

**Non-Metal-Assisted Hydrogenation of Carbon Dioxide with an Extraordinarily
Active Hydride on Ir(III)–Pincer Complex**

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The efficient utilization of carbon dioxide has attracted dramatically increasing attention due to its contribution to global warming. As an abundant C1 source, CO₂ can be used to synthesize many value-added organic compounds. Hydrogenation of CO₂ to produce formic acid is one of these important subjects. Recently, Nozaki and co-workers reported a highly active catalyst for hydrogenation of CO₂ (Chart 1).¹ Treatment of an iridium(III) trihydride complex (IrPNPH₃, PNP = 2,6-(di-isopropylphosphinomethyl)pyridine) with 1 atm CO₂ led to an immediate equilibrium between the trihydride and a dihydrido-iridium(III) formate at room temperature. Exposure of the formate in aqueous KOH to H₂ resulted in the elimination of formate anion and the regeneration of the starting trihydride complex.

All calculations were performed using B3LYP functional with the Gaussian 09 program. Geometry optimizations and frequency calculations were carried out in solution phase. The solvent (water) effects were approximated using polarizable continuum model (IEF-PCM).

Two possible pathways were considered for the formation of the formate (Scheme 1). One is direct hydride addition to CO₂ without the assistance of the metal center. The other is the insertion of CO₂ into the Ir–H bond following the coordination of CO₂ to the metal center. These two pathways represent two mechanisms for CO₂ insertion into metal–hydride bond (Chart 2). Usually route A is more favorable because the cooperation of the metal is involved. But here the direct hydride addition to CO₂ is a preferred pathway. This unusual phenomenon is due to that the Ir(III) trihydride complex has two kinds of hydrides. The hydrides vertical to the pyridine moiety are very active electron donors.

The rate-determining step in the whole reaction cycle is the regeneration of the Ir(III) trihydride complex via H₂ dissociation on the pincer-ligand-dearomatized Ir(III) dihydride complex, which has the highest activation barrier of 16.6 kcal/mol.

Chart 1

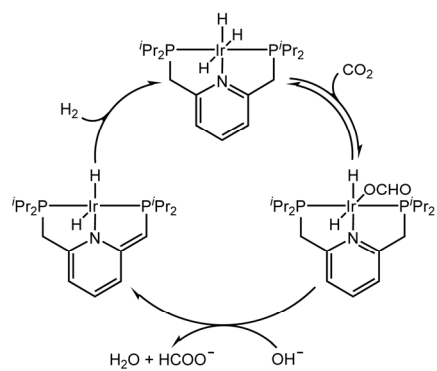
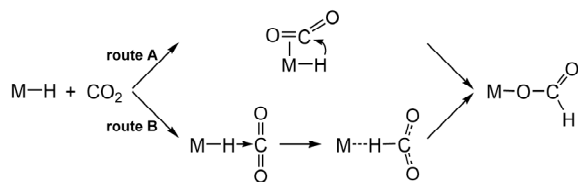


Chart 2



Scheme 1

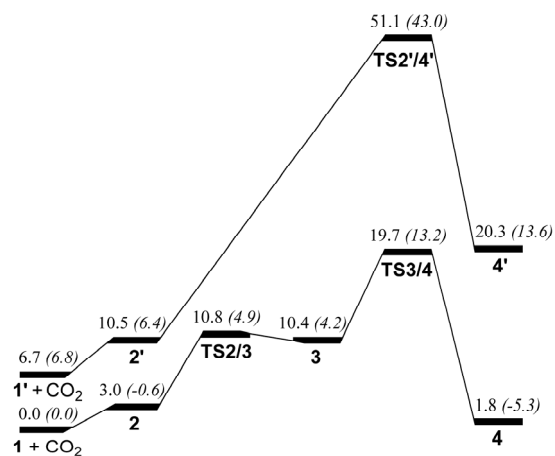
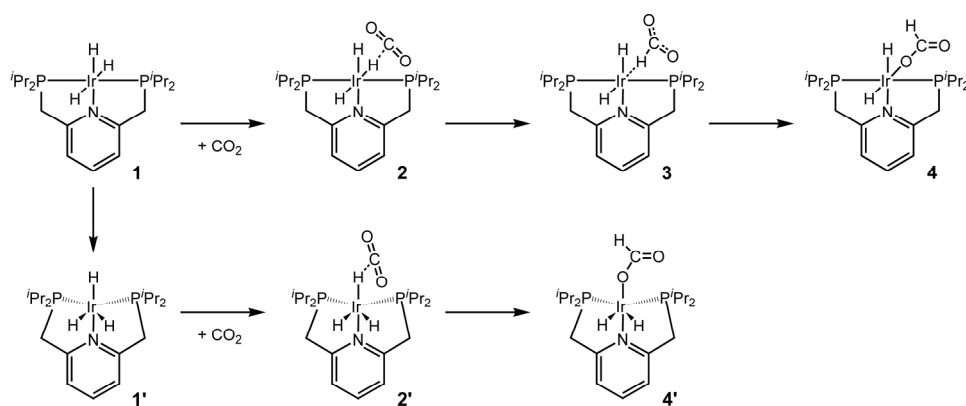


Figure 1. Free energy profile (298 K, in kcal/mol) for two pathways for CO₂ insertion into the Ir-H bond of **1**. The relative enthalpies are also given in parentheses in *italics*.

Reference

[1] Tanaka, R.; Yamashita, M.; and Nozaki, K. *J. Am. Chem. Soc.* **2009**, *131*, 14168.