

An Iridium Precatalyst for Transfer Dehydration of Amides to Nitriles

(¹Graduate School of Pharmaceutical Sciences, Kyoto University, ²Graduate School of Science, Nagoya University, ³Institute for Chemical Research, Kyoto University)

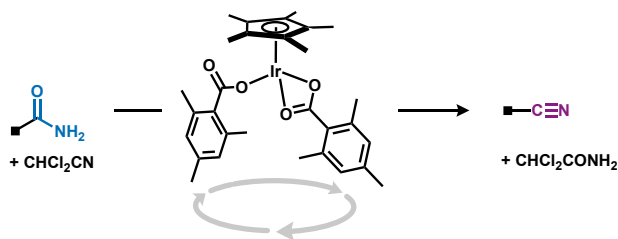
Marie Ono,¹ Toshiki Asai,² Asuka Naraoka,¹ Yasuhiro Ohki,³ Yoshiji Takemoto,¹ ○Hiroshi Naka¹

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Metal-catalyzed, homodesmotic transfer reaction is a valuable synthetic tool for converting a specific functional group to other ones with a minimal loss of chemical energy. A remarkable example is the ruthenium-catalyzed asymmetric transfer hydrogenation of carbonyl compounds developed by Noyori using alcohols as H₂ donors. Homodesmotic transfer catalysis has been recently recognized as a new strategy for reaction development.

The palladium-catalyzed transfer dehydration of primary amides with nitriles is a characteristic homodesmotic transfer reaction.^[1] This reaction can be typically carried out under aqueous conditions in the presence of palladium(II) catalysts (typically PdCl₂) and acetonitrile (H₂O acceptor) at room temperature and is frequently used for producing functionalized nitriles. During our previous studies on the synthetic applications of the palladium-catalyzed transfer dehydration catalysis,^[2] we wondered if the transfer dehydration of amides with nitriles could be catalyzed by other metals, which should offer multiple options for synthetic uses. However, to the best of our knowledge, there has been no metallic species other than palladium known to catalyze homodesmotic transfer dehydration of amides to nitriles using nitriles as water acceptors.^[3]

Herein, we report a structurally well-defined iridium complex, IrCp*(MesCO₂)₂ [Mes = 2,4,6-trimethylphenyl], as an active precatalyst for the transfer dehydration of amides to nitriles. This precatalyst promoted the dehydration of amides using dichloroacetonitrile as a water acceptor with comparable functional group compatibility to previously reported palladium catalysts.^[1,2]



- [1] S. I. Maffioli, E. Marzorati, A. Marazzi, *Org. Lett.* **2005**, 7, 5237-5239.
- [2] H. Okabe, A. Naraoka, T. Isogawa, S. Oishi, H. Naka, *Org. Lett.* **2019**, 21, 4767-4770.
- [3] Our preliminary results were communicated in the CSJ annual meeting 2021 [A16-1am-05].