

Catalytic Hydrodehalogenation of Aryl Halides Mediated by a Long-Range Metal-Ligand Cooperation of Cobalt(I) Complexes Bearing a Tetradentate PNNP Ligand

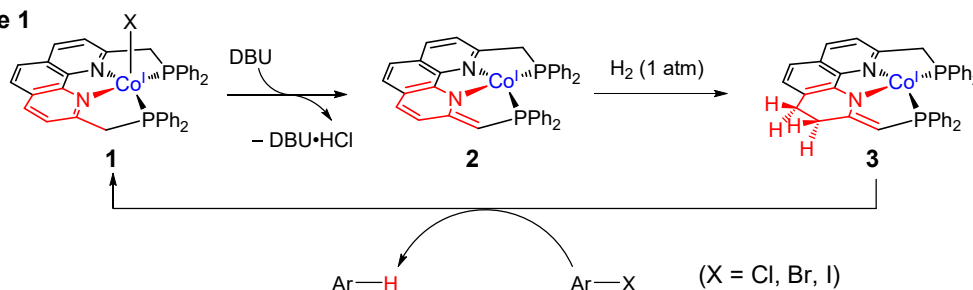
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Metal-ligand cooperation (MLC) is recognized as an important key step for construction of various catalytic reactions.¹ In this study, an intrinsic long-range MLC was demonstrated using a well-defined cobalt(I) system supported by a tetradentate PNNP ligand (2,9-bis((diphenylphosphanyl)methyl)-1,10-phenanthroline).²

PNNP-supported Co(I) chloro complex [CoCl(PNNP)] (**1**) easily underwent deprotonation on the treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in polar solvents to form a four-coordinate-cobalt(I) complex coordinated with an asymmetrical PNNP' ligand with a dearomatized phenanthroline backbone, [Co(PNNP')] (**2**) (Scheme 1). Complex **2** cleaved a H–H bond to form **3**, in which two H-termini were added to the endocyclic double bond of the PNNP backbone. Complex **3** reacted with chlorobenzene to give **1** as well as benzene. Thus, an unprecedented long-range MLC, where the PNNP-backbone behaves as a hydrogen reservoir, was demonstrated. By using this reaction strategy, catalytic hydrodehalogenation of aryl halides with H₂ (1 atm) was performed. The reaction efficiently proceeded in the presence of **1** (2 mol%) and DBU (2 equiv), and a broad substrate scope (> 40 entries) was achieved in good to excellent yields. Radical clock study supported the occurrence of the homolysis of C–X bonds during the reaction. The reaction was accelerated by introducing electron-withdrawing substituents to aryl halides. A series of kinetic parameters showed a good Hammett correlation with the σ_p values of substituents ($\rho = 0.86$). Overall, the single-electron transfer mechanism was suggested.

Scheme 1



1) Milstein, D. *et al. Angew. Chem. Int. Ed.* **2015**, 54, 12236-12273. 2) Nakajima, Y. *et al. Dalton Trans.* **2020**, 49, 14592-14597.