Hydrogenolysis of Esters Catalyzed by a Cobalt(I) Complex Bearing a Phenanthroline-Based Tetradentate PNNP Ligand

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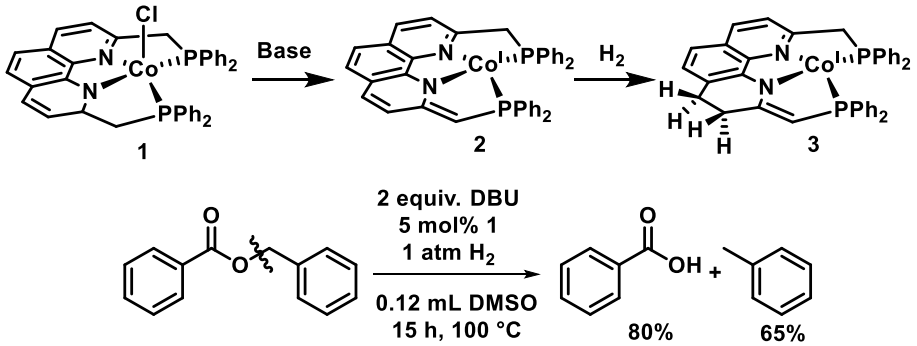
Esters, which are main component of fats and oils in foods, are recognized as one of the important biomass resources. Thus, development of transformation methodologies of esters is of great importance.[1] Among the study, β-C−O cleavage of esters recently draws an increasing attention for the purpose of degradation of biomass as well as a key step of processing lignocellulose to liquid hydrocarbon fuel.[2] One important milestone was made by Marks et al., who applied a tandem homogeneous catalytic system that used metal triflate to selectively cleave esters at the β-C−O bond, and then H_2 gas was activated by palladium as a reductant.[3] In this study, we focus on a cobalt(I) complex bearing a phenanthroline−based tetradentate PNNP ligand.[4] So far, our team demonstrated H_2 activation *via* metal-ligand cooperation of PNNP-Co system. In this process, the phenanthroline backbone accepts two H-atom termini, so that the PNNP ligand act as a hydrogen reservoir. As a result, the resulting complex **3** still possesses a reactive vacant site.[4] We have expected that this PNNP-Co complex can be applied as a single catalyst.

In this study, we have achieved hydrogenolysis of benzyl benzoate and its derivatives *via* β-C−O bond cleavage. In the presence of 5 mol% complex **1**, benzyl benzoate reacted with 1 atm H_2 to afford benzoic acid and toluene in 80% and 65% yields. Kinetic study was performed to support pre-equilibrium process. Further mechanistic details as well as substrate scope will be discussed at the presentation.



1) Corma, A.; Iborra, S.; Velty, A. *Chem. Rev.* **2007**, *107*, 2411. 2) Serrano-Ruiz, J. C.; Wang, D.; Dumesic, J. A. Green Chem. **2010**, *12*, 574. 3) Lohr, T. L.; Li, Z.; Assary, R. S.; Curtiss, L. A.; Marks, T. J. *ACS Catal.* **2015**, *5*, 3675. 4) a) Nakajima, Y. Jheng, N.-Y. *ACS Catal. in revision* b) Jheng, N.-Y.; Ishizaka, Y.; Naganawa, Y.; Sekiguchi, A.; Nakajima, Y. *Dalton Trans.* **2020**, *49*, 14592.