

## MERIT Internship Report (Domestic)

School of Engineering, Department of Applied Chemistry, Yamaguchi Lab. D2

MERIT 5th student Takafumi Yatabe

### 1. Place

National Institute of Advanced Industrial Science and Technology (AIST), Interdisciplinary Research Center for Catalytic Chemistry, Silicon Chemistry Team

### 2. Term

2018.11.12. ~ 2018.12.14.

### 3. Research

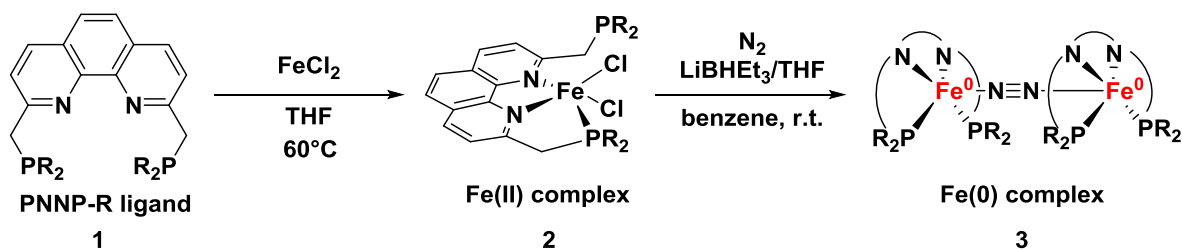
Reaction Field Control of Fe Complexes Possessing Four-dentate PNNP Ligand

### 4. Overview

Although Fe complex catalysts, which are non-toxic and abundant on earth, should be utilized to a variety of application, the research on Fe complexes is behind compared with the other transition-metal complex catalyst researches because of difficult analysis on Fe complexes caused by the paramagnetism of their high-spin states. Strong  $\sigma$ -donating ligands can induce the large ligand field splitting to make diamagnetic Fe complexes with low-spin states, leading to possible analysis on the Fe complexes. The Fe complexes also possess a reactive electron-rich Fe center, which is expected to show high catalytic activities *via* various bond scissions. Recently, in Silicon Chemistry Team, PNNP-R ligands have been designed as strong  $\sigma$ -donating four-dentate ligands, successfully enabling the synthesis of diamagnetic Fe complexes and the catalytic reaction to synthesize organic silicon compounds through Si-H bond scission. In this internship, I studied the additional reactivity of Fe-PNNP-R complexes and sophisticated Fe-PNNP-R complexes by tuning the ligands.

### 5. Content

Recently, in Silicon Chemistry Team, PNNP-R ligands (**1**), which are strong  $\sigma$ -donating four-dentate ligands, have been applied to the synthesis of Fe(II)-PNNP-R complexes (**2**) and reactive Fe(0)-PNNP-R complexes (**3**) (Figure 1). **3** can be also utilized for the efficient catalytic dehydrogenative coupling of silanes and silanols *via* the Si-H bond scission (*Dalton Trans.* **2018**, *47*, 17004). Fe(0)-PNNP-R complexes possess an extremely electron-rich metal center expected to sever various bonds *via* oxidative addition. In this study, I actually confirmed a selective bond scission by an Fe(0)-PNNP-R complex *via* oxidative addition and successfully isolated the oxidative adduct. Additionally, in the course of the studies on reactivity of the oxidative adduct, I was able to synthesize a novel Fe complex, which can dissociate bonds concertedly utilizing a basic site of the PNNP-R ligand close to an Fe center. In addition, the electronic states and steric structures of Fe-PNNP-R complexes can be easily controlled by changing the substituent (= R) of phosphines. I also designed more electron-rich PNNP-R ligands, synthesized novel Fe(II)-PNNP-R complexes, and tried much more difficult bond scissions using the complexes.



**Figure 1.** Synthesis of Fe-PNNP-R complexes.

## 6. Impression

To date, I have been studying on the development of unprecedented organic reactions utilizing unique properties of heterogeneous catalysts for about five years. Therefore, I have never done the experiments on authentic organic synthesis under an inert atmosphere, synthesis of organic metal complexes, or reaction using them, although the contents have something to do with my usual research. Specialty and affiliated associations are also different, which made research contents, experimental operation, and way of thinking fresh and stimulating to me. Nevertheless, I got used to the operation comparatively quickly and did various interesting researches freely because I already had knowledge about the complex chemistry. Thus, I felt that this internship as a doctoral course student was very good to learn many things efficiently. In the future, I have interdisciplinary research plans of novel reaction development by combining the unique properties of heterogeneous catalysts with those of homogeneous complex catalysts, and I will fully draw on the experience during this internship for the plans.

## 7. Acknowledgement

I deeply thank National Institute of Advanced Industrial Science and Technology for accepting this internship. I appreciate a lot of help of those who belong to Interdisciplinary Research Center for Catalytic Chemistry, including Silicon Chemistry Team members, despite their busy schedules. In particular, Dr. Yumiko Nakajima (Team leader) accepted this internship willingly, contrived my research theme, discussed the researches, measured single crystal X-ray structure analysis together, and so on for me. Dr. Shinji Tanaka also helped me a lot from when I asked for this internship acceptance to the end of this internship, including measurement of my samples by dynamic nuclear polarization surface enhanced NMR spectroscopy (DNP SENS). I am deeply indebted to them for the much kind help. Furthermore, I am also grateful to Prof. Kazuya Yamaguchi as my supervisor and Prof. Shū Kobayashi as my MERIT supervisor for the acceptance of this internship. In closing, I express my gratitude to MERIT program for giving me this precious chance of internship.