

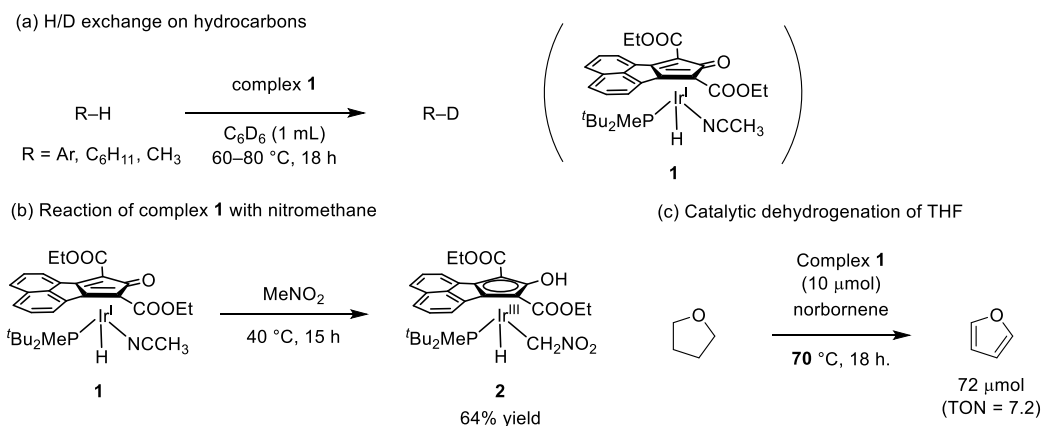
Cleavage of C–H Bonds by Cyclopentadienone Iridium Complex

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Oxidative addition of C–H bonds, which generates reactive intermediates with metal–carbon bonds, has played an essential role in the field of organometallic chemistry.¹ Previously, we reported a new type of sp^3 C–H bond *forming* reaction, “Metal-Ligand cooperative reductive elimination of sp^3 C–H bonds”, which takes place at a hydroxycyclopentadienyl dimethylplatinum(IV) complexes.² Herein we prepared an iridium(I) hydride complex **1** bearing electron-deficient cyclopentadienone ligand toward sp^3 C–H bond oxidative addition. Complex **1** catalyzed H/D exchange of sp^2 C–H bonds in toluene, and sp^3 C–H bonds in hexane and methane in the presence of C_6D_6 (**Scheme 1a**). When complex **1** was treated with nitromethane, hydroxycyclopentadienyl nitromethyliridium(III) complex **2** was formed (**Scheme 1b**), showing the novel elementary reaction, *metal–ligand cooperative C–H bond oxidative addition*. In this reaction, we found that the more electron-deficient the cyclopentadienone ligand is, the more favorable the reaction becomes, in sharp contrast to the classical metal-centered oxidative addition.¹ This trend shows good agreement with the proposed mechanism where the C–H bond cleavage is accompanied by two-electron transfer from the metal center to the cyclopentadienone ligand.³ Complex **1** was further applied to catalytic transfer-dehydrogenation of THF, where 7.2 of catalytic turnover was achieved at 70 °C, the lowest temperature ever reported (**Scheme 1c**).

Scheme 1



1) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, 97, 2879–2932. 2) Higashi, T.; Ando, H.; Kusumoto, S.; Nozaki, K. *J. Am. Chem. Soc.* **2019**, 141, 2247–2250. 3) a) Shvo, Y.; Czarkie, D.; Rahamim, Y.; Chodosh, D. F. *J. Am. Chem. Soc.* **1986**, 108, 7400–7402. b) Higashi, T.; Kusumoto, S.; Nozaki, K. *Angew. Chem. Int. Ed.* 10.1002/anie.202011322.