Promoting Effect of Water in Ruthenium-Catalyzed Hydrogenation of Carbon Dioxide to Formic Acid

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A strong promoting effect of water in the catalytic hydrogenation of CO_2 to formic acid with the solvento metal hydride species $TpRu(PPh_3)(CH_3CN)H$ is observed. High-pressure NMR monitoring of the catalytic reaction shows that CO_2 readily inserts into Ru−H to form the metal formate $TpRu(PPh_3)(CH_3CN)(\eta^1\text{-}OCHO)\cdot H_2O$, in which the formate ligand is intermolecularly hydrogen-bonded to a water molecule. Theoretical calculations carried out at the B3LYP level show that reaction barrier of the CO_2 insertion is significantly reduced in the presence of water. In the transition state of the process, electrophilicity of the carbon center of CO_2 is enhanced by the formation of hydrogen bonds between its oxygen atoms and H_2O. The metal formato species comes into equilibrium with another metal formate rapidly; the second formato species $TpRu(PPh_3)(H_2O)(\eta^1\text{-}OCHO)$ contains a coordinated H_2O, which is intramolecularly hydrogen-bonded with the formate ligand. In view of the stability of these two metal formates under catalytic conditions, it is very likely that they are not within the major catalytic cycle of the reaction. A catalytic cycle, which accounts for the promoting effect of water, is proposed. The key species in the cycle is the aquo metal hydride species $TpRu(PPh_3)(H_2O)H$, which could be generated by a ligand displacement reaction of $TpRu(PPh_3)(CH_3CN)H$ with H_2O. It is proposed that $TpRu(PPh_3)(H_2O)H$ is able to transfer a proton and a hydride simultaneously to CO_2 to yield formic acid in a concerted manner, itself being converted to a transient hydroxo species, which then associates a H_2 molecule. The aquo hydride complex $TpRu(PPh_3)(H_2O)H$ is regenerated via σ-metathesis between the hydroxo and $\eta^2\text{-}H_2$ ligands. Theoretical calculations have been carried out to study the structural and energetic aspects of species involved in this catalytic cycle.

Introduction

Transition-metal-catalyzed CO_2 hydrogenation to formic acid is one of the interesting and attractive reactions of CO_2 fixation. It has attracted much attention in recent years, as it provides a promising approach for utilizing carbon dioxide as a raw material for large-scale chemical synthesis.[1] It was shown in one of the early papers that addition of a small quantity of water was effective to enhance the catalytic hydrogenation of CO_2 to formic acid by combinations of group VIII transition metals and bases.[2] The accelerating effect of small amounts of added water in organic solvents has also been observed in active Rh[3] and Ru[4] systems. Although no compelling experimental and theoretical data have been provided to explain the positive "water effect", it has been speculated that hydrogen-bonding interaction between an H_2O molecule and an oxygen atom of CO_2 enhances the electrophilicity at carbon and facilitates its insertion into the metal−hydride bond.[3]

We have recently found that the ruthenium hydride complex $TpRu(PPh_3)(CH_3CN)H$ (**1**; Tp = hydrotris(pyrazolyl)borate) is a versatile complex exhibiting a wide range of reactivity.[5] It gives, upon protonation with a strong acid such as $HBF_4\cdot Et_2O$ or CF_3SO_3H, the η^2-dihydrogen complex $[TpRu(PPh_3)(CH_3CN)(H_2)]^+$, which has been demonstrated to play an important role in the catalytic hydrogenation of olefins.[5a] It is able to decarbonylate primary alcohols, RCH_2OH, forming the carbonyl complexes $TpRu(PPh_3)(CO)R$.[5b] It also reacts with silane, R_3SiH, to give the highly fluxional $TpRu(PPh_3)$"H_2SiR_3" complex, which contains a η^2-silane moiety.[5c] Continuing our investigation of the reactivity of **1**, we studied the catalytic activity of this complex in

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Table 1. Hydrogenation of CO_2 to Formic Acid with $TpRu(PPh_3)(CH_3CN)H$ (1)[a]

entry	reacn time (h)	turnover no.[b]
1[c,d]	16	trace
2[d]	16	30
3[e]	16	720
4[f]	16	735
5	4	250
6	8	436
7	16	760
8[g]	16	346
9[h]	16	146

[a] Typical reaction conditions: catalyst, 0.013 mmol; NEt_3, 2 mL; solvent, THF/H_2O (15 mL/5 mL); total pressure, 50 atm (CO_2/H_2 = 1/1); temperature, 100 °C. [b] TON = mol of product/mol of **1**. [c] No NEt_3 added. [d] Solvent THF (20 mL). [e] Solvent THF/H_2O (19 mL/1 mL). [f] Solvent THF/H_2O (17.5 mL/2.5 mL). [g] The THF phase of entry 7 was recycled. THF and H_2O were added to make up a (15 mL/5 mL) THF/H_2O solution, and 2 mL of NEt_3 was also added. [h] 0.5 mL of CH_3CN added.

the hydrogenation of carbon dioxide to formic acid. We report here the promoting effect of water in the **1**-catalyzed hydrogenation of CO_2 and provide in situ high-pressure NMR data and theoretical calculations to explain this positive "water effect".

Results and Discussion

Hydrogenation of Carbon Dioxide to Formic Acid with 1. In the presence of triethylamine, and under a total pressure of 50 atm (CO_2/H_2 = 25 atm/25 atm), complex **1**, in anhydrous THF, catalyzed the hydrogenation of carbon dioxide to yield formic acid with a low turnover number of 30 (entry 2, Table 1). Interestingly, changing the solvent to THF/H_2O led to great enhancement of catalytic activity. Phase separation was observed after the catalysis in these mixed-solvent systems. In the one which contained 5% water (entry 3, Table 1), product distributions (as turnover numbers (TON) in units of moles of product per mole of **1**) in the water and THF phases were 501 and 219, respectively. Increasing the water content to 12.5% (entry 4, Table 1) significantly decreased the amount of product in the THF phase (TON = 687 in water phase and TON = 48 in THF phase). When the percentage of water was increased to 25%, the distribution of product in the water phase was nearly exclusive, and only a trace amount of the product was detected by ^1H NMR spectroscopy in the THF phase. On the other hand, visual observation indicated that the catalyst had much higher solubility in the organic phase than the aqueous one, since the former was yellowish in color, and the latter was colorless, before and after the catalysis. The organic phase could be recycled and was found to be active in the catalytic reaction, despite some loss of activity (entry 8, Table 1)

In Situ High-Pressure NMR Studies. To gain more insight into the mechanisms of the catalytic CO_2 hydrogenation reactions by **1** in anhydrous and hydrous THF, we have carried out a series of in situ high-pressure NMR studies. It is hoped that a greater understanding of the enhancement effect of water in the catalytic synthesis of formic acid from CO_2 and H_2 could be acquired.

(a) Reaction of 1 with CO_2/H_2 in Anhydrous THF. A THF-d_8 (anhydrous) solution of **1**, containing 25 equiv of Et_3N, was pressurized with CO_2/H_2 (8 atm/8 atm) at room temperature in a 5 mm Wilmad pressure-valved NMR tube. The solution was allowed to stand at room temperature for 30 min, after which $^{31}P\{^1H\}$ NMR spectroscopy showed that **1** remained unchanged. However, the $^{31}P\{^1H\}$ NMR spectrum taken at 80 °C after the solution was heated at this temperature for 10 min showed that most of the complex **1** was converted to a mixture of $TpRu(PPh_3)(H_2)H$ (**2**; δ 75.0 ppm) and another species **3** corresponding to a signal at δ 54.9 ppm. Complex **2** was formed by displacement of CH_3CN with H_2; its presence was further confirmed by observation of its hydride signal at δ −9.80 ppm (d, $J(HP)$ = 18.4 Hz) in ^1H NMR spectroscopy. We have previously reported that **2** can be synthesized by heating a THF solution of **1** under 40 atm of H_2 for 48 h or by heating **1** in CH_3OH under 6 atm of H_2 for 6 h in a sealed tube.[5b] Prolonged heating (40 h) of the solution at 80 °C led to the formation of the metal carbonyl hydride complex $TpRu(PPh_3)(CO)H$ (**4**) as the major product; a small amount of **2** and a species which exhibited a $^{31}P\{^1H\}$ singlet signal at δ 61.0 ppm were also present. The carbonyl hydride complex **4** was identified by comparison of its $^{31}P\{^1H\}$ NMR signal and its hydride signal (δ −11.83 ppm, $J(HP)$ = 26.8 Hz) with those of an authentic sample.[5b] An independent high-pressure NMR experiment showed that $TpRu(PPh_3)(H_2)H$ in THF-d_8 was slowly converted to **4** under CO_2/H_2 (8 atm/8 atm) at 80 °C; at the conclusion of the experiment (20 h), GC-MS analysis of gases in the headspace of the tube did not show the presence of CO. It is probably true that, in the reaction of **1** with CO_2/H_2 in anhydrous THF-d_8, the carbonyl hydride complex **4** was generated via the intermediacy of $TpRu(PPh_3)(H_2)H$, although at this stage we have no detailed mechanistic information for this transformation. Separate studies, both experimental and theoretical, to unravel the mechanism of this reaction are now in progress. In fact, there are precedents in the formation of metal carbonyl from formic acid or CO_2/H_2. For example, it was known more than three decades ago that decarbonylation reactions of formic acid by group III metal halide complexes could be used to prepare carbonyl complexes.[6] Wilkinson's complex $Rh(PPh_3)_3Cl$ was converted to $Rh(PPh_3)_2(CO)Cl$ when heated in polar aprotic solvents under CO_2/H_2 pressure; the presence of CO in the resulting gas mixture suggested the occurrence of a reverse water-gas shift reaction.[7] It has recently been reported that a pincer ligand iridium dihydride complex interacts with CO_2 to form an intermediate metallo formate complex, which then undergoes disproportionation to give an isolable metallo bicarbonate derivative and a carbonyl hydride complex.[8] The complex $Cp^*Ru(PCy_3)Cl$, which failed to generate the coordinatively unsaturated ruthenium hydride species in its reaction with $NaBH_4$, was able to form the formato complex $Cp^*Ru(PCy_3)(\eta^2\text{-}OCHO)$ when treated with carbon dioxide in the presence of $NaBH_4$. More surprisingly, the initially formed formato complex, in a sealed NMR tube in THF-d_8, was converted to a mixture of the metal carbonyl hydride $Cp^*Ru(PCy_3)(CO)H$ and formic acid in approximately

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(6) Cleare, M. J.; Griffith, W. P. *J. Chem. Soc. A* **1969**, 372.

(7) Koinuma, H.; Yoshida, Y.; Hirai, H. *Chem. Lett.* **1975**, 1223.

(8) McLoughlin, M. A.; Keder, N. L.; Harrison, W. T. A.; Flesher, R. J.; Mayer, H. A.; Kaska, W. C. *Inorg. Chem.* **1999**, *38*, 3223.

a 1:2 ratio. Again, the detailed mechanism is not yet clearly understood.[9]

(b) Reaction of 1 with CO_2 in Anhydrous THF. As mentioned in the preceding paragraph, **1** reacts with CO_2/H_2 in anhydrous THF-d_8 to form $TpRu(PPh_3)(H_2)H$ (**2**) and a second species **3**. To gain knowledge about the structure of **3**, we studied the reaction of **1** with pressurized CO_2 alone with NMR spectroscopy. It was shown by $^{31}P\{^1H\}$ NMR spectroscopy that after an anhydrous THF-d_8 solution of **1** in a 5 mm Wilmad pressure-valved NMR tube was subjected to 15 atm of CO_2 at room temperature for 19 h, complex **3** was formed as the overwhelming product. The ^1H NMR spectrum of the **3** showed, in addition to the nine peaks pertaining to the Tp ligand in the downfield region, a sharp singlet at δ 8.17 ppm; this peak, integrated for 1H, could be ascribed to a formate proton. A sharp singlet, which integrated for 3H and was due to coordinated CH_3CN, appeared at δ 2.25 ppm.

The formato ligand in **3** was further evidenced by ^{13}C NMR study of the reaction of **1** with $^{13}CO_2$ (2 atm) at room temperature in anhydrous THF-d_8 for a prolonged period of time (40 h). In the $^{13}C\{^1H\}$ NMR spectrum of the resulting solution, the formato carbon of **3** appeared as a singlet at δ 170.6 ppm. The off-resonance decoupled spectrum showed a C−H coupling constant of 190.4 Hz. When all the NMR data are taken together, **3** can be identified as the formato complex $TpRu(PPh_3)(CH_3CN)(\eta^1\text{-OCHO})$. In the reaction, a second but smaller formate signal was detected in addition to that of **3**; it appeared as a singlet at δ 175.9 ppm in the $^{13}C\{^1H\}$ NMR spectrum, and the signal was split into a doublet with $J(CH) = 197.0$ Hz in the ^1H-coupled spectrum. We attribute this smaller formate signal to the bidentate formato ligand of $TpRu(PPh_3)(\eta^2\text{-OCHO})$.

Normal CO_2 insertion into the metal−hydride bond to generate a metal formate complex seems to be in operation in most of the successful catalytic systems for the CO_2 hydrogenation reaction. Many previous studies have shown that the stoichiometric reaction of carbon dioxide with a metal hydride complex results in the formation of a metal formate complex.[10] Recently, a number of theoretical studies describing this CO_2 insertion reaction have been reported.[11]

(c) Reaction of 1 with CO_2 and H_2 in Hydrous THF. A THF-d_8 solution of **1** containing 10 vol % of water and 25 equiv of Et_3N was pressurized with 25 atm each of CO_2 and H_2 in a 10 mm sapphire high-pressure NMR tube. The $^{31}P\{^1H\}$ NMR spectrum taken within 10 min at room temperature indicated that the signal of **1** disappeared, and two major singlet signals of roughly equal intensities were seen at δ 54.8 and 57.8 ppm. After heating at 100 °C for 10 min, the intensity of the latter increased at the expense of the former. ^1H NMR spectroscopy now showed the formation of a small amount of formic acid, as indicated by the singlet at δ 8.42 ppm. $^{31}P\{^1H\}$ NMR monitoring over a 4 h period at 100 °C showed the growing in of peaks at δ 68.0, 62.3, 61.8, 57.4, and 28.7 ppm. With the help of ^1H NMR spectroscopy, the first peak was assigned to $TpRu(PPh_3)(CO)H$ (**4**). The last peak was identified as the signal of triphenylphosphine oxide, which was probably formed by CO_2 oxidation of PPh_3. Unfortunately, we have not been able to identify the other phosphorus NMR peaks, which probably are due to some decomposition products of the two initially formed complexes pertaining to the δ 54.8 and 57.8 ppm signals. The ^1H NMR spectrum also revealed the presence of a minute quantity of $TpRu(PPh_3)(H_2)H$, but the amount was too small to be detected by $^{31}P\{^1H\}$ NMR spectroscopy.

(d) Reaction of 1 with CO_2 in Hydrous THF. A THF-d_8 solution of **1** containing 10 vol % of water in a 5 mm Wilmad pressure-valved NMR tube was pressurized with 10 atm of CO_2; the $^{31}P\{^1H\}$ NMR spectrum of the resulting solution recorded within 10 min showed that **1** had already completely reacted. The spectrum showed a singlet at δ 54.8 ppm, and a very small peak at δ 57.8 ppm was also visible. The ^1H NMR spectrum of the same solution clearly showed the set of nine peaks pertaining to the Tp ligand. A singlet at δ 2.30 ppm, integrated for 3H, was assignable to the coordinated CH_3CN, and a singlet (1H) at δ 7.63 ppm could be attributed to the hydrogen of a formate ligand. This last peak disappeared when the deuteride complex $TpRu(PPh_3)(CH_3CN)D$ (**1-*d***) was used in place of **1** in an identical NMR study.

The $^{31}P\{^1H\}$ signal at δ 57.8 ppm gradually gained intensity at the expense of the peak at δ 54.8 ppm. In 20 min time, the ratio of the intensities of the two peaks was roughly 1:3. A concurrent ^1H NMR spectrum showed the free acetonitrile signal at δ 2.17 ppm; the ratio of its intensity to that of the coordinated CH_3CN was also roughly 1:3. These two $^{31}P\{^1H\}$ signals were identical with the two major peaks that first appeared at the initial stage of the reaction of **1** with CO_2/H_2 (vide supra). Therefore, it is clear that in the catalytic CO_2 hydrogenation reactions in hydrous THF, complex **1** reacts rapidly with CO_2 to produce **5** (corresponding to the δ 54.8 ppm signal), and complex **6** (corresponding to the δ 57.8 ppm signal) is then derived from **5** with concomitant CH_3CN dissociation from the latter. Unfortunately, it has not been possible to obtain a spectroscopically pure solution of **6**, since **5** and **6** form an equilibrium mixture.

To verify the existence of the formato moieties in **5** and **6**, reaction of **1** with $^{13}CO_2$ in hydrous THF-d_8 was monitored by NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum recorded after a THF-d_8 (containing 5 vol % of H_2O) solution of **1** was subjected to 2 atm of $^{13}CO_2$ at room temperature for 1 h showed that **1** was completely converted to a mixture of **5** and **6** in an approximately 2:1 ratio. The same solution exhibited, in the $^{13}C\{^1H\}$ NMR spectrum, two singlets at δ 173.1 and 176.2 ppm, which were assignable to the formato ligands of **5** and **6**, respectively. Both peaks were split into doublets in the ^1H-coupled ^{13}C NMR spectrum; the former showed an H−C coupling constant of 193.9 Hz, and that of the latter was 198.2 Hz. The $^1H\{^{13}C\}$ NMR spectra of **5** and **6** showed the formate protons at δ 7.63 and 8.51 ppm, respectively. In the off-resonance decoupled spectra, the

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[9] Yi, C. S.; Liu, N. *Organometallics* **1995**, *14*, 2626.

[10] Some recent examples: (a) Albéniz, M. J.; Esteruelas, M. A.; Lledós, A.; Maseras, F.; Oñate, E.; Oro, L. A.; Soler, E.; Zeier, B. *J. Chem. Soc., Dalton Trans.* **1997**, 181. (b) Whittlesey, M. K.; Perutz, R. N.; Moore, M. H. *Organometallics* **1996**, *15*, 5166. Also see refs 8 and 9.

[11] (a) Hutschka, F.; Dedieu, A.; Eichberger, M.; Fornika, R.; Leitner, W. *J. Am. Chem. Soc.* **1997**, *119*, 4432. (b) Musashi, Y.; Sakaki, S. *J. Chem. Soc., Dalton Trans.* **1998**, 577. (c) Musashi, Y.; Sakaki, S. *J. Am. Chem. Soc.* **2000**, *122*, 3867.

Scheme 1

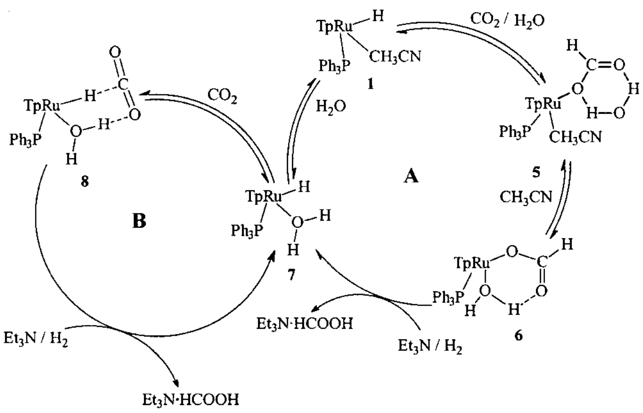
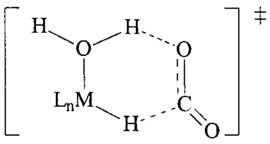


Chart 1



former was split into a doublet with $^1J(\mathrm{HC}) = 193.7$ Hz, while the latter was split into a doublet with $^1J(\mathrm{HC}) = 198.5$ Hz.

If the ^{31}P, ^{13}C, and ^{1}H NMR data of **5** are taken into consideration, it is obvious that the ligand set of the complex consists of a Tp, a PPh_3, a formate, and an acetonitrile; therefore, the molecular formula that can be inferred is $TpRu(PPh_3)(CH_3CN)(\eta^1\text{-}OCHO)$, which seems unlikely because it is identical with that of **3**. As will be shown in a later section, theoretical calculations show that the optimized structure of **5** is a hydrated metal formate complex stabilized by hydrogen bonding of the formate ligand with a water molecule (Scheme 1). Therefore, it seems reasonable that the molecular formula $TpRu(PPh_3)(CH_3CN)(\eta^1\text{-}OCHO)\cdot H_2O$ be assigned to **5**.

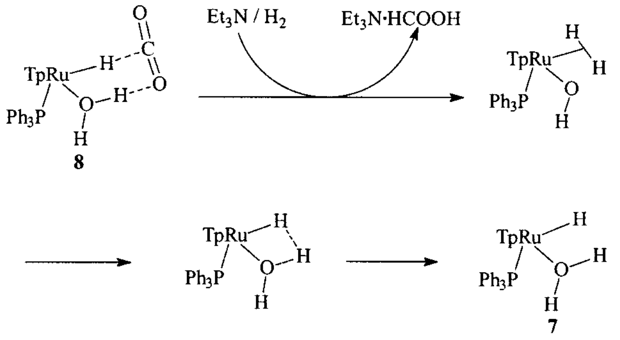
The other formato complex **6**, which is formed at the expense of **5** and is in equilibrium with the latter, is probably the aquo metal formate $TpRu(PPh_3)(H_2O)(\eta^1\text{-}OCHO)$; this complex is also stabilized by a hydrogen-bonding interaction between the formate ligand and H_2O, but intramolecularly, as opposed to the intermolecular interaction in **5** (Scheme 1).

Mechanisms of CO_2 Hydrogenation. The promoting effect of water in CO_2 hydrogenation has been observed in a number of cases, including Pd-,[2] Rh-,[3] and Ru-based[4] catalytic systems. Some authors speculated that water, as an ancillary ligand on the catalyst, could accelerate the insertion of CO_2 into M−H by hydrogen bonding to one of the oxygen atoms of the incoming CO_2 molecule[3,4] (Chart 1).

In this section, we propose a mechanism aimed at explaining the water effect in catalytic hydrogenation of CO_2 with **1**, and theoretical data in support of the proposed mechanism will be provided in the next section.

In the CO_2 hydrogenation reactions in hydrous THF, complex **1** reacts readily with CO_2 to form the hydrated metal formate **5**. That this insertion reaction is facile is probably due to stabilization of the transition state by a hydrogen-bonding interaction between the approaching CO_2 and a noncoordinating H_2O molecule; such an interaction increases the electrophilicity of the carbon atom of the former and therefore facilitates its insertion into Ru−H. Complex **5** then equilibrates with **6**, and the two complexes are observable by high-pressure NMR spectroscopy during the catalytic process. In light of the Halpern axiom that observations of "likely" intermediates in a catalytic cycle generally signal, in fact, a nonproductive, sluggish loop of the pathway,[12] one would reasonably expect that the production of formic acid via **5** and **6** is slow. Therefore, the sequence in cycle A of Scheme 1 may not be the productive route of the catalytic process. On the other hand, we propose that the sequence in cycle B is productive and is therefore the major route. The key species in this cycle is **7**, which is mainly formed by displacement of the acetonitrile ligand of **1** by H_2O. That the availability of **7** has a profound effect on the overall efficiency of the catalytic system is supported by the fact that the presence of a small amount of CH_3CN in the system results in a very substantial decrease of the turnover number of the catalytic reaction (entry 9, Table 1). A feature of this productive cycle is that a hydride and a proton are simultaneously transferred to an approaching CO_2 molecule to form the formic acid in a concerted manner via the intermediacy of **8**. Noyori and co-workers have proposed a simultaneous transfer of H^- and H^+ from the Ru−amide bond to a carbonyl function in the study of the ruthenium(II)-catalyzed hydrogen transfer between alcohols and carbonyl compounds.[13] Very recently, Morris et al. have reported similar concerted dihydrogen transfer from cis hydride and N−H groups of a ruthenium complex to the ketone or imine substrate followed by heterolytic dihydrogen splitting.[14] Although it is not shown in cycle B of Scheme 1, elimination of formic acid from **8** probably generates a transient hydroxo species, which then associates a dihydrogen molecule and undergoes a σ-bond metathesis reaction to regenerate **7** (Scheme 2).

Scheme 2



σ-Bond metathesis reactions are well-recognized reactions in the field of early-transition-metal, lanthanide, and actinide chemistry;[15] recent experimental[16] and theoretical[17] findings, however, suggest that these reactions could also occur with middle- and late-transition-metal systems. A theoretical assessment on the σ-bond

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[12] (a) Halpern, J. *Science* **1982**, *217*, 401. (b) Halpern, J. *Inorg. Chim. Acta* **1981**, *50*, 11.

[13] Yamakawa, M.; Ito, H.; Noyori, R. *J. Am. Chem. Soc.* **2000**, *122*, 1466.

[14] Abdur-Rashid, K.; Lough, A. J.; Morris, R. H. *Organometallics* **2000**, *19*, 2655.

metathesis reaction of water with a palladium hydride complex to yield hydrogen has been reported; the calculations show that such a reaction is feasible and that it can in some instances be competitive with an oxidative-addition/reductive-elimination sequence.[18] Although we have not been able to identify the intermediates **7** and **8**, our theoretical calculations to be presented in the next section strongly support the proposed mechanism of the catalytic cycle.

In the case of CO_2 hydrogenation in anhydrous THF, the formato complex **3** is a stable intermediate detectable in in situ high-pressure NMR spectroscopy throughout the catalytic process. Its formation is not as facile as for its hydrated counterpart **5**, probably due to the relatively higher activation energy in the reaction pathway. In view of the stability of **3**, it is expected that the generation of product from this species will not be a low-energy process, and therefore, this catalysis, unlike the one in hydrous THF in which there is another low-energy pathway, has a low turnover number.

Theoretical Study. Experimentally, it is found that reactions of $TpRu(PPh_3)(CH_3CN)H$ (**1**) with CO_2 under hydrous and anhydrous conditions differ significantly in reaction rates. In hydrous THF solution **1** reacts with CO_2 rapidly to form the formato complex **5**, while in the anhydrous THF solution, the reaction goes more slowly to generate complex **3**. To understand the experimental observations, theoretical calculations have been carried out at the B3LYP level of density functional theory to study the formation of **3** from the reaction of **1** with CO_2.

(a) Influence of the Water Molecule on CO_2 Insertion into the Ru−H Bond. Figure 1a shows the calculated free energies for species involved in the reaction under anhydrous conditions. The mechanism here is similar to those found in the literature for CO_2 insertion into M−H bonds.[11] The transition state involves the breaking of the metal−hydride bond and the formation of both the C−H and Ru−O bonds. The CO_2 molecule is reduced by the hydride through an electrophilic reaction and a structural rearrangement to form the η^1-formato complex $TpRu(PH_3)(CH_3CN)(\eta^1\text{-}OCHO)$ (**3**).

The transition state (**TS**) of this reaction has been optimized and confirmed by the frequency calculation. The relative free energy of **TS** is 31.8 kcal/mol at room temperature. Consistent with the experimental observation, this high activation energy implies a slow reaction at room temperature. Structurally, **TS** is a late transition state regarding the hydrogen-transferring process. The Ru−H and H−C bonds in **TS** are 2.322 and 1.154 Å, respectively (see Figure 2). On the basis of the structural feature of the transition state, we can infer that the high reaction barrier is mainly determined by the breaking of the metal−hydride bond (transferring the hydrogen from the metal hydride to CO_2) and the stability of the product **3** is due to the formation of the Ru−O bond. One thus expects that an enhancement of the electrophilicity at the carbon center of CO_2 can reduce the reaction barrier and accelerate the metal formate formation. Hydrous conditions are confirmed to be able to serve the purpose.

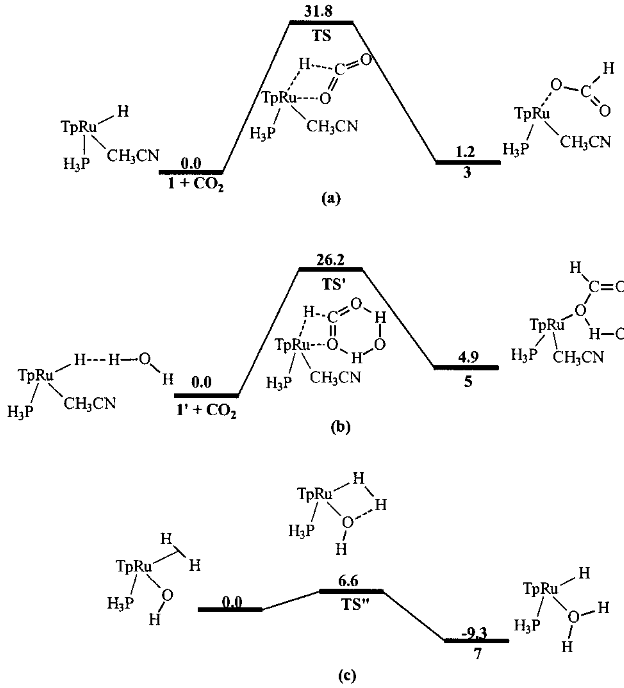

Figure 1. Free energy profiles for the reactions of $TpRu(PH_3)(CH_3CN)(H)$ and CO_2 (a) without and (b) with a water molecule and for (c) transformation of $TpRu(PH_3)(OH)(H_2)$ to $TpRu(PH_3)(H_2O)(H)$. The relative energies shown are in units of kcal/mol.

To model the hydrous conditions, we study the same reaction by adding a water molecule in our calculations. Figure 1b shows the calculated free energies for the reaction of **1** and CO_2 in the presence of a water molecule. The transition state (**TS′**) is now 26.2 kcal/mol higher in free energy than the reaction **1′** + CO_2. Clearly, this activation energy is significantly lower than that found for the reaction without a water molecule (Figure 1a). Comparing the geometries of **TS** and **TS′** (see Figure 2), one sees that the Ru−H distance in **TS′** (2.361 Å) is longer than that in **TS** (2.322 Å), but the C−H distance in **TS′** (1.141 Å) is shorter than that in **TS** (1.154 Å). The differences suggest that **TS′** is an even later transition state regarding the hydrogen transfer in this reaction. In addition, the Ru−O bonds in **TS′** and **TS** are the same (2.923 Å). Therefore, interaction of the water molecule with CO_2 enhances the electrophilicity at the carbon center of the latter, resulting in significant reduction of the reaction barrier.

(b) Structural and Energetic Aspects of Species Involved in the Catalytic Cycle. To study the structural and energetic aspects of the species in Scheme 1, we also calculated complexes **6**−**8**, shown in Figure 2. The calculations show that **6** + CH_3CN is thermodynamically more stable than **5** by 12.6 kcal/mol in free

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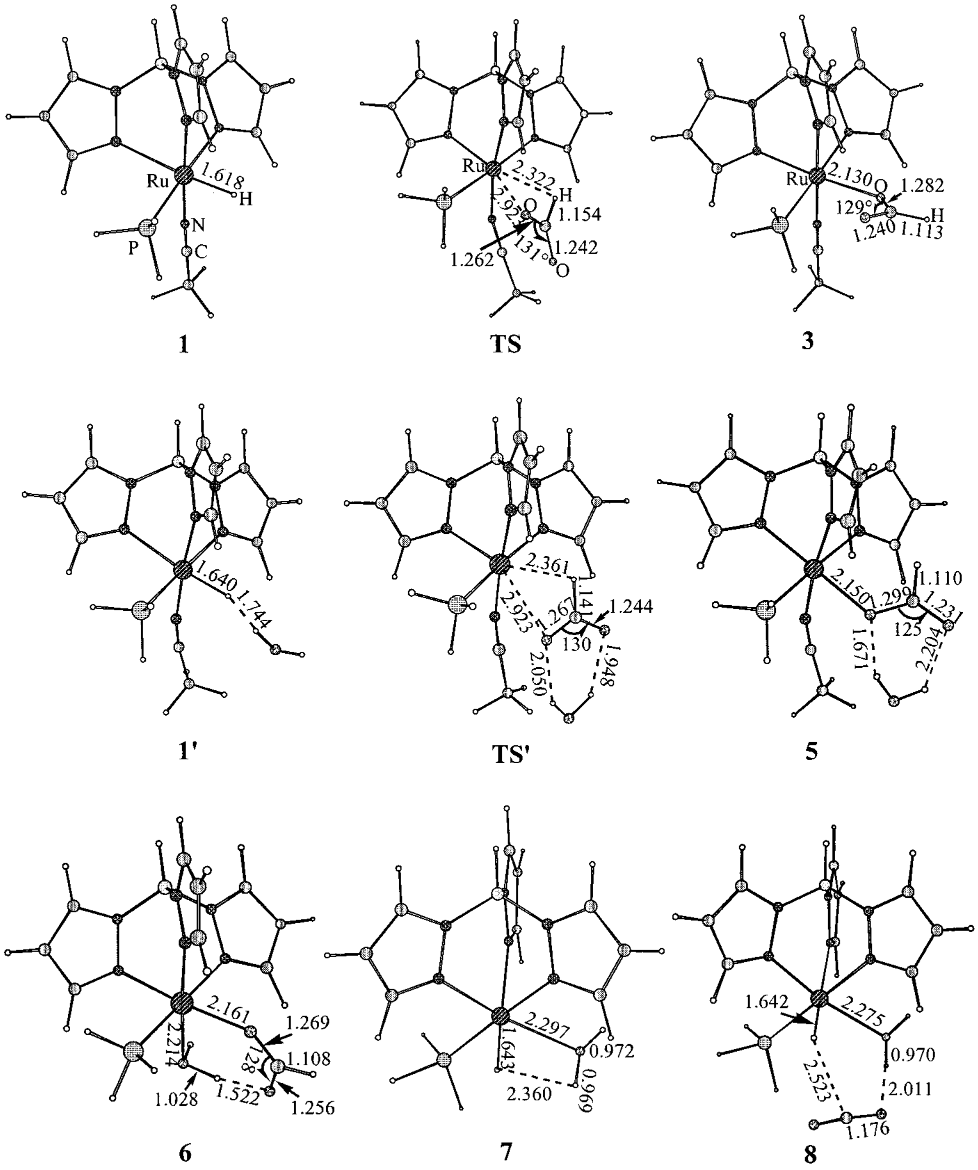

Figure 2. Optimized structures with selected structural parameters for species involved in the catalytic cycle shown in Scheme 1.

energy, although experimentally they are found in equilibrium. The inconsistency is believed to be due to overestimation of the entropy contribution to the stability of **6** + CH_3CN because the electronic energy difference between **5** and **6** + CH_3CN is 1.6 kcal/mol in favor of the former. We suspect that the solvent effect might also play a role here. However, the solvation energy calculations based on the SCRF model (solvent = acetonitrile) show that the solvent effect reduces the energy difference only by 2 kcal/mol.

Structure **7** is calculated to be a hydride in which the Ru–H bond is appreciably lengthened when compared to that in **1**. The lengthening can be related to its dihydrogen bonding with a proton of the water ligand (H- - -H = 2.360 Å). Complex **8** shows a strong hydrogen bond between one proton of the water ligand and one of the two oxygen atoms of CO_2. The free energy calculations shows that complex **8** is 5.8 kcal/mol more stable than **7** + CO_2. Elimination of formic acid from **8** under the added Et_3N/H_2 to form the stable Et_3N·HCOOH adduct regenerates complex **7**. The reaction of **8** with H_2 and NEt_3 is unlikely to be a concerted termolecular process because such steps are extremely rare; it probably proceeds stepwise, and the sequence of steps is not known. However, the actual barrier for the regeneration of **7** from **8** should be smaller than the assumed process, in which the formic acid is directly removed from **8** in the presence of NEt_3. The direct removal of the formic acid from **8** to generate a transient hydroxo species and the HCOOH·NEt_3 adduct requires only 17.0 kcal/mol in free energy. This result indicates that the process does not have a high barrier and should be easily achieved.

According to Scheme 2, once the transient hydroxo species $TpRu(PPh_3)(OH)$ is formed, the addition of H_2 gives a dihydrogen hydroxo complex, which can be easily transformed to complex **7** with a small free energy barrier of 6.6 kcal/mol (Figure 1c).

Conclusion

We have studied experimentally the promoting effect of water in the catalytic hydrogenation of CO_2 to formic acid with $TpRu(PPh_3)(CH_3CN)H$. With the support of a theoretical study, we have proposed a reaction mechanism to account for such an effect. One of the features of the proposed catalytic cycle is the simultaneous transfer of a hydride and a proton from the aquo ruthenium hydride intermediate $TpRu(PPh_3)(H_2O)H$ to the CO_2 molecule to give formic acid in a concerted manner. The other feature is that the usual metal formate intermediates resulting from CO_2 insertion into M−H in most of the successful catalytic CO_2 hydrogenation reactions with metal hydride complexes are probably not within the main catalytic cycle in the present case. Failure to generate the aquo ruthenium hydride intermediate in the absence of water is probably the reason for the low activity of CO_2 hydrogenation reactions in anhydrous solutions.

Experimental Section

Ruthenium trichloride, $RuCl_3{\cdot}3H_2O$, pyrazole, and sodium borohydride were obtained from Aldrich. Triphenylphosphine was purchased from Merck and was recrystallized from ethanol before use. The complex $TpRu(PPh_3)(CH_3CN)H$ was synthesized according to published procedures.[5b] Solvents were distilled under a dry nitrogen atmosphere with appropriate drying agents (solvent/drying agent): tetrahydrofuran/Na−benzophenone, diethyl ether/CaH_2, acetonitrile/CaH_2, *n*-hexane/Na. High-purity hydrogen gas and carbon dioxide were supplied by Hong Kong Oxygen.

Proton NMR spectra were obtained from a Bruker DPX 400 spectrometer. Chemical shifts were reported relative to residual protons of the deuterated solvents. ^{31}P and ^{13}C NMR spectra were recorded on a Bruker DPX 400 spectrometer at 161.70 and 100.60 MHz, respectively. ^{31}P chemical shifts were externally referenced to 85% H_3PO_4 in D_2O. ^{13}C chemical shifts were internally referenced to the residual peak of deuterated solvents. High-pressure NMR studies were carried out either in a commercial 5 mm Wilmad pressure-valved NMR tube or a 10 mm sapphire HPNMR tube; the sapphire NMR tube was purchased from Saphikon, Milford, NH, while the titanium high-pressure valve was constructed at the ISSECC-CNR, Firenze, Italy.

Catalytic Hydrogenation of CO_2 with $TpRu(PPh_3)(CH_3CN)H$ (1). The reactions were performed in a 100 mL stainless steel autoclave. In a typical run, ∼0.013 mmol of **1** in 20 mL of THF/H_2O (3/1 by volume) and 2 mL of NEt_3 were added to the autoclave. After being flushed with H_2 three times, the system was heated with stirring at 100 °C and under 50 atm of CO_2/H_2 (1/1). At the end of the required length of time, the autoclave was cooled rapidly and vented carefully. The resulting biphasic solutions were carefully poured into a measuring cylinder, and the exact volumes of the two phases were measured. A 0.2 mL aliquot of the aqueous solution was syringed into a NMR tube, to which 0.3 mL of D_2O and 6 μL of DMF (internal standard) were added. The relative intensities of the formato proton of the product and the amido proton of the internal standard were measured, and with help of a calibration curve, the TON of the catalysis was derived. The organic phase was analyzed in an analogous manner.

Computational Details. In our calculations, the PPh_3 ligand was modeled using a PH_3 group. Geometry optimizations and frequency calculations were carried out for all species (reactants, precursors, products, and transition states) involved in the reactions using the Gaussian 98 program[19] installed on Pentium III personal computers with Linux (Red Hat) operating systems.

Molecular geometries of the model complexes were optimized at the Becke3LYP (B3LYP) level of density functional theory.[20] The LANL2DZ effective core potentials and basis sets[21] were used to describe Ru and P. Polarization functions (ξ(d) = 0.340)[22] were also added for P. Because of the large size of systems studied, we used a STO-3G basis set for those atoms which are not metal-coordinated in the Tp ligand and for the hydrogen atoms in the PH_3 ligands. The standard 6-31G** basis set was used for all other atoms. These basis sets were designated as **BS1**. Since we were interested in the relative energies, we expected that the errors produced by **BS1** could be canceled when the relative energies were computed. Indeed, single-point energy calculations using the better and more consistent basis set described below indicated that the changes in the relative energies were within 2 kcal/mol. The better basis set (**BS2**) replaced STO-3G with 6-31G. With this better basis set, single-point calculations based on the **BS1**-optimized structures were performed to recalculate the energies (reported in the text). The entropy contributions were evaluated through the **BS1** frequency calculations of the optimized structures.

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