

Metal-complexes can be given diverse functions by a precise design. Based on experimental and theoretical mechanistic studies, Nagashima has focused on functional metal-complexes for two types of reactions such as photo-induced reactions and noncovalent interaction-driven reactions by employing various metals/metalloids such as rhodium (Rh), tin (Sn), and boron (B).

(1) Photoexcitation-oriented metal-complexes

Photoinduced reactions have received much attention as a powerful tool to access kinetically or thermodynamically prohibited reactions on the ground state. However, these reactions have been developed mainly by using specific transition-metals such as Cu, Pd, Ni, Ru, and Ir. On the other hand, Nagashima revealed the nature of rhodium (Rh), tin (Sn), and boron (B) on the excited state to develop the highly reactive and selective photoinduced reactions.

For photoexcitation-oriented rhodium(Rh)-complex, Nagashima designed the functionalized cyclopentadienyl (Cp) Rh(III) complex, which can be subjected to photo-induced *in situ* reduction to anionic CpRh(II) ate complexes ([J. Am. Soc. Chem. 2021, 143, 11325](#)). This photocatalytic system enabled more chemoselective *ortho*-C-H borylation of arenes than previously reported C-H borylations. Mechanistic studies revealed that only basic groups act as directing groups because ligand-to-metal charge transfer (LMCT) of Rh(III) intermediates is necessary on the excited state. In addition, Nagashima also developed the visible-light-harvesting spirocyclic-Rh(I) complex, which can extend the scope of C-H borylations and [2+2+2] cycloaddition of alkynes to challenging substrates under blue LED irradiation ([Nature Synth. 2023, accepted for publication](#)).

For photoexcitation-oriented tin(Sn)-complex, Nagashima designed stannyl anion complexes to generate the excited triplet (T1) stannyl diradicals by photoexcitation ([J. Am. Soc. Chem. 2021, 143, 5629](#)). These species showed the orthogonality to traditional reagents (cations, anions, and radicals) to enable hydrostannylation of alkynes and defluorostannylation of fluoroarenes.

For photoexcitation-oriented boron(B)-complex, Nagashima designed the anionic photo-absorbing borate complex to enable a quadruple borylation reaction of terminal alkynes ([J. Am. Soc. Chem. 2019, 141, 9819](#)). Moreover, Nagashima also developed photo-induced reduction of silyl-borate complexes to enable *in situ* generation of diverse silyl radicals ([J. Org. Chem. 2022, in press](#)) and dearomative carbo-silaboration reactions of quinolines without the need for any catalyst ([Nature Commun. 2023, accepted for publication](#)).

(2) Noncovalent interaction-oriented metal-complexes

Noncovalent interactions (NCIs) are important to control reactivities and/or selectivities in catalytic reactions. However, there are few investigations and explorations of NCIs in Rh-catalyzed [2+2+2] cycloadditions.

Nagashima first revealed that the coordinative interaction between enamides and cationic Rh(I) significantly improved the selectivity of Rh-catalyzed [2+2+2]

trimerizations by computational studies ([Nature Synth. 2022, 1, 365](#)). Based on the above theoretical studies, Nagashima explored NCI-oriented Rh-complexes and revealed that the coordinative interaction between ester moieties and cationic Rh(I) realized synthesis of axially chiral styrene carboxylic esters ([Angew. Chem. Int. Ed. 2022, 61, e202202542](#)). In this reaction, the coordinative interactions can surpass steric repulsions to improve the enantioselectivity.

In addition to these coordinative interactions, Nagashima explored NCI-oriented Rh-complexes and found that $\pi \dots \pi$ and C–H... π interactions on substrates and/or ligands accelerates sterically demanding [2+2+2] cycloadditions using 1,8-dialkynyl naphthalenes ([ACS Catal. 2023, 13, in press](#)). These NCIs can stabilize the transition states rather than induce steric repulsions to realize synthesis of sterically demanding fluoranthenes.