Science and Technology Group
Annual Report FY2020

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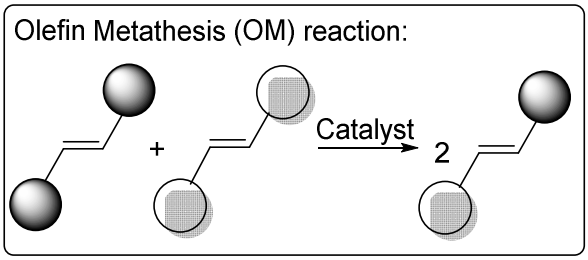
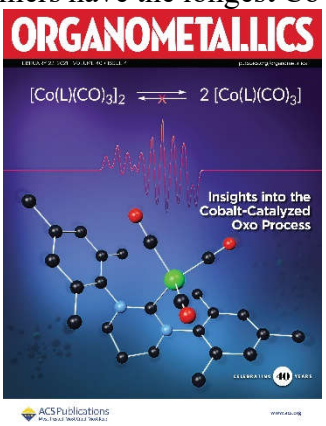
1 Introduction



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

During this study, I found that bulky NHC ligand can stabilize unprecedented 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. This result was presented at 101st CSJ annual meeting and published in Organometallics. The work was featured as a cover of Organometallics Volume 40, Issue 4. A related chemistry with cobalt complexes and manganese complexes will be reported in FY2021 or Fy2022.



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 of Mononuclear [Co(ligand)(CO)$_3$] Metalloradicals and Its H_2 Activation Mechanism.* The 101st CSJ annual meeting, online, March 19-22, 2021.

Publication

(1) Takebayashi, S.; Fayzullin, R. R., [Co(NHC)(CO)$_3$]: Isolation and Reactivity Study of a Model 17-Electron Species in the Oxo Process. *Organometallics* **2021**, *40* (4), 500-507.