

Theoretical and Experimental Investigations of an Aldol-type Reaction with Rh Complex

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The chemical transformation of nitrile groups plays an important role in the field of organic synthesis. Goto *et al.* reported an aldol-type reaction of organonitriles under mild conditions in 2008 [1] with a Rh catalyst. In the present study we theoretically and experimentally investigate the origin for its high catalytic efficiency, leading to the observed high yield of the corresponding β -hydroxynitrile product.

In the theoretical investigations, all stationary points on the potential energy surfaces, including transition states, were optimized using the density functional theory (DFT) with the B3PW91 functional. The PCy₃ (Cy = cyclohexyl) ligand is explicitly treated. We chose a moderate basis set size (6-31G(d) for non-metal elements and LanL2DZ for Rh) for geometry optimization, and the refined energies were computed using ONIOM(DF-LCCSD(T):DF-SCS-LMP2) with a larger basis set ((aug-)cc-pVTZ and ECP28MWB). To evaluate the solvent effect (dimethyl sulfoxide (DMSO)), we performed RISM-SCF-SEDD [2] calculations at RI-SCS-MP2/(aug-)cc-pVTZ+cc-pVDZ, and the energetic contribution due to the solvation was added to the ONIOM free energy. We investigated several reaction pathways with monomer and dimer catalysts, and proposed a plausible catalytic cycle as shown in Figure 1.

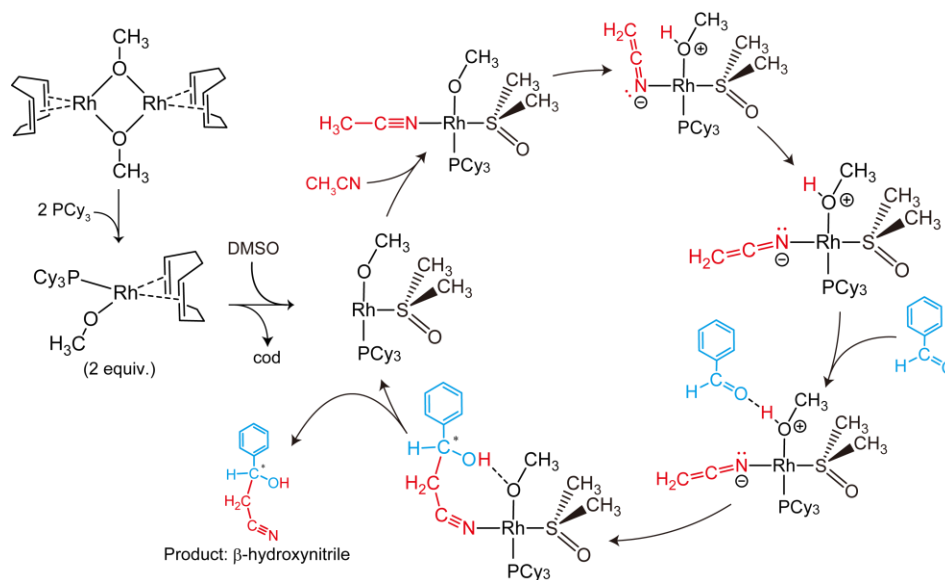


Figure 1. Proposed catalytic cycle

[1] Goto, A., Endo, K., Saito, S. *Angew. Chem. Int. Ed.*, 47:3607-3609, 2008.

[2] Yokogawa, D., Sato, H., Sakaki, S. *J. Chem. Phys.*, 126:244504, 2007.