Y. FAN, H. ZHENG, S. LABALME, W. LIN^{*} (THE UNIVERSITY OF CHICAGO, USA) Molecular Engineering of Metal-Organic Layers for Sustainable Tandem and Synergistic Photocatalysis *J. Am. Chem. Soc.* **2023**, *145*, 4158–4165, DOI: 10.1021/jacs.2c12599.

Photocatalytic Dehydrogenative Amination of Cyclohexanones



Significance: A metal organic layer (MOL) Hf–Ir composite was prepared from a photosensitizing Ir–BBA complex and HfCl₄ under solvothermal conditions. A cobaloxime unit was added to the resulting Hf–Ir MOL with a pyridylpropionate (PPA) tether to give Hf–Ir–CoPPA. The Hf–Ir–CoPPA promoted a dehydrogenative amination of cyclohexanones to give the corresponding *N*-alkyl anilines with photo irradiation by blue LED. The amination of a steroidal 3,17-diketone took place with excellent chemoselectivity to give the corresponding A-ring amination product exclusively.

Comment: ICP analysis of Hf–Ir–CoPPA revealed that the MOL composite had a Hf/Ir/Co ratio of 1.0/0.54/0.40. A 2D-monolayered double-decker structure of Hf–Ir–CoPPA was constructed with Hf₁₂ cluster units and bridging-ligand units Ir–BBA. Hf–Ir–CoPPA was recovered by centrifugation and reused 8 times without significant loss of its catalytic performance. Hf–Ir–CoPPA also catalyzed the Heck-type coupling of alkyl iodides with styrenes to give the corresponding β-substituted styrenes.

Category

Polymer-Supported Synthesis

Key words

photpcatalysis

metal-organic layer

cobalt catalyst

dehydrogenative amination



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