CeO_2 Supported Au–Pd Alloy Nanoparticle Catalyst for Heterogeneously Catalyzed Decarbonylation of 1,2-Diketones

([1]*School of Engineering, The University of Tokyo*) ○Takehiro Matsuyama,[1] Takafumi Yatabe,[1] Tomohiro Yabe,[1] Kazuya Yamaguchi[1]

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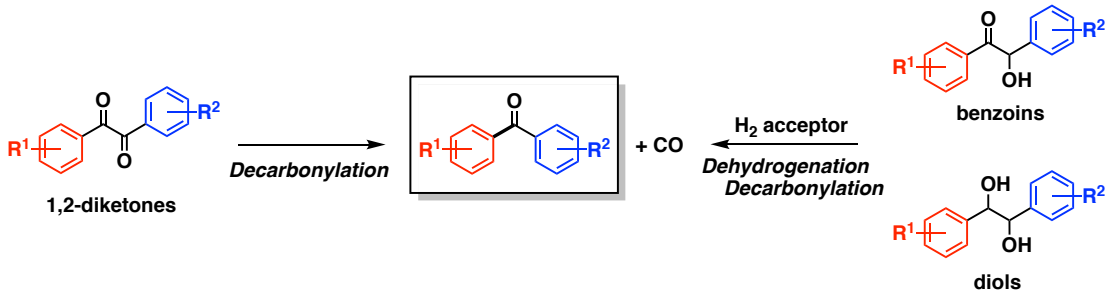
Ketone is an essential moiety in the synthesis of pharmaceuticals, agrochemicals, and natural products, and various synthetic methods of ketones, including Friedel–Crafts acylation, have been developed to date. A new approach to ketone synthesis via 1,2-diketones has been paid attention to due to the possibility of utilizing various starting materials such as alkynes, alkenes, and aldehydes. However, reported decarbonylation of 1,2-diketones to ketones mostly depended on a kind of benzilic acid rearrangement utilizing a stoichiometric amount of base and anilines,[1)] and a few reports of 1,2-diketones decarbonylation involving oxidative addition demonstrated limited substrate scopes such as aliphatic diketones[2)] or alkynyl 1,2-diketones.[3)] To the best of our knowledge, no report of decarbonylation of diaryl 1,2-diketones involving oxidative addition has been reported.

In this study, we have developed heterogeneously catalyzed decarbonylation of 1,2-diketones to ketones involving oxidative addition using a CeO_2-supported Au–Pd alloy nanoparticle catalyst (Au−Pd/CeO_2), which demonstrates a wide substrate scope and functional group tolerance. In addition, we have also reported tandem reactions starting from benzoins or diols to synthesize diaryl ketones using the catalyst with a hydrogen acceptor. Au−Pd/CeO_2 was confirmed to function as a heterogeneous catalyst by hot filtration and ICP-AES analysis of the filtrate, and the catalyst can be recycled. In this presentation, we will discuss the alloy effect and the support effect in detail based on the thorough catalyst characterization, kinetic analysis, and control experiments.



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