

Visible Light Induced C-H Bond Activation of Arenes by PSP-Pincer Rhodium Hydride Complexes

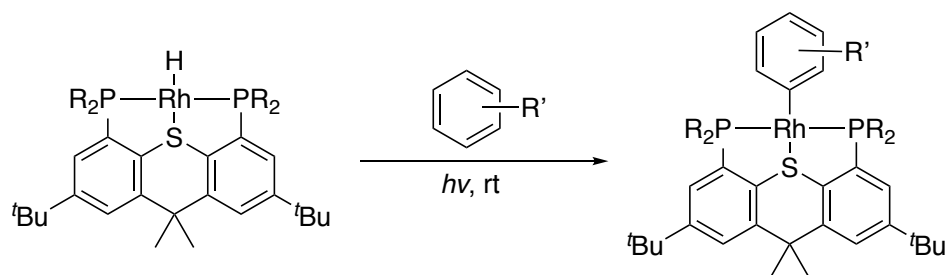
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Dehydrogenative C-H bond activation with transition metal hydride complexes is a promising method as a highly atom- and step-economical functionalization due to its facile regeneration of active metal hydride species by various reductants or β -hydride elimination. However, the number of such reports is still limited. One of the recent examples is a thermal C-H bond activation of simple arenes using a rhodium hydride complex with a POP-type xantphos ligand.¹⁾

We have recently achieved rhodium-catalyzed (*Z*)-selective hydroboration of terminal alkynes by using a PSP-type thioxantphos pincer ligand, demonstrating the advantage of more rigid and electron-rich nature of PSP-rhodium complexes compared with POP-rhodium complexes.²⁾ We expected that the dehydrogenative C-H bond activation of arenes using rhodium hydride complexes could also proceed under milder conditions with higher efficiency by using PSP ligands due to the more electron-rich rhodium center.

Herein we report a visible light-induced C-H bond activation of arenes by PSP-pincer thioxantphos rhodium hydride complexes. After examination of various thermal and photochemical conditions, it was found that PSP-rhodium hydride complexes reacted with benzene efficiently to give corresponding phenyl rhodium complexes at room temperature under irradiation of blue LEDs. This is in contrast to the previous example of the slow C-H bond activation by a POP-rhodium hydride complex under heating, showcasing the clear difference between PSP- and POP-rhodium complexes. This photo-induced C-H bond activation by PSP rhodium hydride complexes was applicable to a series of arenes. Detailed computational studies for the effect of photo-irradiation and the difference between PSP- and POP-ligands will also be presented.



1) M. A. Esteruelas, *et al.*, *Organometallics* **2015**, 34, 1911. 2) N. Iwasawa, *et al.*, *Org. Lett.* **2021**, 23, 9262.