Reactivity of Iron Sandwich Complexes with Oxocyclohexadienyl Ligands toward Proton-Coupled Electron Transfer Reactions

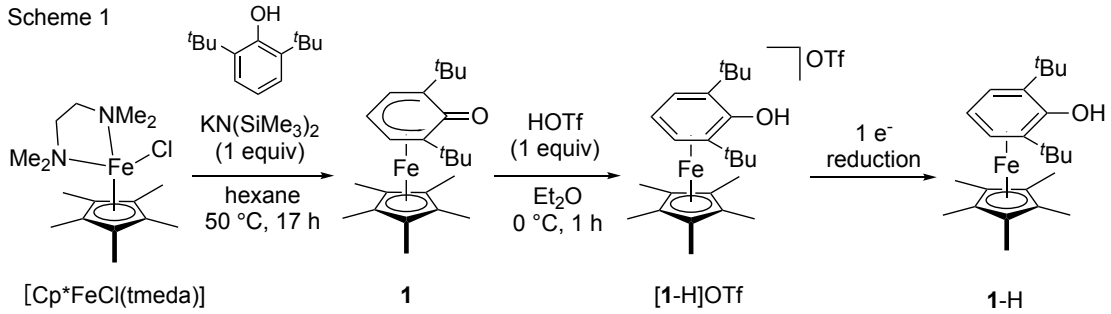
(*Graduate School of Engineering, The University of Tokyo*) ○Yuye Zhang, Shogo Kuriyama, Yoshiaki Nishibayashi

Keywords: Iron Complexes; Proton-Coupled Electron Transfer (PCET); Bond Dissociation Free Energy; Oxocylohexadienyl Ligand; Electrochemistry

Electrochemical synthesis of ammonia as an environmental-friendly replacement for the traditional Haber-Bosch process has been an attractive target. We previously reported the molybdenum-catalyzed ammonia formation using SmI_2 as a reductant and H_2O as a proton source, where a proton-coupled electron transfer (PCET) process between a samarium-aqua complex and the molybdenum catalyst occurred.[1] Because this reaction requires a stoichiometric amount of expensive SmI_2 as a reductant, the development of new PCET mediators for electrochemical ammonia synthesis is desired. Here, we have envisaged that π-bonded η^5-oxocyclohexadienyl iron complexes, which have the iron center as a redox cite and the oxocyclohexadienyl group as a proton transfer cite, would promote electrochemical PCET reactions.

An iron sandwich complex [Cp*Fe(η^5-2,6-^{t}Bu$_2$C$_6$H$_3$O)] (**1**, Cp* = η^5-C_5Me_5) was newly synthesized from the reaction of [Cp*FeCl(tmeda)] with 2,6-^{t}Bu$_2$C$_6$H$_3$OH in the presence of $KN(SiMe_3)_2$ (Scheme 1). Protonation of **1** with HOTf (OTf = SO_3CF_3) afforded a cationic iron complex bearing a π-bound phenol ligand ([**1**-H]OTf). The pK_a value of [**1**-H]OTf was determined as 9.92 in THF through UV-vis spectroscopy. One-electron reduction of [**1**-H]OTf to **1**-H proceeded electrochemically at -2.08 V vs ferrocene$^{0/+}$. Based on the definition of bond dissociation free energy (BDFE),[2] the BDFE of the O–H bond in **1**-H was estimated as 26.0 kcal mol^{-1}, which is small enough for **1**-H to work as a hydrogen atom donor in PCET reactions. The reactivity of these iron complexes toward PCET reactions such as ammonia formation will be presented.

Scheme 1



1) Ashida, Y.; Arashiba, K.; Nakajima, K.; Nishibayashi, Y. *Nature* **2019**, *568*, 536–540.
2) Warren, J. J.; Tronic, T. A.; Mayer, J. M. *Chem. Rev.* **2010**, *110*, 6961–7001.

This paper is based on results obtained from a project, JPNP21020, commissioned by the New Energy and Industrial Technology Development Organization (NEDO).