学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Studies on Cooperative Organometallic Catalysis for Organic Synthesis

（有機合成への応用を指向する協働作用触媒に関する研究）

Cooperative catalysis is one of the most attractive tools for achieving highly efficient organic transformation, in which the catalysts activate multi-reactants at once. Various kinds of organometallic cooperative catalysts have been developed; however, quenching between two active sites in the cooperative catalysts are usually an issue towards achieving high catalytic efficiency for organic transformation. Thus, conceptually new catalyst designs are still demanded.

The author has developed cooperative catalysis for nucleophilic addition towards alkynes and for transformation of stable C—O bonds. The catalytic systems are rationally designed with an imidazo[1,5-a]pyridine-3-ylidine ligand template and an anthracenide scaffold, and these cooperative activities of catalysts were supported through control experiments and DFT calculations.

Chapter 1 describes the demonstration for the effective cyclization of alkyne-tethered carboxylic acids by using the original cooperative catalysts bearing an imidazo[1,5-*a*]pyridine-3-ylidine ligand. A substituent at the C5 position of the ligand was expected to impact the catalytic environment around the metal atom, which is bound to the carbene at the C3-position. Hence, an imidazole moiety was introduced as an organic basic site to the C5 position, and 5-imidazolyl imidazo[1,5-*a*]pyridin-3-ylidene silver complexes were prepared as highly efficient catalysts for the cyclization of alkyne-tethered carboxylic acids (Figure 1). Due to the rigidity of the imidazo[1,5-*a*]pyridin-3-ylidene backbone, the basic imidazole moiety at the C5 position was fixed in the vicinity of the silver metal. In fact, the cyclization was accelerated due to a cooperative effect of an assisted deprotonation by the imidazole moiety and the Lewis acidity of the silver metal. DFT calculations supported the cooperativity between silver and imidazole.

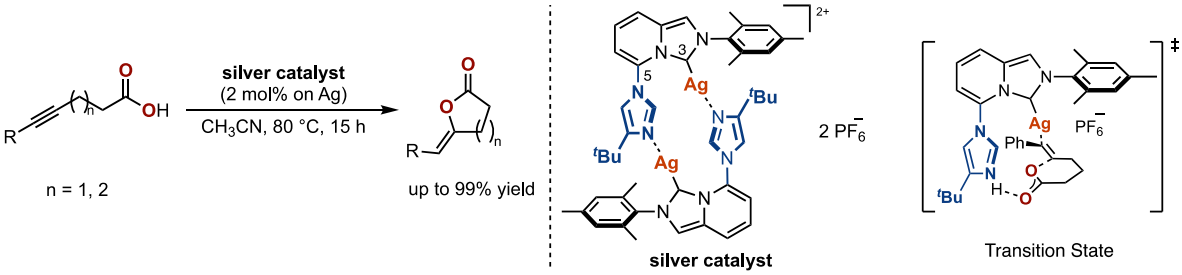

Figure 1. Cyclization of alkyne tethered carboxylic acids catalyzed by a designed silver carbene complex.

Chapter 2 describes the development of highly active catalysts towards challenging intermolecular nucleophilic additions with non-activated alkynes (Figure 2). The author prepared novel imidazo[1,5-*a*]pyridin-3-ylidene gold complexes including a bipyridine coordination site at the C5 position, which enabled the formation of hetero-bimetallic cooperative catalysts through the binding of a hard metal at the bipyridine site. The rigid imidazo[1,5-*a*]pyridin-3-ylidene skeleton caused the two metals, gold and zinc, to be located in close proximity and displayed cooperative effects in facilitating intermolecular reactions. The catalytic activities of the heterobimetallic complexes were investigated, in which *in situ* generated heterobimetallic complexes bearing a cationic gold atom and $Zn(acac)_2$ showed high catalytic performance toward hydrocarboxylation and hydroalkoxylation of non-activated alkynes. The cooperative action of the Au-Zn hetero-bimetallic complexes was supported by DFT calculations. Interestingly, it was found that nucleophilic addition of carboxylic acids toward non-activated alkynes can proceed through two different pathways, either direct nucleophilic attack of the zinc carboxylate or nucleophilic attack of deprotonated carboxylic acids resulting from hydrogen-bonding at zinc carboxylate oxygen atom.

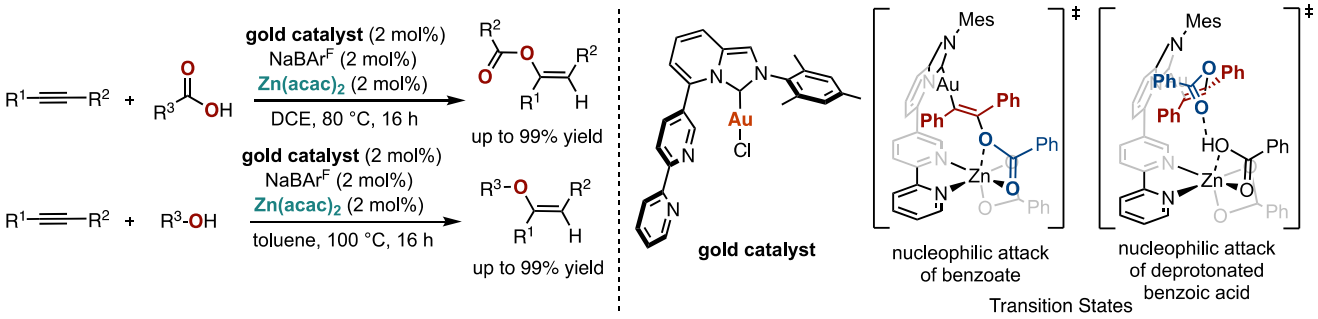

Figure 2. Hydrocarboxylation and alkoxylation of non-activated alkynes catalyzed by a designed gold carbene complex.

Chapter 3 describes the development of Ni-Mg cooperative catalytic systems for the homo-coupling of aryl ethers (Figure 3). Aryl ethers are attractive substrates for reductive homo-coupling in terms of readily availability and low toxicity. The author developed a protocol using inexpensive Mg(anthracene)(thf)$_3$ (**1**) as a reductant under mild conditions (60 °C). Optimization of the reaction conditions revealed that reductant **1** was crucial for the homo-coupling. Using simple metal reductants such as Mg^0, Zn^0, and Mn^0 powder did not promote the reaction. The role of specific reductant **1** was investigated by DFT calculations, in which the nickel(0)-ate complexes were proposed as reasonable active species. It was proposed that the nickel(0)-ate complex allows cleavage of the C–O bond with a low energy barrier (12.1 kcal/mol) through activation of the C–O bond by cooperative Lewis acid activation at the magnesium metal site.

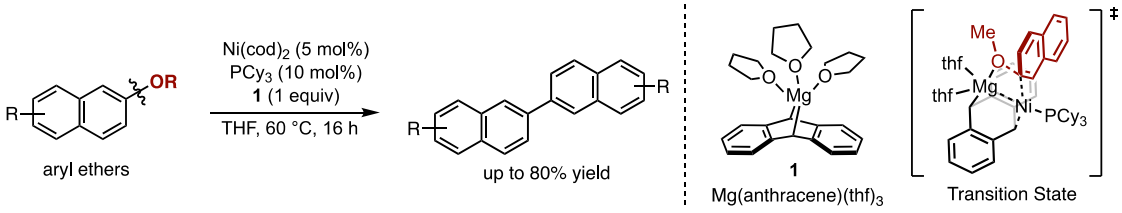

Figure 3. Nickel-catalyzed homocoupling of aryl ethers using Mg(anthracene)(thf)$_3$ reductant.