

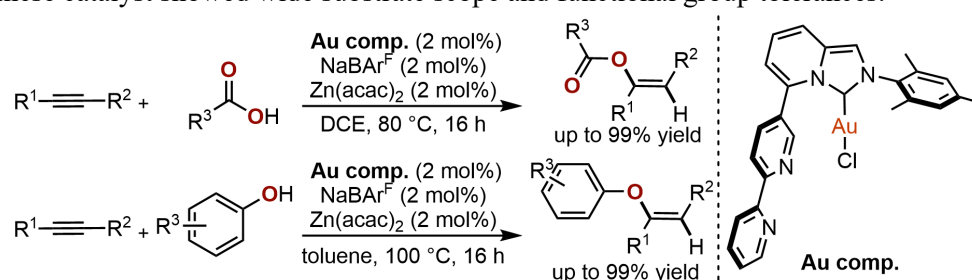
Nucleophilic Addition of Carboxylic Acids and Phenols towards Non-activated Alkynes Catalyzed by Gold-Zinc Bimetallic Complexes Including [1,5-*a*]pyridine-3-ylidene Ligands

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Keywords: Gold Catalyst; *N*-Heterocyclic Carbene; Cooperative Catalysis; Nucleophilic Addition

Imidazo[1,5-*a*]pyridin-3-ylidene¹ is an attractive *N*-heterocyclic carbene (NHC) platform for designing organometallic catalysts, since the substituent at the C5-position impacts the catalytic environment of metal atom bound to carbene at the C3-position. In fact, we reported that 5-imidazolyl-imidazo[1,5-*a*]pyridin-3-ylidene silver cationic complexes served as a highly active catalyst toward cyclization of alkyne-tethered carboxylic acids through acid-base cooperative actions.² This contribution will report the development of gold complexes bearing imidazo[1,5-*a*]pyridin-3-ylidene including coordinative *N*-heteroaromatics at the C5-position, in which *N*-heteroaromatics served as a ligand for constructing hetero-bimetallic complexes with hard metal salts.

For evaluating the catalytic activity of the gold complexes, we attempted hydrocarboxylation and hydrophenoxylation of non-activated alkynes by the use of the hetero-bimetallic complexes generated through pre-mixing the gold complex with non-coordinative anion sources and metal salts. These nucleophilic addition was plausibly accelerated through cooperative action of the Lewis acidic gold atom for activating alkynes and the basic metal for increasing nucleophilicity of carboxylic acids or phenols through deprotonation of acidic protons.³ We found that the gold-zinc hetero-bimetallic complexes showed highly catalytic performance toward hydrocarboxylation and hydrophenoxylation of non-activated alkynes, and these catalyst showed wide substrate scope and functional group tolerances.



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