Synthesis and Properties of Iron Complexes Bearing SiCN-Type Pincer Ligands

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Replacing traditional noble metal catalysts with iron catalysts has attracted attention from a standpoint of sustainability. [1] We have recently developed iron catalyst $\bf A$ bearing a strongly σ -donating silyl-NHC chelate ligand, which promotes double hydroboration of nitriles under UV irradiation. [2] Moreover, our recent study revealed that related silyl-NHC-pyridine pincer complex $\bf B$ acts as a catalyst for the same reaction under visible-light irradiation by blue LED. [3]

In this work, to explore more efficient visible-light driven catalysts, we designed and synthesized an analogous pincer complex by extending the π conjugation of the pyridine unit of **B** to a quinoline unit.

The reaction of imidazolium salt 1 with Fe₃(CO)₁₂ in the presence of KN(SiMe₃)₂ afforded NHC-quinoline chelate iron complex 2 in 49% yield (Scheme 1). Complex 2 was then converted to silyl-NHC-quinoline pincer complex 3 in 78% yield upon irradiation with red LED and repeated degassing. The UV-visible spectrum of complex 3 showed an absorption band in the visible light region of ca. 450–500 nm, which is red-shifted from that of complex B by ca. 50 nm. Furthermore, we investigated the catalytic activity of complex 3 for the double hydroboration of p-tolunitrile with pinacolborane (HBpin) under irradiation by blue LED (440–450 nm) at room temperature, which gave N,N-bis(boryl)amine in 47% NMR yield. Exploration of substrate scope of hydroboration catalyzed by 3 and B, and mechanistic investigation are currently underway.

Scheme 1. Synthesis and catalysis of a silyl-NHC-quinoline pincer-ligated iron complex

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