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Reactivity of PSP-Pincer Rhodium Complexes: Z-Selective Hydroboration of Terminal Alkynes and Photoinduced C–H Bond Activation of Arenes

In this doctor's thesis, I have synthesized thioxantphos-based Rh-PSP complexes and examined their reactivities with the expectation that thioxantphos would provide not only higher stability but also more electron density to its transition metal centers than its POP-congener xantphos because of the lower electronegativity and the softer Lewis basicity of the sulfur atom compared to the oxygen atom. Using these Rh complexes, I have developed 1) catalytic Z-selective hydroboration of terminal alkynes and 2) C-H bond activation of arenes. Through this study, I have also made a comparison of reactivities between xantphos and thioxantphos to clarify the characteristic features of PSP-pincers compared with POP-pincers.

The first chapter describes catalytic Z-selective hydroboration of terminal alkynes. While hydroboration of alkynes is an important method to synthesize alkenyl boronates, Z-selective hydroboration of terminal alkynes is less common. In the very rare example of Rh-catalyzed Z-selective hydroboration of terminal alkynes by Miyaura and co-workers, Rh-vinylidene species is proposed as the key intermediate for the unusual Z-selectivity. Since vinylidene formation is known to be facilitated by more electron-rich transition metal centers, I have investigated the applicability of thioxantphos-Rh catalysts to Z-selective hydroboration. Using 4-phenyl-1-butyne as a model substrate, the reaction was found to proceed smoothly with high Z-selectivity by carrying out the reaction with HBpin, $[\text{Rh}(\text{nbd})_2]\text{BF}_4$, and a thioxantphos-type ligand at 30 °C. While the ligand was exchanged to a xantphos-type ligand, it gave the product in low yield with moderate Z-selectivity. These results showcase the significant difference between PSP and POP ligands in hydroboration reactions. This hydroboration was applicable to a wide range of terminal alkyl alkynes having various functional groups such as ether, sulfonate, ester, ketone, imide, and halide with high Z-selectivity. It should be noted that the carbonyl moiety was not reduced under the reaction conditions.

From deuterium labeling experiments using deuterated alkyne, terminal proton entirely migrated to internal carbon, which supported generation of a Rh-vinylidene complex as the active species. Thus, the electron-rich and rigid thioxantphos ligand was supposed to lead to facile generation of the Rh-vinylidene species.

The second chapter describes C-H bond activation of arenes. C-H bond activation of simple arenes by transition metal complexes is a useful methodology for organic synthesis. However, use of metal hydride for C-H bond activation has rarely been realized. I expected electron-rich thioxantphos ligands could facilitate dehydrogenative C-H bond activation of arenes by Rh complexes under mild conditions, since oxidative addition of arenes to Rh(I) hydride complexes would be accelerated with PSP ligands. As a result of screening of reaction conditions, a thioxantphos-Rh hydride complex was found to be active for C-H bond activation, and the catalytic C-H borylation reaction was achieved.

In conclusion, by utilizing the rigid and electron-rich thioxantphos-Rh complexes, I have achieved highly Z-selective hydroboration of terminal alkynes and C-H bond activation of arenes. These reactions demonstrate superiority of PSP-type pincer ligands over POP-type ligands in several reactions and would lead to further development of utilization of PSP-type pincer ligands in transition metal catalyzed reactions.