

Development of Ruthenium Complexes Bearing a Tetradentate Hemilabile Ligand and Their Catalytic Reactivity

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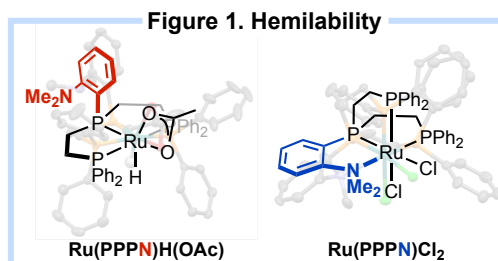
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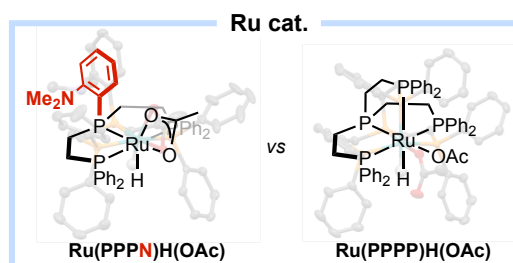
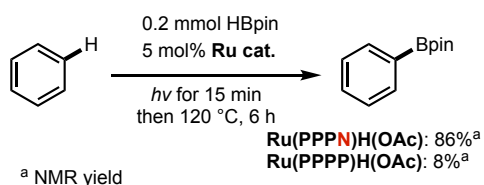
Ru complexes supported by tetradentate ligands have been studied mainly on its stoichiometric chemistry rather than the catalytic reactivity. Among the stoichiometric reactivities, the ability to activate a C–H bond of simple arenes by a Ru complex bearing a tetradentate phosphine ligand is attractive, but no catalytic application has been reported¹. One of the biggest reasons owes to the 18-electron saturated structure of the resulting complex, which is inert to further transformation.

Herein, we envision that the introduction of a nitrogen-containing group as one of the coordinating sites of the tetradentate ligands, which can flexibly dissociate from the metal center to create an open coordination site, could significantly enhance the reactivity of the Ru complex as a catalyst for C–H functionalization of simple arenes.

Upon complexation of a new PPPN ligand and Ru precursors, Ru(PPPN)H(OAc) and Ru(PPPN)Cl₂ complexes were obtained. Interestingly, X-ray analysis clarified a different coordination behavior of –NMe₂ group, which coordinates to Ru in Ru(PPPN)Cl₂, but dissociates from Ru in Ru(PPPN)H(OAc). It clearly demonstrated the hemilabile feature of a PPPN ligand in Ru complexes (**Figure 1**). After various investigations of catalytic reactivity of these complexes, the Ru-catalyzed C–H borylation of unactivated arenes is found to proceed more efficiently with the hemilabile PPPN ligand than with a tetradentate phosphine ligand (**Scheme 1**). Mechanistic study has also been conducted for gaining further insight into the effect of the labile coordinating group during the reaction. This result is an important demonstration of hemilabile ligand-enabling synthetically significant catalytic reaction.



Scheme 1.



1) R. Osman *et al.* *J. Am. Chem. Soc.* **1997**, *119*, 8459-8473