Science and Technology Group
Annual Report FY2019

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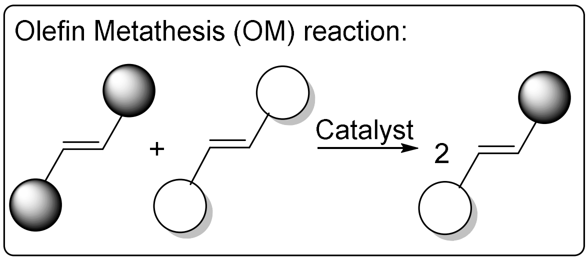
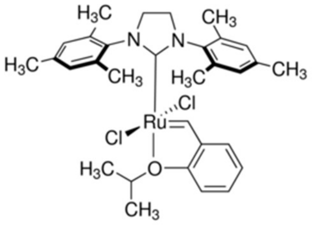
1 Introduction



The olefin metathesis reaction is among the most widely applicable catalytic reactions for carbon-carbon double bond formation. Currently, molybdenum- and ruthenium-carbene catalysts are the most common choices for this reaction. It has been anticipated that base metal catalyst would be a desirable economical and biocompatible substitute of the ruthenium-catalysts. *In this project, we are going to develop such base metal catalyzed olefin metathesis reactions using* ***manganese*** *organometallic complexes.* This project is founded by KAKENHI early-career scientists program, project number 18K14230, from FY2018 to FY2020. URL: https://kaken.nii.ac.jp/grant/KAKENHI-PROJECT-18K14230/

2 Activities and Findings



At the onset of this project, manganese (Mn) catalyst was designed based on known ruthenium-N-heterocyclic carbene (NHC) catalysts (right figure). The most common d^6 Mn (I) precursor, $MnBr(CO)_5$, was chosen as a starting point to synthesize a d^6 Mn(I) carbene complex that is isoelectronic to d^6 Ru(II) carbene complexes. Several Mn(I) complexes and a Mn(I) carbene complex were prepared, however none of these complexes were active towards olefin metathesis reaction.

During this study, I found that bulky NHC ligand can stabilize monomeric Mn(0) metalloradicals which usually exists as a dimer. Application of this strategy to an industrially important cobalt (Co) hydroformylation catalyst $[Co(ligand)(CO)_3]_2$ (ligand = CO or PR_3) resulted in unprecedented isolation of monomeric $[Co(NHC)(CO)_3]$ metalloradicals. When less bulky NHC ligands were used $[Co(NHC)(CO)_3]_2$ dimers were obtained. Single crystal XRD analysis revealed that these dimers have the longest Co-Co bonds reported for $[Co(ligand)(CO)_3]_2$ complexes. The equilibrium between monomer and dimer was confirmed by EPR and NMR spectroscopies, and thermodynamic parameters for this equilibrium was determined. Isolation of the $[Co(NHC)(CO)_3]$ metalloradicals enabled us to investigate its reactivity towards H_2 for the first time. Kinetic studies showed that this complex reacts with H_2 by a bimolecular mechanism instead of the previously proposed termolecular mechanism. $[Co(NHC)(CO)_3]_2$ dimer reacted with H_2 in dissociative mechanism and formed Co-hydride complex $[HCo(NHC)(CO)_3]$ under unusually mild conditions. Solid state structure of a $[HCo(NHC)(CO)_3]$ complex was determined using single crystal XRD analysis.

3 Collaborations

This research was carried out by corroboration with

- Dr. Robert Fayzullin (Arbuzov Institute of Organic and Physical Chemistry, FCR Kazan Scientific Center, Russian Academy of Sciences)
  Single crystal X-ray crystallography analysis

4 Publications and other output

Presentation

(1) Takebayashi, S. Fayzullin, R. *Isolation and Reactivity Study of 17-electron Metalloradical $[Co(NHC)(CO)_3]$.* The 100th CSJ annual meeting, Chiba, March 22-25, 2019.

(2) Takebayashi, S. *New metalloradical complexes discovered in OIST.* OIST Internal seminar, Okinawa, July 12, 2019.