**Transition-Metal Catalysis: From Synthetic Transformation to Applications**

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Transition-metal catalyzed transformation of organic compounds has been attracted attention in many fields such as synthetic organic chemistry, medicinal chemistry, and even materials chemistry. This chemistry provides the most promising way to achieve an environmentally benign process with a high efficiency and selectivity and atom economy.

The first part of the talk shows the transformations of vinylsilanes were achieved by using transition metals such as Rh(I) and Ir(I) with HCl for preparing silyl ether (alkoxysilane) and organic group-functionalized silica or glass surface (hybrid material). Highly efficient O-silylation of alcohol with vinylsilane was developed using a catalyst system consisting of [(COE)2RhCl]2 and HCl. In this reaction, a key intermediate is chlorosilane, generated from vinylsilane and HCl, which can be regenerated in the catalytic cycle. From this observation, a novel and efficient grafting method of functional organic compound with vinylsilane onto silica or glass surface by transition-metal catalysis was developed. Vinylsilanes are stable enough to introduce various functional groups, and resulting functional vinylsilanes was successfully grafted onto inorganic surface. Furthermore, more efficient method to prepare organic-inorganic hybrid materials is also devised using divinylsilane as a mediator. In this reaction, one of vinyl groups is used for direct C–C bond formation between functional organic molecule and vinylsilanyl group while the other is for immobilizing alkylsilanyl group onto silica surface.

The second part of the talk describes dehydroformylation of aldehydes to generate olefins that features the transfer of a formyl group and hydride from an aldehyde substrate to a strained olefin acceptor. A Rhodium(Xantphos)(benzoate) catalyst activates aldehyde carbon-hydrogen (C–H) bonds with high chemoselectivity to trigger carbon-carbon (C–C) bond cleavage and generate olefins at low loadings and temperatures. This mild protocol can be applied to various natural products and was used to achieve a three-step synthesis of (+)-yohimbenone.

Last part of the talk deals with the development of new desymmetrization method of ,-bis(allyl)aldehyde by Rh(I) catalyst. Desymmetrization has emerged as the way to access chiral quaternary-carbon motifs, which are among the most challenging stereocenters to generate with enantiocontrol. Strategies involving C−H bond activation are especially promising yet rare. Given this challenge, we have recently disclosed a Rh-catalyzed desymmetrization of all-carbon quaternary centers from prochiral ,-bis(allyl)aldehyde by a cascade featuring isomerization and hydroacylation. A BIPHEP ligand promotes enantioselective formation of -vinylcyclopentanones. Mechanistic studies support irreversible and enantioselective olefin-isomerization followed by olefin-hydroacylation. We have also demonstrated a desymmetrization of prochiral ,-bis(allyl)aldehyde to form scaffolds bearing quaternary centers *via* carboacylation to generate [2.2.1]-bicycloheptanone. Finally, we have established a metal-catalyzed isomerization to generate cyclohexenecarboxaldehydes bearing -quaternary centers. This Rh-catalyzed method provides enantioselective access to a 3,3,5-trisubstituted cyclohexene motif that is inaccessible by the well-established Diels-Alder and therefore complements conventional cycloadditions.