

研究论文

钌配合物催化氢化CO<sub>2</sub>生成甲酸反应中的醇促进效应

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摘要 在水合钌配合物[TpRu(PPh<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)]BF<sub>4</sub> [Tp=hydrotris(pyrazolyl) borate]

催化氢化二氧化碳生成甲酸的反应中观察到醇对反应的促进作用.

利用原位高压核磁共振跟踪催化反应过程的结果表明, 在甲醇溶液中, [TpRu(PPh<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)]BF<sub>4</sub>在三乙胺和H<sub>2</sub>

作用下转化为TpRu(PPh<sub>3</sub>)<sub>2</sub>H. 二氧化碳插入Ru—H生成甲酸根配合物TpRu(PPh<sub>3</sub>)<sub>2</sub>(η<sup>1</sup>-OCHO)•HOCH<sub>3</sub>,

其中的甲酸根配体与醇分子间形成分子间氢键. 该甲酸根配合物随即转化为另一个甲酸根配合物TpRu(PPh<sub>3</sub>)

(CH<sub>3</sub>OH)(η<sup>1</sup>-OCHO)并与之达成平衡, 后者由于存在分子内氢键而稳定.

考虑到这两个甲酸根配合物在催化反应中的稳定性, 它们应该不在主要的催化循环内. 提出了配合物[TpRu(PPh<sub>3</sub>)

<sub>2</sub>(H<sub>2</sub>O)]BF<sub>4</sub>在几种醇溶液中催化氢化二氧化碳生成甲酸的催化循环机理, 催化循环的关键中间体可能是TpRu

(PPh<sub>3</sub>)(ROH)H. 该中间体能同时转移负氢及醇配体中的氢质子到接近的二氧化碳分子上生成甲酸, 并吸收H<sub>2</sub>

生成过渡态TpRu(PPh<sub>3</sub>)(OR)(H<sub>2</sub>). 该过渡态经过σ-复分解反应重新生成TpRu(PPh<sub>3</sub>)(ROH)H完成催化循环.

关键词 [钌配合物](#) [醇效应](#) [原位高压核磁共振](#) [催化机理](#)

分类号

**Promoting Effect of Alcohol in Hydrogenation of CO<sub>2</sub> to Formic Acid Catalyzed by Ruthenium Complex**

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**Abstract** The promoting effect of alcohols in the catalytic hydrogenation of CO<sub>2</sub> to formic acid with the solvento complex [TpRu(PPh<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)]BF<sub>4</sub> [Tp=hydrotris(pyrazolyl) borate] is observed. High-pressure NMR monitoring of the catalytic reactions shows that the observable intermediate is a formate complex TpRu(PPh<sub>3</sub>)<sub>2</sub>(η<sup>1</sup>-OCHO)•HOCH<sub>3</sub>, which is formed from CO<sub>2</sub> insertion into Ru—H bond of TpRu(PPh<sub>3</sub>)<sub>2</sub>H and stabilized by hydrogen-bonding interaction between the formate ligand and a methanol molecule. The metal formate species comes into equilibrium with another metal formate TpRu(PPh<sub>3</sub>)(CH<sub>3</sub>OH)(η<sup>1</sup>-OCHO); the second metal formate species contains a coordinated methanol, which is intramolecularly hydrogen-bonded with the formate ligand. In view of the stability of these two formates under catalytic conditions, it is very likely that they are not within the major catalytic cycle of the reaction. The productive catalytic cycle of the reactions conducted in a variety of alcohols is proposed. The key species in the cycle is the transient alcohol hydride intermediate, TpRu(PPh<sub>3</sub>)(ROH)H. It is proposed that TpRu(PPh<sub>3</sub>)(ROH)H is able to transfer a hydride and a proton simultaneously to an approaching CO<sub>2</sub> molecule to produce formic acid, itself being converted to a transient alkoxo species, which then associates a H<sub>2</sub> molecule to regenerate TpRu(PPh<sub>3</sub>)(ROH)H via σ-metathesis between the alkoxo and η<sup>1</sup>-H<sub>2</sub> ligands.

**Key words** [ruthenium complex](#) [alcohol effect](#) [in situ high-pressure NMR](#) [catalytic mechanism](#)

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