Mechanistic Investigation of the Rhodium-catalyzed Transfer Hydroarylation between Tertiary Alcohols and Ketones

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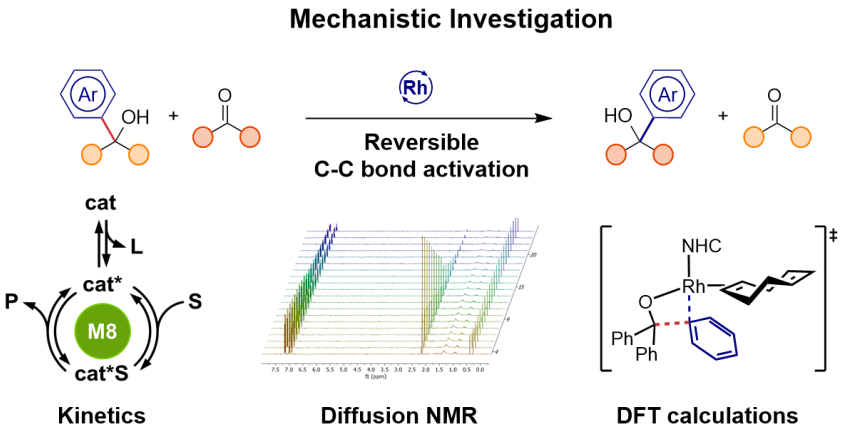
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Carbon–carbon bonds are among the most abundant yet least reactive chemical bonds in organic molecules. The targeted activation of these bonds in a general sense remains challenging yet offers great potential to break down and reorganize small molecules without the need for prefunctionalization.

We recently disclosed a catalytic shuttle arylation reaction to interconvert triaryl alcohols and ketones by realizing C–C bond activation via reversible β-carbon elimination.[1] Using this method, unprotected alcohols serve as a benign alternative to stoichiometrically employed organometallic reagents to access value-added alcohol products from ketones. Our method exhibits high chemoselectivity and tolerates functional groups that are vulnerable to traditional nucleophilic and basic reagents encountered in carbonyl addition.

The mechanism of this isofunctional transformation was subsequently investigated by experimental and computational methods including kinetic studies, in situ spectroscopic monitoring, and density functional theory (DFT) calculations, supporting a fully reversible β-carbon elimination/insertion mechanism.[2] The gained insight allowed to develop improved protocols with air-stable precatalysts.

This work highlights the advantages of using alcohols as mild aryl donor reagents in carbonyl addition and sheds light on the mechanism of rhodium-catalyzed C–C bond activation, possibly initiating the development of novel chemical transformations using alcohols as latent carbon-centered nucleophiles.



[1] Lutz, M. D. R.; Gasser, V. C. M.; Morandi, B. *Chem* **2021**, *7*, 1108.
[2] Lutz, M. D. R.; Roediger, S.; Morandi, B. *in preparation*.