Ruthenium-Catalyzed Hydrogenation of Carbon Dioxide to Formic Acid in Alcohols

Siu Man Ng,[a] Chuanqi Yin,[a] Chi Hung Yeung,[a] Tak Chung Chan,[a] and Chak Po Lau*[a]

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Catalytic hydrogenation of CO_2 to formic acid with the (solvento)metal hydride complex, $TpRu(PPh_3)(CH_3CN)H$ [Tp = hydrotris(pyrazolyl)borate], in various alcohols was studied. High-pressure NMR monitoring of the catalytic reaction in non-acidic methanol shows that the observable intermediate is a formate complex resulting from CO_2 insertion into the Ru–H bond and is stabilized by the hydrogen-bonding interaction between the formato ligand and a methanol molecule. However, in the case of the acidic alcohol, CF_3CH_2OH, the observable intermediates are $[TpRu(PPh_3)(CH_3CN)_2]^+$-$CF_3CH_2O^-$ and the alkyl carbonate complex, $TpRu(PPh_3)(\eta^2$-$O_2COCH_2CF_3)$, which are formed by the reaction of CO_2 with the alkoxide species, $TpRu(PPh_3)(CH_3CN)(OCH_2CF_3)$, generated by a very facile reaction between $TpRu(PPh_3)(CH_3CN)H$ and CF_3CH_2OH. We propose that the productive catalytic cycles of the reactions conducted in a variety of alcohols are similar to the one we formulated for the catalytic hydrogenation of CO_2 in hydrous THF. The formic acid is produced by the transfer of a hydride and a proton from the transient alcohol hydride intermediate, $TpRu(PPh_3)(ROH)H$, to an approaching CO_2 molecule. The activity of $TpRu(PPh_3)(CH_3CN)H$ is higher in CF_3CH_2OH than in methanol and other non-acidic alcohols and it is probably due to the enhanced electrophilicity of the carbon atom of CO_2, which results from the strong interaction between the proton of the highly acidic alcohol in $TpRu(PPh_3)(CF_3CH_2OH)H$ and an oxygen atom of CO_2. The electrophilic carbon atom of CO_2 could in turn abstract the hydride from Ru–H in a more facile manner.

Introduction

Transition-metal-catalyzed CO_2 hydrogenation to formic acid remains an area of interest, as it provides a promising approach for utilizing carbon dioxide as a raw material for large-scale chemical synthesis.[1] Although it has been known for some time that addition of water to active Pd,[2] Rh,[3] and Ru[4] systems is effective in enhancing the catalytic hydrogenation of CO_2 to formic acid, no compelling experimental and theoretical data had been provided to explain the positive "water effect" until the publication of our recent work on the promoting effect of water in the catalytic hydrogenation CO_2 with the ruthenium complex $TpRu(PPh_3)(CH_3CN)H$ (**1**) [Tp = hydrotris(pyrazolyl)borate]. With the support of high-pressure NMR spectroscopy and theoretical calculations, we proposed a reaction mechanism to account for the "water effect". The key intermediate in the catalytic cycle is an (aquo)ruthenium hydride species, $TpRu(PPh_3)(H_2O)H$, which is generated through ligand displacement by H_2O. It transfers a hydride and a proton of the coordinated H_2O to the approaching CO_2 molecule to give formic acid and is converted into a transient hydroxo species, which then associates an H_2 molecule to regenerate $TpRu(PPh_3)(H_2O)H$ by σ-metathesis between the hydroxo and the η^2-H_2 ligands.[5]

Continuing our investigation on the catalytic hydrogenation of CO_2 to formic acid with **1**, we studied the **1**-catalyzed reactions in alcohols. The accelerating effects of certain alcohols on the hydrogenation of carbon dioxide, catalyzed by (trimethylphosphane)ruthenium complexes, have recently been reported.[6]

Results and Discussion

Hydrogenation of Carbon Dioxide to Formic Acid with 1

We have previously learned that **1** catalyzes the hydrogenation of carbon dioxide to yield formic acid with a low turnover number in anhydrous THF (see Entry 1, Table 1), but the catalytic activity of **1** was greatly enhanced when 5% (by volume) of water was added to the system (Entry 2, Table 1).[5] Perusal of Table 1 reveals significant increase in the catalytic activity of **1** in alcohols too (relative to that of **1** in anhydrous THF), although the enhancement effects are not as large as in THF/H_2O, except for the acidic alcohol, CF_3CH_2OH. In the catalytic reactions using alcohols as solvents, the yields of the ester side products are very low. Also noteworthy is the trend of decreasing turnover numbers of

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[a] Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University
Hung Hom, Kowloon, Hong Kong, China
Fax: (internat.) + 852-2364-9932
E-mail: bccplau@inet.polyu.edu.hk

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Table 1. Hydrogenation of CO_2 to formic acid with $TpRu(PPh_3)(CH_3CN)H$ (**1**) in alcohols

Entry[a]	Solvent	Turnover no. of formic acid[b]	Turnover no. of ester[b]
1	THF	30	–
2	THF/H_2O[c]	720	–
3	THF/H_2O[c,d]	250	
4	CH_3OH	388	75
5	C_2H_5OH	230	11
6	C_2H_5OH[d]	127	4
7	n-C_3H_7OH	213	12
8	i-C_3H_7OH	141	–
9	t-C_4H_9OH	72	15
10	CF_3CH_2OH	1815	–

[a] Typical reaction conditions: catalyst 0.013 mmol; NEt_3 2 mL; solvents 20 mL; total pressure 50 atm (CO_2/H_2 = 1:1); temperature 100 °C; reaction time 16 h. [b] Turnover no: mol of product/mol of complex. [c] THF/H_2O (19 mL/1 mL). [d] Reaction time 4 h.

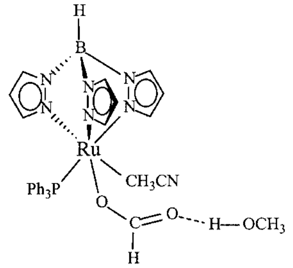
formic acid with increasing bulkiness of the alcohols (Entries 4−9, Table 1).

In Situ High-Pressure NMR Studies

To gain more insight into the mechanisms of the catalytic CO_2-hydrogenation reactions by **1** in alcohols, we carried out a series of in situ high-pressure NMR studies.

(a) Reaction of 1 with CO_2 in Methanol/THF

A CH_3OH/[D_8]THF (1:1 by volume) solution of **1** in a 5-mm Wilmad pressure-valved NMR tube was pressurized with 6 atm of $^{13}CO_2$ at room temperature. The $^{31}P\{^1H\}$ NMR spectrum of the resulting solution recorded after 10 min shows the disappearance of **1** and the presence of a new complex **2** which gives a singlet at δ = 52.9 ppm. The $^1H\{^{13}C\}$ NMR spectrum of the same solution clearly shows the set of nine peaks pertaining to the Tp ligand. A singlet at δ = 2.30 ppm, integrated for 3 H, is assignable to the coordinated CH_3CN, a singlet (1 H) at δ = 7.63 ppm can be attributed to the hydrogen atom of a formate ligand. This signal is split into a doublet in the ^{13}C-coupled ^1H NMR spectrum by the formato carbon atom, half of it is unfortunately masked by the peaks of the Tp and PPh_3 ligands. The $^{13}C\{^1H\}$ NMR spectrum of the solution exhibits a singlet at δ = 174.7 ppm, pertaining to the formato carbon atom, which is split into a doublet in the ^1H-coupled ^{13}C NMR spectrum with an H-C coupling constant of 194.9 Hz. If the ^{31}P, ^1H, and ^{13}C NMR spectroscopic data of **2** are taken together, it is obvious that the ligand set of the complex consists of a Tp, a PPh_3, a formate, and an acetonitrile ligand. With reference to our recently reported formate complex, $TpRu(PPh_3)(CH_3CN)(\eta^1\text{-}OCHO)$, generated by CO_2 insertion into the Ru−H bond of **1** in anhydrous THF, and $TpRu(PPh_3)(CH_3CN)(\eta^1\text{-}OCHO)\cdot H_2O$, which is formed by the reaction of **1** with CO_2 in hydrous THF and stabilized by hydrogen-bonding interactions between the formato ligand and a water molecule,[5] we propose that the molecular formula of **2** is $TpRu(PPh_3)(CH_3CN)(\eta^1\text{-}OCHO)\cdot HOCH_3$. The formato ligand in **2** is hydrogen-bonded to a methanol molecule. Unfortunately, we have not been able to observe any downfield-shifted OH proton signals due to the hydrogen-bonded CH_3OH, probably because of its undergoing rapid exchange with the molecules in the bulk, or because the signal is masked by the large number of peaks due to the Tp and phosphane ligands in the region.



2

Attempts to synthesize **2** on a preparative scale by treating **1** with pressurized CO_2 were frustrated by its decomposition to the hydride species and some intractable materials during workup, in which the CO_2 pressure has to be removed. Similar problems were encountered in our previous efforts to isolate the formate complexes, $TpRu(PPh_3)(CH_3CN)(\eta^1\text{-}OCHO)$ and $TpRu(PPh_3)(CH_3CN)(\eta^1\text{-}OCHO)\cdot H_2O$.[5] Treatment of the chloro complex $TpRu(PPh_3)(CH_3CN)Cl$ with sodium formate also resulted in the formation of the hydride complex **1** as the major product. It seems that all these (Tp)ruthenium formate species are only stable under CO_2 pressure.

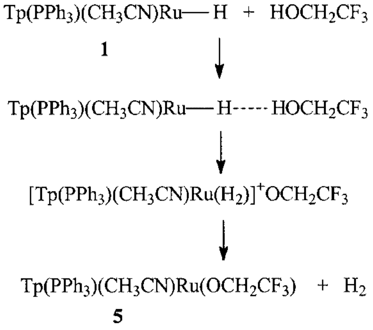
(b) Reaction of 1 with CO_2 and H_2 in Methanol/THF

A CH_3OH/[D_8]THF (1:1 by volume) solution of **1** containing 20 equiv. of Et_3N was pressurized with 6 atm of $^{13}CO_2$ and H_2 in a 5-mm Wilmad pressure-valved NMR tube; the $^{31}P\{^1H\}$ and ^1H NMR spectra of the solution taken within 10 min at room temperature shows the disappearance of **1** and the formation of **2**. A minute amount of formic acid, indicated by a very small doublet at δ = 8.60 ppm ($J_{C,H}$ = 189 Hz) in the ^1H NMR spectrum, was formed. After heating the tube at 100 °C for 3 h, ^1H NMR spectroscopy showed a very significant increase of the formic acid signal. In the downfield region, in addition to the set of peaks pertaining to the Tp ligand of **2**, some minute peaks were also visible. The $^{31}P\{^1H\}$ spectrum, however, shows only one singlet due to **2**. The CO_2-hydrogenation reaction was basically complete within 3 h because the ^1H NMR spectrum taken 3 h later did not show any visible increase in the formic acid signal. It is, however, worth noting that, after heating the solution at 100 °C for 2 d, the ^1H NMR spectrum showed that the amount of formic acid decreased, while the downfield region of the spectrum became relatively complex, indicating the presence of a few sets of Tp signals. A doublet of doublets ($J_{H,P}$ = 26.4, $J_{C,H}$ = 9.3 Hz) is observed in the upfield region at δ = −11.81 ppm, which can be assigned to the carbonyl hydride complex TpRu(PPh$_3$)(CO)H (**3**), which we have previously reported.[7] The ^{31}P{^{1}H} spectrum exhibits a major singlet at δ = 52.9 ppm, which is due to **2**. A singlet at δ = 66.1 ppm is assignable to **3**, while the singlet at δ = 30.9 ppm is identified as the signal of triphenylphosphane oxide, which was probably formed by CO$_2$ oxidation of PPh$_3$. A number of small, unidentified signals can be observed in the region between the signals of **2** and **3**. After heating at 100 °C for 3 d, a further decrease in the amount of formic acid was evidenced by ^{1}H NMR spectroscopy and a set of Tp signals of TpRu(PPh$_3$)(CO)H (**3**) was observed in the downfield region. The hydride signal of **3** also shows enhanced intensity. The ^{31}P{^{1}H} NMR spectrum was also simplified, showing a major peak at δ = 66.1 ppm, which is due to **3**. The phosphane oxide peak at δ = 30.9 ppm and an unidentified peak at δ = 63.3 ppm are the only two minor signals in the spectrum. In our previous work, high-pressure NMR spectroscopy monitoring of the catalytic CO$_2$ hydrogenation with **1** in hydrous THF revealed that the carbonyl hydride complex **3** was the major ruthenium-containing species after prolonged heating at 100 °C. Moreover, in the course of the reaction, a very small amount of TpRu(PPh$_3$)(H$_2$)H (**4**)[7] was also detected by ^{1}H NMR spectroscopy. Independent NMR experiments showed that **4** reacted slowly with formic acid in [D$_8$]THF to yield TpRu(PPh$_3$)(CO)H. We believe that in the course of the **1**-catalyzed CO$_2$ hydrogenation in CH$_3$OH/[D$_8$]THF, the carbonyl hydride complex **3** was formed by the reaction of TpRu(PPh$_3$)(H$_2$)H (**4**) with formic acid and the dihydrogen hydride species was present in such low concentration that it eluded detection by NMR spectroscopy. Examples relevant to the formation of **3** can be found in the literature.[8−10] An authentic sample of **3** was found to be inactive in catalyzing CO$_2$ hydrogenation in methanol.

Reaction of CF$_3$CH$_2$OH with 1

In view of the superiority of CF$_3$CH$_2$OH in promoting the CO$_2$-hydrogenation reaction, studies to gain insight into its role in the catalytic reaction were carried out. The ^{1}H NMR spectrum taken a few minutes after the dissolution of **1** in CF$_3$CH$_2$OH/[D$_8$]THF (1:1 by volume) in a 5-mm Wilmad pressure-valved NMR tube showed that the alkoxide complex TpRu(PPh$_3$)(CH$_3$CN)(OCH$_2$CF$_3$) (**5**) was formed and **1** was no longer detectable. The spectrum shows a new set of nine peaks pertaining to the Tp ligand. A singlet at δ = 2.27 ppm integrated for 3 H is assignable to the coordinated acetonitrile. Two multiplets, each integrated for 1 H, are observed at δ = 3.04 and 3.45 ppm; these peaks can be attributed to the methylene hydrogen atoms of the coordinated −OCH$_2$CF$_3$ group. A singlet at δ = 4.65 ppm signals the presence of free hydrogen. The trifluoroalkoxo ligand was verified by ^{19}F NMR spectroscopy, which shows the signal of −OCH$_2$CF$_3$ as a triplet at δ = −75.05 ppm ($J_{\mathrm{H,F}}$ = 10 Hz). The ^{31}P{^{1}H} NMR spectrum shows a singlet at δ = 52.8 ppm.

Formation of **5** probably resulted from protonation of the hydrido ligand of **1** by CF$_3$CH$_2$OH via a dihydrogen-bonded intermediate Tp(PPh$_3$)(CH$_3$CN) Ru−H···H−OCH$_2$CF$_3$ and the η^2-dihydrogen complex (see Scheme 1). The relevancy of dihydrogen bonding to the protonation reaction is suggested by independent NMR studies involving reactions of **1** with limited amounts of CF$_3$CH$_2$OH. Upon addition of 1.5 and 7.5 equiv. of CF$_3$CH$_2$OH to [D$_8$]toluene solutions of **1**, the ^{1}H NMR spectra of the solutions show that the hydride signal of **1** becomes broadened and shifted upfield by 0.16 and 0.63 ppm, respectively. Variable-temperature T_1 measurements for the hydrido ligand of **1** yielded a T_1(min) of 252 ms (at 400 MHz and 235 K) and 65 ms (at 400 MHz and 233 K) for the **1**/1.5 equiv. CF$_3$CH$_2$OH and the **1**/7.5 equiv. CF$_3$CH$_2$OH solutions, respectively. The two T_1(min) values are much lower than that of the hydrido ligand of **1** in [D$_8$]toluene in the absence of CF$_3$CH$_2$OH (540 ms at 400 MHz and 257 K). These T_1(min) measurements thus suggest the presence of Ru−H···H−OCH$_2$CF$_3$ dihydrogen-bonding interaction. Reactions of acidic alcohols with transition-metal hydride complexes to generate M−H···H−OR dihydrogen-bonded species are well documented.[11] For example, a dynamic equilibrium between the dihydrogen-bonded ruthenium hydride species and the η^2-dihydrogen complex (dppm)$_2$HRu−H···H−OR [(dppm)$_2$HRu(H$_2$)]$^+$OR$^-$ is established in the presence of phenol. The more acidic alcohol, hexafluoro-2-propanol, shifts the equilibrium to the side of the η^2-dihydrogen complex and eventually yields the alkoxide complex (dppm)$_2$Ru[OCH(CF$_3$)$_2$]$_2$.[11c]



Scheme 1

Attempts to synthesize **5** on a preparative scale, unfortunately, were not successful, due to its decomposition into some intractable materials during the workup processes. It seems that **5** is only stable in CF$_3$CH$_2$OH solutions.

Reaction of TpRu(PPh$_3$)(CH$_3$CN)(OCH$_2$CF$_3$) (5) with CO$_2$

Et$_3$N (20 equiv.) was added to a CF$_3$CH$_2$OH/[D$_8$]THF solution of **5**; ^{31}P{^{1}H} NMR spectroscopy indicated that **5** was unaffected by the base. The solution was then subjected to 8 atm of CO$_2$ at room temperature; NMR spectroscopy showed that **5** was converted into a 1:1 mixture of [TpRu(PPh$_3$)(CH$_3$CN)$_2$]$^+$ (**6**) and another complex **7** after 2 h. Complex **6**, which we have previously reported,[12] can be easily identified by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The ^1H NMR spectrum of the mixture clearly shows two sets of signals (six peaks each) in the downfield region, one of which pertaining to the Tp ligand of complex **6**, while the other set belongs to the Tp ligand of **7**. A six-peak pattern for the Tp ligand implies that two of the three legs *trans* to the Tp ligand in an octahedral configuration are equivalent. The assumption that the two legs in **7** are due to the bidentate alkyl carbonato ligand $CF_3CH_2OCO_2^-$ is supported by the ^{13}C NMR study of an identical reaction using $^{13}CO_2$ in place of the unlabeled carbon dioxide. The ^{13}C NMR spectrum of the resulting solution shows a characteristic carbonate singlet resonance at δ = 172.3 ppm. Since only one carbonate signal was detected in the ^{13}C NMR spectrum, the counterion of **6** is not a free alkyl carbonato anion but it is the alkoxide anion $CF_3CH_2O^-$, which is confirmed by ^{19}F NMR spectroscopy showing a triplet signal at $\delta = -76.02$ ($J_{H,F} = 10$ Hz). The methylene hydrogen signals of the $CF_3CH_2OCO_2$ ligand are unfortunately masked by a huge peak in the ^1H NMR spectrum due to the free alcohol. The $^{31}P\{^1H\}$ spectrum of the solution shows two singlets: one at $\delta = 50.8$ ppm pertaining to **6** and another one at $\delta = 63.9$ ppm, ascribable to the phosphane ligand of **7**. When all the NMR spectroscopic data are taken together, **7** can be identified as the alkyl carbonato complex $TpRu(PPh_3)(\eta^2\text{-}O_2COCH_2CF_3)$. Apparently, **7** was formed by CO_2 insertion into the $Ru-OCH_2CF_3$ bond of **5** [see Equation (1)]. Insertion of CO_2 into metal−oxygen bonds of metal alkoxides and phenoxides to form metal carbonate species is well documented.[13]

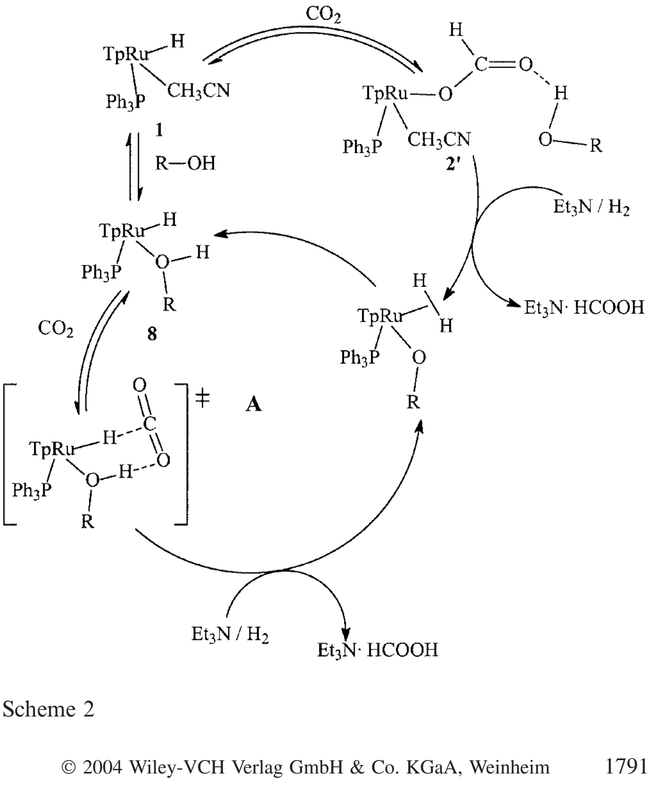
$$2\ \underset{\mathbf{5}}{TpRu(PPh_3)(CH_3CN)(OCH_2CF_3)} + CO_2 \longrightarrow \underset{\mathbf{6.CF_3CH_2O^-}}{[TpRu(PPh_3)(CH_3CN)_2]^+\ CF_3CH_2O^-} + \underset{\mathbf{7}}{TpRu(PPh_3)(\eta^2\text{-}O_2COCH_2CF_3)} \quad (1)$$

Reaction of 1 with CO_2/H_2 in CF_3CH_2OH/[D$_8$]THF

A CF_3CH_2OH/[D$_8$]THF (1:1 by volume) solution of **1** containing 20 equiv. of Et_3N was pressurized with 6 atm of CO_2 and H_2 at room temperature in a 5-mm Wilmad pressure-valved NMR tube. The $^{31}P\{^1H\}$ NMR spectrum taken 1 h later at room temperature indicates the formation of a 1:1 mixture of **6** and **7**. ^1H NMR spectroscopy shows, in addition to **6** and **7**, a small amount of formic acid, evidenced by a small singlet at $\delta = 8.42$ ppm. A few hours later, ^1H NMR measurements showed that the amount of formic acid increased, and it also suggested the presence of a minute amount of $TpRu(PPh_3)(CO)H$ (**3**), as evidenced by a very small doublet at $\delta = -11.83$ ppm ($J_{H,P}$ = 26.8 Hz). After heating the NMR tube at 100 °C for 1 d, it was found by ^1H and $^{31}P\{^1H\}$ studies that **6** and **7** disappeared and **3** was the only ruthenium complex present in the solution.

Mechanism of CO_2 Hydrogenation in Non-Acidic Alcohols

Our high-pressure NMR studies show that reactivity of **1** in the CO_2-hydrogenation reaction in methanol is very similar to that in hydrous THF and it is therefore reasonable to propose that the mechanism of **1**-catalyzed CO_2-hydrogenation reactions in non-acidic alcohols (Entries 4−9, Table 1) is analogous to that of the catalysis in hydrous THF. Therefore, in analogy to the active aquo hydride species $TpRu(PPh_3)(H_2O)H$ in hydrous THF, the key intermediate in the catalytic cycle **A** (see Scheme 2) is the transient alcohol hydride species **8**, which is mainly formed by displacement of the acetonitrile ligand of **1** by ROH. The interaction of the OH proton of the alcohol in **8** with one of the oxygen atoms of the approaching CO_2 increases the electrophilicity of the carbon atom, which is then able to abstract the hydride from Ru−H. The turnover numbers of the catalytic reactions decrease with increasing bulkiness of the alcohols (Entries 3−7, Table 1) and this observation supports the fact that the availability of **8** might have a large effect on the overall efficiency of the catalytic system. It is more difficult for a hindered alcohol to displace the acetonitrile ligand of **1**. In view of the detection of a small amount of $TpRu(PPh_3)(H_2)H$ (**4**) by NMR spectroscopy in our previous study of **1**-catalyzed CO_2 hydrogenation in hydrous THF, we propose that **4** is present in a minute amount in the alcohols, although it has not been successfully detected by NMR spectroscopy. Reaction of $TpRu(PPh_3)(H_2)H$ with formic acid to yield $TpRu(PPh_3)(CO)H$ was verified by an independent experiment.



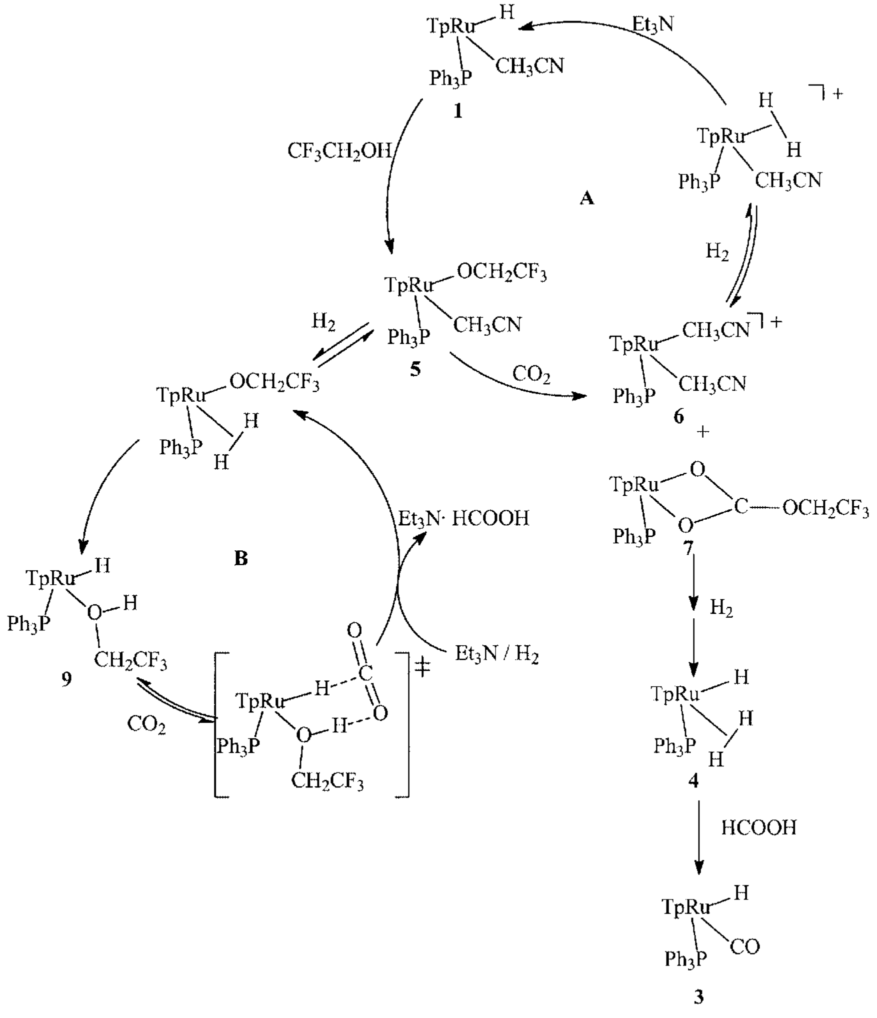
Scheme 2

Mechanism of CO_2 Hydrogenation in Acidic Alcohol CF_3CH_2OH

Unlike the CO_2-hydrogenation reaction in methanol, no metalloformate intermediate is observable in the course of the catalysis in CF_3CH_2OH because complex **1** reacts rapidly with the acidic alcohol to form the metal alkoxide **5**, which then reacts with CO_2 to give the observable intermediate species $[TpRu(PPh_3)(CH_3CN)_2]^+$ (**6**) and $TpRu(PPh_3)(\eta^2\text{-}O_2COCH_2CF_3)$ (**7**). Although the observable intermediates in the catalyses in methanol and CF_3CH_2OH are different, we propose that the sequence in cycle **B** (see Scheme 3), which is basically identical to the catalytic cycle **A** of Scheme 2, is the productive route for the catalytic process in trifluoroethanol. Under H_2 pressure, a minute quantity of the active alcohol hydride species $TpRu(PPh_3)(CF_3CH_2OH)H$ (**9**) might be generated through the alkoxo dihydrogen intermediate $TpRu(PPh_3)(OCH_2CF_3)(H_2)$. The much higher catalytic activity of **1** in CF_3CH_2OH than in the non-acidic alcohols is probably related to the much stronger interaction of the proton of the coordinated CF_3CH_2OH in **9** with an oxygen atom of CO_2, which enhances significantly the positive charge at the carbon atom of the molecule, making the hydride abstraction from Ru−H facile. Again, the final ruthenium complex $TpRu(PPh_3)(CO)H$ results from the reaction of formic acid with $TpRu(PPh_3)(H_2)H$ (**4**) after prolonged heating. The action of H_2 on the alkyl carbonato intermediate **7** is believed to be one of the routes to generate **4**, although the sequence of the reaction is unknown.

Conclusion

Continuing our study on the promoting effect of water in the **1**-catalyzed hydrogenation of CO_2 to formic acid, we have studied the effect of alcohols on the catalysis. Our study suggests that, although the NMR-detectable intermediates in the catalysis in methanol (and probably in other non-acidic alcohols) and in acidic CF_3CH_2OH are different, the catalytic cycles of CO_2 hydrogenation in both cases are probably identical. The key species of the catalytic process, $TpRu(PPh_3)(ROH)H$, is the alcohol analogue of the aquo hydride complex that we have proposed for our previously studied hydrous THF system. The exceptionally



Scheme 3

high promoting effect of CF_3CH_2OH among the alcohols studied is due to the stronger interaction of the highly acidic hydrogen of the trifluoroethanol in $TpRu(PPh_3)(CF_3CH_2OH)H$ with an oxygen atom of the approaching CO_2, greatly enhancing the electrophilicity of the carbon atom of the molecule, and enabling its abstraction of the hydride from Ru−H.

Experimental Section

General Remarks: Ruthenium trichloride, $RuCl_3 \cdot 3H_2O$, pyrazole, and sodium borohydride were obtained from Aldrich. Triphenylphosphane 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.[13] Solvents were distilled under dry nitrogen with appropriate drying agents.[14] High-purity hydrogen gas and carbon dioxide were supplied by Hong Kong Oxygen. ^1H NMR spectra were obtained with a Bruker DPX 400 spectrometer. Chemical shifts are reported relative to residual protons of the deuterated solvents. ^{31}P, ^{19}F, and ^{13}C NMR spectra were recorded with a Bruker DPX 400 spectrometer at 161.70, 376.31 and 100.60 MHz, respectively. ^{31}P NMR chemical shifts were externally referenced to 85 % H_3PO_4 in D_2O. ^{19}F NMR chemical shifts were externally referenced to $CFCl_3$ in $CDCl_3$. ^{13}C NMR chemical shifts were internally referenced to the residual peak of the deuterated solvents. High-pressure NMR studies were carried out in commercial 5-mm Wilmad pressure-valved NMR tubes.

Safety Warning: It is advisable not to add more than 12 atm of gas(es) to the 5-mm Wilmad pressure-valved NMR tubes at room temperature.

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, about 0.013 mmol of **1** in 20 mL of alcohol and 2 mL of NEt_3 was added to the autoclave. After being flushed with H_2 three times, the system was heated whilst stirring at 100 °C 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 formic acid in the resulting solution was analyzed by ^1H NMR spectroscopy. The relative intensities of the formato hydrogen signal of the product and the formato hydrogen signal of the internal standard (DMF) were measured, and with the help of a calibration curve, the turnover number of the catalysis was derived.

Acknowledgments

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