, is a less-well-appreciated, but also versatile, approach. With the objective of achieving *enantioselective* nucleophilic catalysis, we have developed “planar-chiral” derivatives of 4-(dimethylamino)pyridine (DMAP), which is perhaps the most versatile nucleophilic catalyst that has been reported to date (Fig. 3).

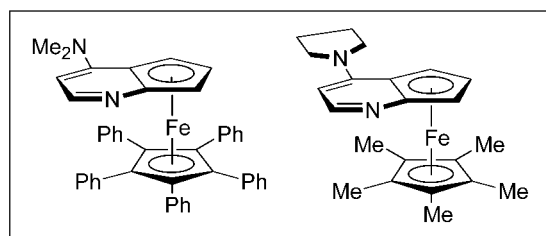
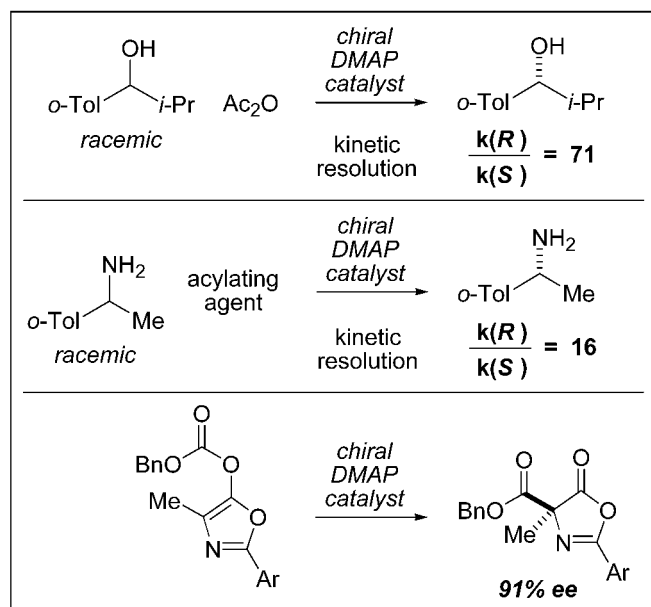


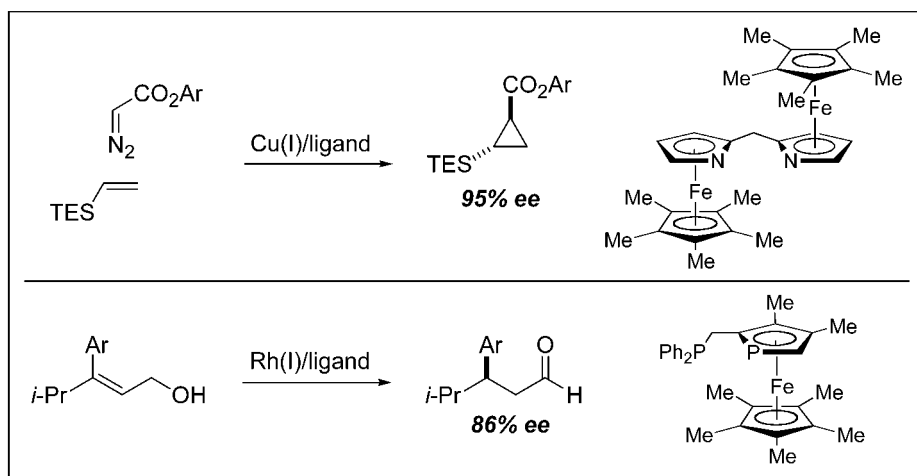
Fig. 3 “Planar-chiral” derivatives of 4-(dimethylamino)pyridine (DMAP).

We have determined that these chiral derivatives of DMAP serve as effective catalysts for a number of interesting processes, including the kinetic resolution of alcohols and amines and the enantioselective *O*-to-*C* rearrangement of *O*-acylated enolates (Fig. 4) [3,4].

In related work, we have employed planar-chiral heterocycles as chiral ligands in transition metal-catalyzed reactions. Our efforts in this area have focused on azaferrocenes and phosphoferrocenes, which we have shown to be effective in processes such as copper-catalyzed cyclopropanations of olefins and rhodium-catalyzed isomerizations of allylic alcohols (Fig. 5) [5].



**Fig. 4** Examples of reactions catalyzed by planar-chiral derivatives of DMAP.



**Fig. 5** Examples of applications of planar-chiral heterocycles as ligands in transition metal-catalyzed reactions.

## ACKNOWLEDGMENTS

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