

二氧化碳插入单氢钌配合物反应中的水效应研究

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摘要 分别研究了在干燥THF及H₂O/THF条件下CO₂与TpRu(PPh₃)(CH₃CN)H [Tp=Hydrotris(pyrazolyl)borate]的反应,发现水对CO₂插入TpRu(PPh₃)(CH₃CN)H的反应具有显著促进作用.

原位高压¹H, ³¹P和¹³C核磁共振研究显示,在水存在下,CO₂插入Ru-H键形成水合甲酸盐配合物TpRu(PPh₃)(CH₃CN)(η¹-OCHO)·H₂O键而得到增强,进而显著降低CO₂插入TpRu(PPh₃)(CH₃CN)H中Ru-H键的活化能. TpRu(PPh₃)(CH₃CN)(η¹-OCHO)·H₂O很快部分转化为另一甲酸盐配合物TpRu(PPh₃)(η¹-OCHO),二者最后达成平衡,后者由于甲酸盐配体与水分子配体间形成分子内氢键而稳定.

关键词 [二氧化碳](#) [钌络合物](#) [甲酸 P](#) [氢键](#) [活化能](#)

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Study on Effect of Water in CO₂ Insertion into Ruthenium Hydride Complex

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Abstract A promoting effect of water on CO₂ insertion into TpRu(PPh₃)(CH₃CN)H [Tp = Hydrotris(pyrazolyl)borate] is observed. In situ high-pressure ¹H, ³¹P and ¹³C NMR monitoring shows that CO₂ readily inserts into Ru-H to form the hydrated metal formate TpRu(PPh₃)(CH₃CN)(η¹-OCHO)·H₂O in which the formate ligand is intermolecularly H-bonded to a water molecule. Theoretical calculations carried out at the B3LYP level show that electrophilicity of the carbon center of CO₂ is enhanced by the formation of H-bonds between its oxygen atoms and H₂O in the transition state of the process, and thus reaction barrier of the CO₂ insertion is significantly reduced in the presence of water. The hydrated formate species TpRu(PPh₃)(CH₃CN)(η¹-OCHO)·H₂O comes into equilibrium rapidly with another metal formate species TpRu(PPh₃)(η¹-OCHO), in which the coordinated H₂O is intramolecularly H-bonded with the formate ligand.

Key words [CARBON DIOXIDE](#) [RUTHENIUM COMPLEX](#) [FORMIC ACID P](#) [HYDROGEN BONDS](#) [ACTIVATION ENERGY](#)

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