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博士の専攻分野の名称 博士（理学） 氏名 Deliang Zhang

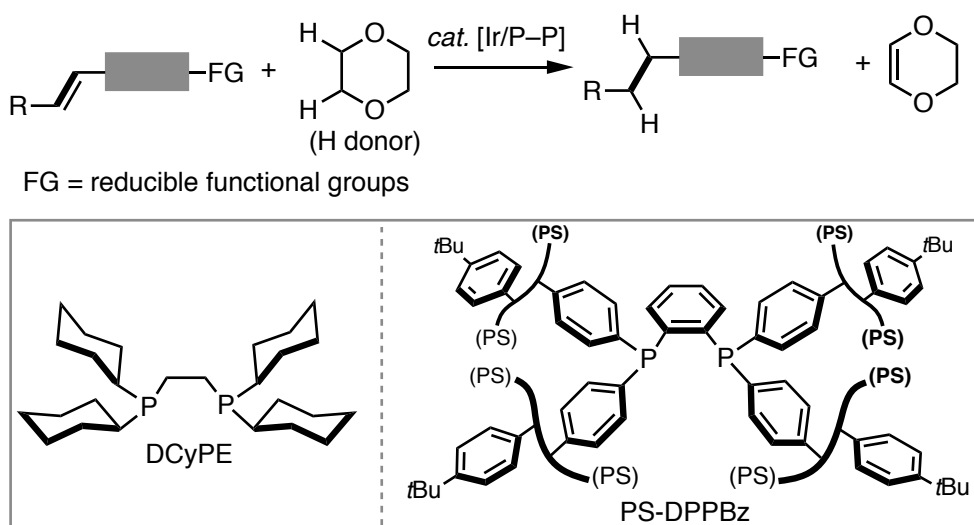
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Catalytic Hydrogenation and Dehydrogenation of Heterocyclic Compounds through sp^3 -C-H Bond Activation

(触媒的 sp^3 -C-H 結合活性化によるヘテロ芳香族化合物の水素化と脱水素化反応)

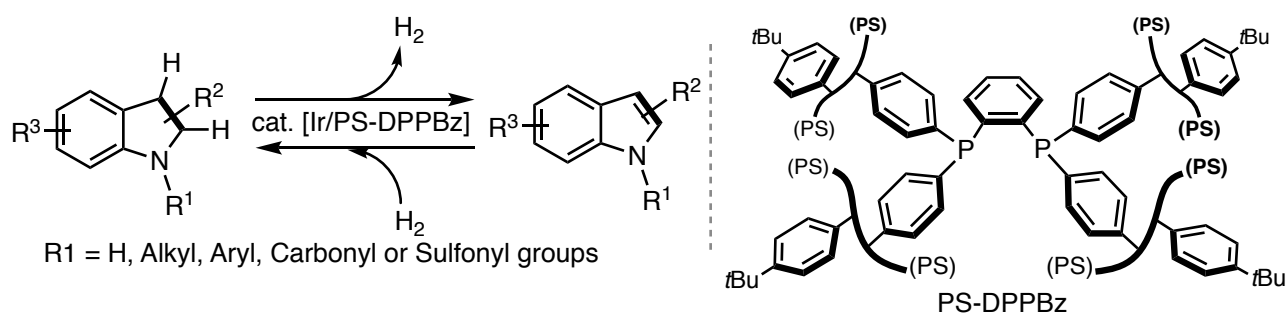
The functionalization of sp^3 -C-H bond in heterocycles to produce more value-added scaffolds is a challenge that has piqued the interest of chemists for a several decades. Despite many efforts have been devoted to this area, the application of ligand-modified active but relatively stable metal-dihydride intermediate through $\text{C}(\text{sp}^3)$ -H bond activation followed by βH elimination of heterocycles for hydrogen transfer processes has been rarely studied.

In Chapter 1, the iridium-catalyzed transfer hydrogenation of alkenes using 1,4-dioxane as a hydrogen donor is described. The use of 1,2-bis(dicyclohexylphosphino)ethane (DCyPE), featuring bulky and highly electron-donating properties, led to high catalytic activity. A polystyrene-cross-linking bisphosphine PS-DPPBz produced a reusable heterogeneous catalyst (Scheme 1). These homogeneous and heterogeneous protocols achieved chemoselective transfer hydrogenation of alkenes over other potentially reducible functional groups such as carbonyl, nitro, cyano, and imino groups in the same molecule.



Scheme 1. Ir-catalyzed transfer hydrogenation of alkenes using 1,4-dioxane as H donor

In chapter 2, the polystyrene-cross-linking bisphosphine ligand PS-DPPBz for the Ir-catalyzed reversible acceptorless dehydrogenation/hydrogenation of *N*-heterocycles is described (Scheme 2). Notably, this protocol is applicable to the dehydrogenation of *N*-substituted indoline derivatives with various *N*-substituents with different electronic and steric natures. The same Ir catalyst was also applicable to backward hydrogenation of *N*-heteroarenes with molecular hydrogen.



Scheme 2. Ir-catalyzed reversible acceptorless dehydrogenation/hydrogenation of *N*-heterocycles

Overall, a bulky and electron-rich ligand DCyPE modified iridium catalyst enabled the C(sp³)-H activation of 1,4-dioxane to produce iridium dihydride species that was utilized for versatile chemoselective transfer hydrogenation of alkenes. A polymer-supported ligand PS-DPPBz was taken as a reusable catalyst. Besides, the same PS-DPPBz in combination with iridium was also found as a good catalyst for reversible acceptorless dehydrogenation/hydrogenation of heterocycles.