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Rh 錯体を用いたアルドール型反応に関する理論的研究

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Theoretical investigation of an aldol-type reaction with a Rh complex

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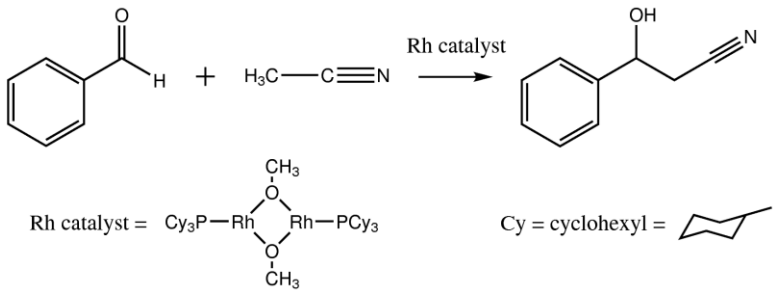
The chemical transformation of nitrile groups plays an important role in the field of organic synthesis. In particular, aldol-type reactions of organonitriles with aldehydes provide β-hydroxynitriles, which are potential precursors for pharmaceutically important functionality. We previously reported that Rh^I complexes efficiently catalyzed aldol-type reactions of nitriles under mild conditions [1]. However, the mechanism for activation of nitrile group in this Rh catalysis was not clear. Because of the difficulty in functionalizing the nitrile group, it is of great importance to elucidate the mechanism of such an efficient catalytic reaction. Here, we conducted theoretical investigations to clarify the mechanism for the Rh catalysis (Scheme 1).



Scheme 1 Target aldol-type reaction

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 PCy_3 (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.

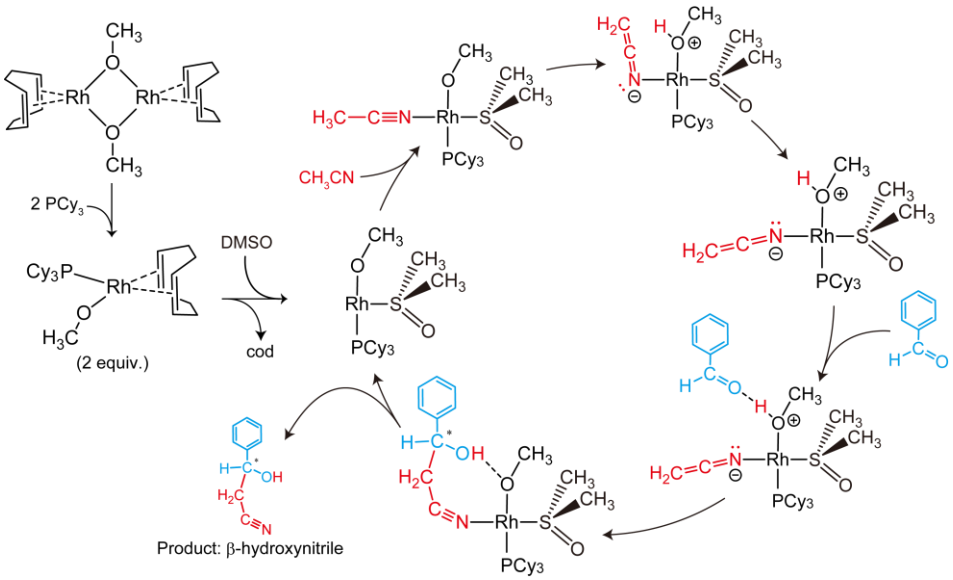


Figure 1 Proposed catalytic cycle

Our calculations show that the barrier height of the proposed pathway is 22.48 kcal/mol, and is comparable to the experimental result (22.4 kcal/mol) of the reaction calorimetry.

References

[1] A. Goto, K. Endo, Y. Ukai, S. Irle, S. Saito, *Chem. Commun.* **2008**, 2212-2214.

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