Reductive C(sp^3)–O Silylation by Cooperative Rhodium/Lewis Acidic Metal Catalysis

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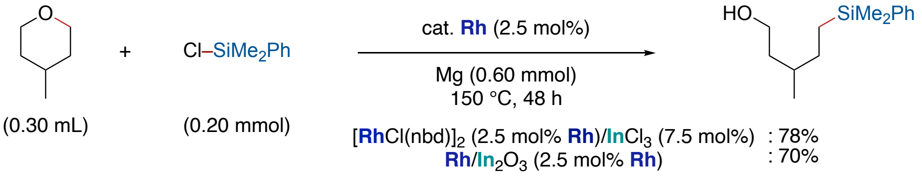
Alcohol and ethers represent ubiquitous structural motifs in both feedstock and fine chemicals. Abundant biopolymers such as cellulose and lignin, characterized by their primary skeletons composed of multiple C–O bonds, are anticipated as sources for organic compounds. Furthermore, the industrial synthetic process for alcohols and ethers has been established. C–O bond transformations directly edit the main skeleton of these molecules and allow access to a wide range of molecules from simple feedstock. However, the formidable chemical stability of alcohols and ethers, arising from the diminished leaving group ability of alkoxides and hydroxides, makes this difficult. Conventional transformations of alcohols and ethers have heavily relied on conversion to more facile leaving groups, such as sulfonates and phosphates, and the direct conversion of C–OR (R = alkyl, H) bonds has proven to be intricate. Recently, the Dong group[1] and the Miura and Shishido group[2,3] have reported the C(sp^3)–O bond functionalization of alkyl ethers. As elucidated above, this type of transformation has garnered substantial attention recently.

We have found that reductive C(sp^3)–O silylation catalyzed cooperatively by rhodium and Lewis acidic metals in the presence of magnesium powder. For instance, the reaction of 4-methyltetrahydropyrane (0.30 mL) with chlorodimethylphenylsilane (0.20 mmol) in the presence of $[RhCl(nbd)]_2$ (2.5 mol%), $InCl_3$ (7.5 mol%), and magnesium powder (0.60 mmol) afforded the ring-opened and C(sp^3)–O silylated product in 78% yield. We also found that rhodium nanoparticles supported on indium oxide catalyzed the same type of transformation. Experiments have suggested that the reaction is catalyzed by nanoparticles containing multi-metallic species in both conditions. We will present the results focusing on chemo-selectivity and the reaction mechanism.



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