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Rhodium-Catalyzed Hydrogenation of Carbon Dioxide to Formic Acid[†]

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Abstract: The complex $[Rh(NBD)(PMe_2Ph)_3]BF_4$ (**2**; NBD = norbornadiene) has been found to serve as a precatalyst for the hydrogenation of carbon dioxide to formic acid at moderate temperatures in THF solution, with turnover numbers of 10–60/day. Water accelerates formic acid production, whereas PMe_2Ph is an inhibitor. Kinetic studies show that the rate of formic acid appearance is first order each in [**2**], p_{H_2}, and p_{CO_2} in the range 50–300 psi (following prehydrogenation). In situ high-pressure IR and NMR experiments reveal that the addition of H_2 to $[Rh(NBD)(PMe_2Ph)_3]BF_4$ (**2**) produces rhodium dihydride complexes $[H_2Rh(PMe_2Ph)_3(S)]BF_4$ (**4**, **5**; S = H_2O, THF) and $[H_2Rh(PMe_2Ph)_4]BF_4$ (**3**). IR and NMR studies of the reaction of **3**–**5** with CO_2 indicate that **3** is unreactive toward CO_2 but that **4** and **5** insert CO_2 to give species **6** and **7**, formulated as formato complexes $[HRh(S)(PMe_2Ph)_2(\eta^2\text{-}OCHO)]BF_4$ and $[HRh(S)_{1,2}(PMe_2Ph)_{3,2}(\eta^1\text{-}OCHO)]BF_4$, respectively; complexes **6** and **7** are also detected under catalytic conditions by IR spectroscopy. Aquo dihydride complex **4** has been found to insert CO_2 more rapidly than the THF complex **5**. $[H_2Rh(PMe_2Ph)_3(S)]BF_4$ (**4**, **5**) also catalyze the decomposition of formic acid to CO_2 and H_2. Combined kinetic and spectroscopic results suggest that reductive elimination of formic acid from the intermediate formato complexes is the rate-limiting step in the catalytic cycle.

The attractiveness of carbon dioxide as a potential chemical feedstock and its perceived inertness have stimulated widespread interest in the organometallic chemistry,[1] the metal-mediated electrochemistry,[2] and, to a limited extent, the metal-mediated photochemistry[3] of this most abundant of carbon resources. Further stimulus for the development of practical methods for regenerating organic compounds from carbon dioxide has been provided by the growing concern over its contribution to the global greenhouse effect.

In fact, the hydrogenation of carbon dioxide to methanol and/or methane over heterogeneous catalysts has been known for many years and has received increased mechanistic attention recently.[4] In contrast, the corresponding homogeneous catalytic processes have been little studied. The initial stage of CO_2 reduction can produce either carbon monoxide (reverse water gas shift reaction) or formic acid (eq 1). Both of these reactions are thermodynamically unfavorable,[5] and perhaps for this reason, they have received little synthetic or mechanistic attention as CO_2 reduction processes. On the other hand, several examples of homogeneous, metal-mediated versions of the thermodynamically favored reverse reactions, the water gas shift reaction[6] and formic acid decomposition,[7] have been reported.

$$CO + H_2O \longleftarrow CO_2 + H_2 \longrightarrow HCO_2H \qquad (1)$$

Only two prior reports in the open literature have described the homogeneous hydrogenation of CO_2 to formic acid.[8] This reaction is catalyzed by late transition metal complexes with the most active being $Pd(Ph_2PCH_2CH_2PPh_2)_2$,[8a] $RuH_2(PPh_3)_4$,[8a] and $RuCl_3(EDTA)$.[8b] Although a possible reaction mechanism involving the intermediacy of carbon dioxide and metallo carboxylic acid complexes was proposed for the last system, no compelling experimental data were provided. Hydrogenations of CO_2 catalyzed by soluble metal catalysts with added alcohols,[9] alkyl halides,[10] or secondary amines[11] to produce formate esters or formamides are thermodynamically enhanced by the formation of water or HX. Darensbourg and co-workers have provided important mechanistic insight into the reactions involving alkyl halides[10] and alcohols.[9] In a practical sense, formic acid itself is a valuable compound, finding important applications as a pickling agent, as a reducing agent, in animal silage manufacture, and as an intermediate for the production of oxalic acid, formate esters, and amides such as DMF;[12a–c] it has also been suggested as a convenient hydrogen storage agent.[12d] Formic acid has been produced commercially by the hydration of carbon monoxide under basic conditions, via hydrolysis of methyl formate, and as a by-product in the partial oxidation of hydrocarbons.[12a]

As part of a program in our laboratory directed toward fundamental studies of CO_2 activation by transition metal com-

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[†] Patent pending.

(1) Reviews: (a) Behr, A. *Carbon Dioxide Activation by Metal Complexes*; VCH Publishers: Weinheim, Germany, 1988. (b) Ito, T.; Yamamoto, A. In *Organic and Bioorganic Chemistry of Carbon Dioxide*; Inoue, S., Yamazaki, N., Eds.; Halstead Press: New York, 1982; Chapter 3, pp 79–151. (c) Darensbourg, D.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129. (d) Kolomnikov, I. S.; Lysyak, T. V. *Russ. Chem. Rev.* (*Engl. Transl.*) **1990**, *59*, 344.

(2) Reviews: Reference 1d. *Catalytic Activation of Carbon Dioxide*; Ayers, W. M., Ed.; ACS Symposium Series 363; American Chemical Society: Washington, DC, 1988; Chapters 5 and 6. Recent ref: DuBois, D. L.; Meidaner, A. *J. Am. Chem. Soc.* **1987**, *109*, 113. Pugh, J. R.; Bruce, M. R. M.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1991**, *30*, 86 (and references therein).

(3) Lehn, J.-M.; Zeissel, R. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 701. Hawecker, J.; Lehn, J.-M.; Zeissel, R. *J. Chem. Soc., Chem. Commun.* **1983**, 536. Lehn, J.-M.; Ziessel, R. *J. Organomet. Chem.* **1990**, *382*, 157. Kutal, C.; Corbin, A. J.; Ferraudi, G. *Organometallics* **1987**, *6*, 553. Tinnemans, A. H. A.; Koster, T. P. M.; Thewissen, D. H. M.; Mackor, A. *Recl. Chim. Pays-Bas* **1984**, *103*, 228. Grant, J. L.; Goswami, K.; Spreer, L. O.; Otvos, J. W.; Calvin, M. *J. Chem. Soc., Dalton Trans.* **1987**, 2105.

(4) Reviews: Sneeden, R. P. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1985; Vol, 8, p 225. Solymosi, F.; Erdohelyi, A. *J. Mol. Catal.* **1980**, *8*, 471. Inui, T.; Funabiki, M. *Chem. Lett.* **1978**, 251.

(5) Quoted values for $\Delta G°$ of these reactions vary significantly depending upon the state of the reactants and/or products and the temperature; values for the reverse WGSR and for HCO_2H formation are ca. +4–9 and ca. +4–12 kcal/mol, respectively.

(6) Reviews: *Catalytic Activation of Carbon Monoxide*; Ford, P. C., Ed.; ACS Symposium Series 152; American Chemical Society: Washington, DC, 1980; Chapters 5–9. Ford, P. C. *Acc. Chem. Res.* **1981**, *14*, 37.

(7) Coffey, R. S. *J. Chem. Soc., Chem. Commun.* **1967**, *923*. Aguilo, A. *J. Catal.* **1969**, *13*, 283. Paonessa, R. S.; Trogler, W. C. *J. Am. Chem. Soc.* **1982**, *104*, 3529. Strauss, S. H.; Whitmire, K. H.; Shriver, D. F. *J. Organomet. Chem.* **1979**, *174*, C59. Yoshida, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3941.

(8) (a) Inoue, Y.; Izumida, H.; Sasaki, Y.; Hashimoto, H. *Chem. Lett.* **1976**, *863*. (b) Khan, M. M. T.; Halligudi, S. B.; Shuka, S. *J. Mol. Catal.* **1989**, *51*, 47. (c) Hashimoto, Y.; Inoue, Y. Jpn. Pat. 76.138.614, 1976; *Chem. Abstr.* **1977**, *87*, 67853v. (d) Tijin Ltd. Jpn. Kokai Tokkyo Koho 81.166.146, 1981; *Chem. Abstr.* **1982**, *96*, 122211x. (e) Tijin Ltd. Jpn. Kokai Tokkyo Koho 81.140.948, 1981; *Chem. Abstr.* **1982**, *96*, 68352d.

(9) Tijin Ltd. Jpn. Pat. 76.138.614, 1976. Darensbourg, D.; Ovalles, C. *J. Am. Chem. Soc.* **1984**, *106*, 3750. Darensbourg, D.; Ovalles, C.; Pala, M. *J. Am. Chem. Soc.* **1983**, *105*, 5937.

(10) Darensbourg, D.; Ovalles, C. *J. Am. Chem. Soc.* **1987**, *109*, 3330.

(11) Anderson, J. J.; Drury, D. J.; Hamlin, J. E.; Kent, A. G. WO 85-GB443, 1985; GB 84-24672, 1984.

(12) (a) *Ullmann's Encylopedia of Industrial Chemistry*, 5th ed.; Elvers, B., Hawkins, S., Ravenscroft, M., Rounsaville, J. F., Schulz, G., Eds.; Verlag Chemie: Weinheim, FRG, 1986; pp 13–32. (b) *Concise Encyclopedia of Chemical Technology*; Kirk, Othmer, Eds.; Wiley Interscience: New York, 1985; p 528. (c) Weissermel, K.; Arp, H. J. In *Industrial Organic Chemistry*; Verlag Chemie: Weiheim, FRG, 1978; pp 38–40. (d) Williams, R.; Crandall, R. S.; Bloom, A. *Appl. Phys. Lett.* **1978**, *33*, 381.

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Table I. Catalytic Hydrogenation of CO_2 by $[Rh(NBD)(PMe_2Ph)_3]BF_4$ (**2**)

expt	p_{H_2}, psi	p_{CO_2}, psi	conditions[a]	(TN/Rh)/day
1	700	700	dry THF	11
2	700	700	wet THF (0.4% H_2O)	26
3	700	700	pretreat with H_2, wet THF	64
4	700	700	add 3 equiv of PMe_2Ph	<2
5			50 atm of CO, 1% H_2O	<2

[a] All reactions carried out at 40 °C in THF solvent.

plexes,[13] we recently discovered the stoichiometric reduction of coordinated carbon dioxide in $(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}CO_2)$ (**1**) by acidic transition metal hydride complexes, resulting in the conversion of coordinated carbon dioxide to carbon monoxide.[13d] This finding should be contrasted with several reported reactions of metal hydrides with free CO_2 producing metal formate complexes.[14] In an effort to elucidate the factors controlling the selectivity of CO_2 reduction by metal hydride complexes (i.e. to carbon monoxide or to formate) and possibly to develop new catalytic CO_2 reduction processes, we have investigated the interaction of CO_2 (both free and complexed) with cationic rhodium hydride complexes, $[H_2Rh(L)_n(S)_{4-n}]Z$[15] (**3**; L = PMe_2Ph, S = solvent, Z = BF_4^-). These species are active hydrogenation catalysts for alkenes,[16] alkynes,[17] and ketones.[18] As a result of these investigations, we report herein our discovery of a new active catalyst system for the hydrogenation of carbon dioxide to formic acid as well as the first detailed mechanistic study of this CO_2 reduction process, including spectroscopic characterization of probable catalytic intermediates.

Results

Interaction of $[RhH_2(PMe_2Ph)_x(THF)_y]BF_4$ with $(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}CO_2)$. Continuing our studies of the stoichiometric reactions of metal hydrides with coordinated CO_2 in $(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}CO_2)$ (**1**),[13d] we first examined the interaction of **1** with the cationic hydrides $[RhH_2(PMe_2Ph)_x(THF)_y]BF_4$, derived from addition of dihydrogen to $[Rh(NBD)(PMe_2Ph)_3]BF_4$[15] (**2**; NBD = norbornadiene). However, in THF or CH_2Cl_2 solution at room temperature, no reaction was detected during IR or NMR monitoring over several hours.

Catalytic Hydrogenation of CO_2 by $[Rh(NBD)(PMe_2Ph)_3]BF_4$—Activity, Promotion, and Inhibition. In view of the proven ability of the $[Rh(PR_3)_x(S)_{4-x}]^+$ catalyst systems to promote hydrogenation of polar functional groups, e.g. ketones,[18] we decided to investigate the capability of **2** to catalyze the hydrogenation of carbon dioxide itself. Indeed, when a 1.4 mM solution of **2** in THF was pressurized with 750 psi each of CO_2 and H_2 at room temperature, formic acid was produced with a turnover number of 34 mol/mol of Rh after 3 days, as determined by IR analysis of withdrawn aliquots (eq 2, Table I); no other organic products were detected by IR or GC/MS analysis. Interestingly, the formic acid turnover number increased to 78 in 3 days when the reaction was carried out in the presence of a small amount of added H_2O (0.4% v/v). Although H_2O is not an essential component in the system, its presence does significantly increase the rate of reaction, an effect which we have investigated mechanistically (vide infra). Finally, the formic acid production was further increased to a turnover of 128 after 2 days by pretreatment of **2** with molecular hydrogen for 3–6 h prior to the introduction of CO_2.

$$CO_2 + H_2 \xrightarrow[\text{THF}]{[Rh(NBD)(PMe_2Ph)_3]BF_4} HCO_2H \quad \text{(10-60 turnovers/day)} \qquad (2)$$

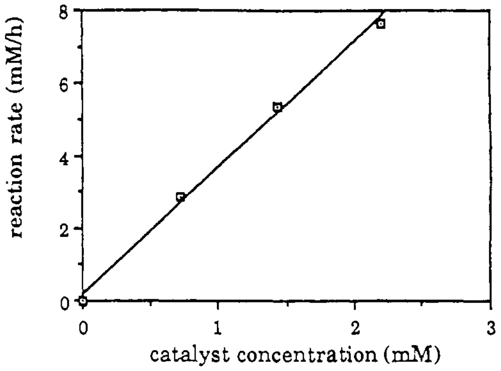

Figure 1. Effect of catalyst concentration on the rate of formic acid appearance.

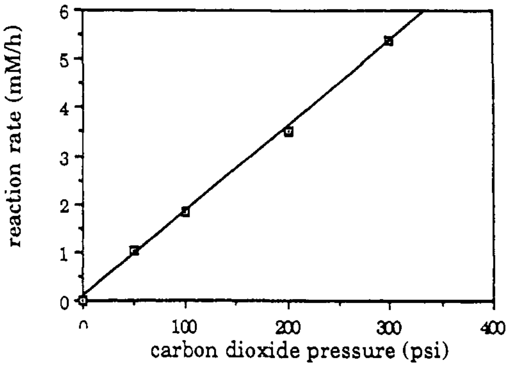

Figure 2. Effect of CO_2 pressure on the rate of formic acid appearance.

The influence of added phosphine on the catalysis was briefly assessed. In one run, 3 equiv of PMe_2Ph/**2** was added to the reactor and the system pressurized as usual. No formic acid was detectable by IR monitoring after 3 days at 40 °C.

Finally, to evaluate the possible role of the reverse water gas shift reaction in formic acid production, after activation of **2** with dihydrogen in wet THF, the autoclave was pressurized with CO (500 psi). After 3 days at room temperature, IR analysis of a withdrawn aliquot indicated the absence of an appreciable quantity of formic acid.

Reaction Kinetics. The kinetics of the catalytic reaction were examined by varying the concentration of catalyst precursor **2** and the pressures of CO_2 and H_2. Experiments were conducted using a standard protocol of pretreatment of **2** with 400 psi of H_2 (6 h, 20 °C) in THF solution containing 0.4% added H_2O by volume. The formic acid concentration was determined by analyzing withdrawn aliquots by IR spectroscopy and by comparison with a working curve derived from standard solutions. The concentration of **2** was varied in the range 0.72–2.2 mM while the CO_2 and H_2 pressures were maintained at 300 psi each and the temperature was maintained at 40 °C. Initial rates were obtained from the linear region of the [formic acid]/time plot (<10% of reaction). As shown in Figure 1, a first-order plot of the rate of formic acid appearance was linear with a slope of 1, indicating

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(13) (a) Belmore, K. A.; Vanderpool, R.; Tsai, J. C.; Khan, M. A.; Nicholas, K. M. *J. Am. Chem. Soc.* **1988**, *110*, 2004. (b) Farmer, M.; Khan, M.; Nicholas, K. M. *J. Chem. Soc., Chem. Commun.* **1988**, 1384. (c) Tsai, J. C.; Khan, M.; Nicholas, K. M. *Organometallics* **1989**, *8*, 2967. (d) Tsai, J. C.; Khan, M.; Nicholas, K. M. *Organometallics* **1991**, *10*, 29. (e) Fu, P. F.; Khan, M.; Nicholas, K. M. *Organometallics* **1991**, *10*, 382. (f) Tsai, J. C.; Wheeler, R. A.; Khan, M. A.; Nicholas, K. M. *Organometallics* **1991**, *10*, 1344. (g) Ziegler, W.; Nicholas, K. M. *J. Organomet. Chem.* **1992**, *423*, C35.

(14) (a) Darensbourg, D. J.; Rockicki, A. *Organometallics* **1982**, *1*, 1685. (b) Darensbourg, D. J.; Fisher, M. B.; Schmidt, R. E. J.; Baldwin, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 1297. (c) Darensbourg, D. J.; Rockicki, A.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1981**, *103*, 3223. (d) Smith, S. A.; Blake, D. M.; Kubota, M. *Inorg. Chem.* **1972**, *11*, 660. (e) Johnson, B. F. G.; Johnston, R. D.; Lewis, J.; Williams, I. G. *J. Chem. Soc. A* **1971**, 689. (f) Pu, L. S.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1968**, *90*, 3896. (g) Bradley, M. G.; Roberts, D. A.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 379. (h) Roberts, D. A.; Geoffroy, G. L. *J. Organomet. Chem.* **1980**, *198*, C75. (i) Komiya, S.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 784. (j) Kolomnikov, I. S.; Gusev, A. I.; Aleksandrov, G. G.; Lobeeva, T. S.; Struchkov, Y. T.; Vol'pin, M. E. *J. Organomet. Chem.* **1973**, *59*, 349. (k) Komiya, S.; Yamamoto, A. *J. Organomet. Chem.* **1972**, *46*, C58.

(15) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397.

(16) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 2134.

(17) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 2143.

(18) Review: (a) Heil, B.; Marko, L.; Toros, S. *Homogeneous Catalysis with Metal Phosphine Complexes*; Plenum Press: New York, 1983; Chapter 10. (b) Schrock, R. R.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1970**, 567. (c) Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1975**, 617.

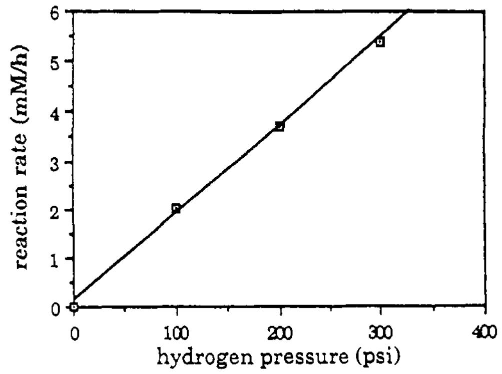


Figure 3. Effect of H_2 pressure on the rate of formic acid appearance.

a first-order dependence on the concentration of **2**.

To determine the rate dependency on carbon dioxide concentration, its pressure was varied in the range 50–300 psi with the H_2 pressure maintained at 300 psi, the catalyst concentration at 1.44 mM, and the reaction temperature at 40 °C. In this pressure range, CO_2 adheres to Henry's law.[19] Under these conditions the rate of formic acid production was cleanly first order with respect to CO_2 pressure (and hence concentration) (Figure 2).

Finally, to establish the rate dependence on hydrogen concentration, its pressure was varied in the range 100–300 psi with the CO_2 pressure maintained at 300 psi and the same concentration of **2** and temperature as previously indicated. As can be seen in Figure 3, the rate of formic acid appearance was also first-order dependent on the H_2 pressure. In summary then, the rate of formic acid production is first order each in **2**, CO_2, and H_2.

In Situ Spectroscopic Studies. (a) IR Spectra under Catalytic Conditions. A solution of **2** in dry or "wet" (0.4% v/v H_2O) THF was pressurized with 700 psi each of H_2 and CO_2 in a high-pressure IR reactor cell at ambient temperature. IR monitoring over a few-hour period revealed (Figure 4a), in addition to the growth of the formic acid peak (1725 cm^{-1}), a set of weak, broad bands in the Rh–H stretching region (1900–2150 cm^{-1}), two prominent absorptions at 1620 and 1567 cm^{-1}, and two moderate bands at 1361 and 1331 cm^{-1}. The latter peaks are in the region typical of metal formato complexes[14] (vide infra). When the pressure in the cell was released, the absorption at 1620 cm^{-1} disappeared within minutes while the 1557-cm^{-1} band persisted for a least a day. In order to further identify the species produced in the catalytic reaction and to elucidate its mechanism, we conducted in situ high-pressure IR and NMR studies of the interaction of **2** with the individual reactant gases.

(b) Reaction of 2 with H_2 and CO_2 Separately. When a solution of complex **2** was pressurized with 300–700 psi of CO_2, no new absorptions appeared in the 1500–2000-cm^{-1} IR region; thus **2** does not readily form a CO_2 adduct. In regard to the reaction of **2** with dihydrogen, despite the well-known function of $[(R_3P)_xRh(diene)]Z$ as hydrogenation catalysts and the elegant preparative and spectroscopic studies by Schrock and Osborn,[15–18] detailed information on the precise species produced when complex **2** (L = PMe_2Ph) reacts with dihydrogen was lacking. Accordingly, the interaction of **2** with H_2 in THF solution was examined, in both the presence and the absence of added H_2O. The in situ IR spectrum obtained after **2** was pressurized with 700 psi of H_2 in THF containing 0.4% H_2O showed three new absorptions at 2129, 2003, and 1925 cm^{-1}, tentatively assigned to Rh–H stretching vibrations[14] (Figure 4b). The ^1H NMR spectrum of **2** in THF-d_8 (containing 3% added H_2O) under 200 psi of H_2 (Figure 5) showed the presence primarily of two hydride complexes, **3** and **4**; a trace of a dark precipitate was also present in the solution. The less abundant hydride species **3** exhibited a high-field resonance at −10.15 ppm, appearing as the AA′ portion of a AA′MXX′Y_2 pattern with a large trans P–H coupling (J_{P-H} = 153.3 Hz). The dominant rhodium hydride species **4** displayed two resonances (1:1) at −8.92 (very broad at room temperature) and −21.77 ppm. At −40 °C the resonance at −8.92 ppm appeared as the A part of an AA′MXY_2 system with a large trans P–H coupling (J_{P-H} = 163.4 Hz) whereas the resonance at −21.77 ppm corresponded to the A′ part, lacking a large P–H coupling.

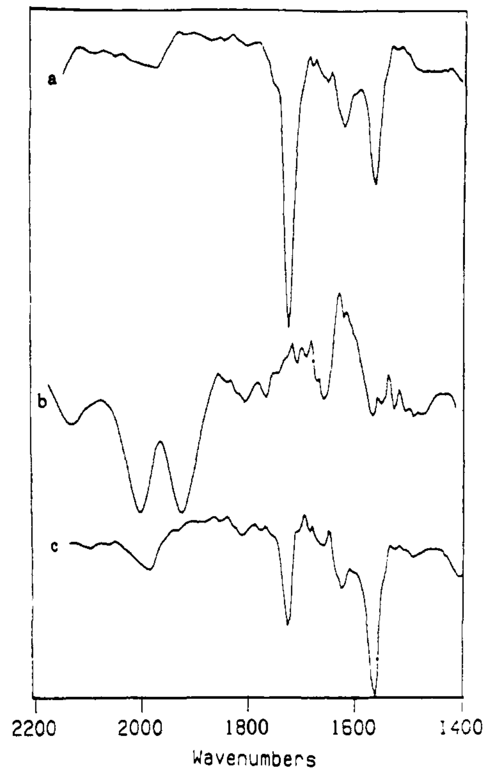
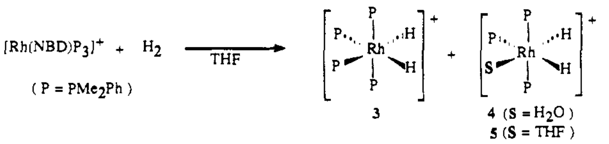


Figure 4. In situ IR spectra: (a) under catalytic conditions—$[Rh(NBD)(PMe_2Ph)_3]BF_4$ (**2**) + CO_2 (700 psi) + H_2 (700 psi) in wet THF after 8 h; (b) **2** + H_2 (700 psi) in wet THF → **3** + **4**; (c) rhodium hydrides **3** and **4** + CO_2 (700 psi) in THF → **6** + **7**.

The identities of **3** and **4** were fully established by the $^{31}P\{^1H\}$ NMR spectrum of the solution (Figure 6). The minor species **3** exhibited two resonances (1:1) at 0.93 (dt; J_{Rh-P} = 98.2 Hz, J_{P-P} = 24.4 Hz) and −11.03 ppm (dt; J_{Rh-P} = 86.2 Hz, J_{P-P} = 24.4 Hz), which, on the basis of selective decoupling of the methyl protons of the PMe_2Ph ligand, is indicative of a phosphine trans to a hydride (J_{P-H} = 153 Hz) and one cis to a hydride ligand. These NMR data and the presence of the Rh–H IR band at 2003 cm^{-1} establish the identity of **3** as the previously reported [*cis*-$H_2Rh(PMe_2Ph)_4]BF_4$.[15] The $^{31}P\{^1H\}$ NMR resonances (2:1) associated with the major hydride species **4** appeared at 6.06 (dd; J_{Rh-P} = 105.9 Hz, J_{P-P} = 25.3 Hz) and −8.37 ppm (dt; J_{Rh-P} = 90.9 Hz, J_{P-P} = 25.3 Hz). The $^{31}P\{^1H, (CH_3)_2PPh\}$ NMR spectrum revealed that the phosphine resonating at −8.37 ppm is situated trans to a hydride ligand (J_{P-H} = 163.4 Hz). These NMR spectroscopic data, together with the Rh–H IR absorption bands at 2129 and 1925 cm^{-1}, implicate a tris(phosphine) dihydride composition for **4**, which we formulate as $[H_2Rh(PMe_2Ph)_3(S)]BF_4$ (eq 3). Consistent with this assignment, it was found



(3)

by ^{31}P NMR monitoring that the mixture of **3** and **4** was completely transformed to **3** following treatment with 3 equiv of PMe_2Ph. The presence of water as a ligand in **4** (in wet THF) was supported by in situ NMR studies of the reaction of complex **2** with molecular hydrogen in the absence of added H_2O (vide infra). At −40 °C it was also possible to detect (by ^{31}P NMR monitoring) a small amount of a phosphine complex tentatively identified as $[RhH_2(PMe_2Ph)_2S_2]BF_4$ [S = THF or H_2O; $^{31}P\{^1H\}$

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[19] Darensbourg, D. *Catalytic Activation of Carbon Dioxide*; Ayers, W. M., Ed.; ACS Symposium Series 363; American Chemical Society: Washington, DC, 1988; Chapter 4, p 27.

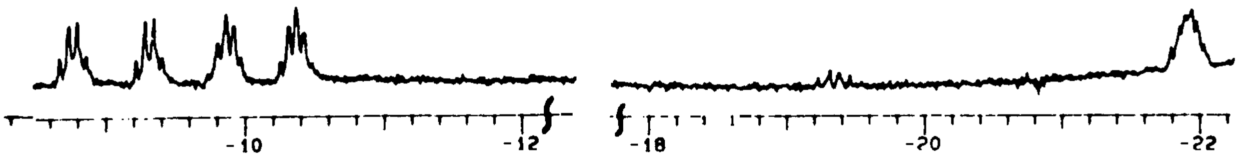


Figure 5. In situ ^{1}H NMR spectrum of **2** + H_2 (700 psi) in wet THF → **3** + **4**.

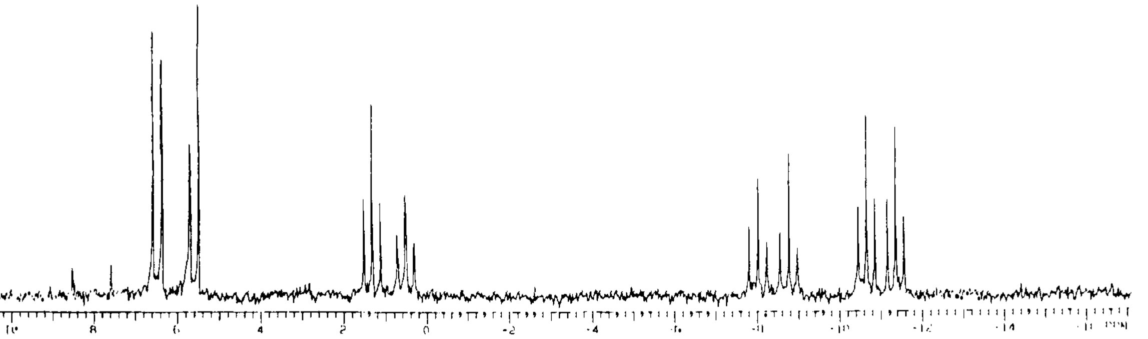


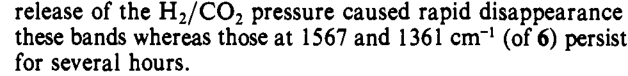
Figure 6. In situ $^{31}P\{^{1}H\}$ NMR spectrum of **2** + H_2 (700 psi) in wet THF → **3** + **4**.

NMR δ 8.07 (dd; J_{Rh-P} = 114.5 Hz)]; related species (e.g. with S = CH_3CN) have been characterized by Schrock and Osborn.[16]

When H_2O was intentionally omitted from the system, a new hydride species **5** was detected. The $^{31}P\{^{1}H\}$ NMR spectrum obtained upon treating a solution of **2** in "dry" THF with 200 psi of H_2 and cooling to −50 °C showed the presence of tetrakis complex **3** accompanied by two double doublets at 5.8 (J_{Rh-P} = 105.39 Hz, J_{P-P} = 26.3 Hz) and 4.9 ppm (J_{Rh-P} = 104.1 Hz, J_{P-P} = 26.0 Hz) and two double triplets at −8.6 (J_{Rh-P} = 90.7 Hz, J_{P-P} = 25.2 Hz) and −13.6 ppm (J_{Rh-P} = 88.1 Hz, J_{P-P} = 26.2 Hz). The resonances at 5.8 and −8.6 ppm are derived from a small amount of the aquo complex **4** (resonances slightly temperature shifted); the absorptions at 4.9 and −13.6 ppm are associated with an identical AA'MX$_3$ spin system and are assigned to the corresponding THF complex $[H_2Rh(PMe_2Ph)_3(S)]BF_4$ (**5**). Likewise the ^{1}H NMR spectrum of the solution at −60 °C showed resonances for complexes **3** (−10.15 ppm) and **4** (−8.92 and −21.8 ppm) and those associated with $[H_2Rh(PMe_2Ph)_3(THF)]BF_4$ (**5**) (broad d; −8.92 and −22.95 ppm). Consequently, when H_2O is intentionally omitted from the system, dihydrogen addition to complex **2** produces tetrakis complex **3**, a small amount of aquo complex **4** (presumably arising from H_2O present in the commercial THF-d_8), and the THF complex **5** (eq 3).

(c) Interaction of Rhodium Hydride Complexes 3–5 with CO_2. In order to examine the reactivity of the rhodium hydrides **3–5** with CO_2 while limiting their subsequent transformations (e.g. to formic acid), we conducted in situ IR and NMR experiments following release of the H_2 pressure and repressurization with CO_2. We note that IR and NMR spectra of these solutions showed that the hydrides **3–5** remained after release of the H_2 pressure. IR monitoring of the reaction between rhodium dihydride species **3** and **4** and carbon dioxide (700 psi) in "wet" THF showed the 2003-cm^{-1} band remaining, while the 2129- and 1925-cm^{-1} Rh–H bands of **4** disappeared within a few hours. New absorptions simultaneously appeared at 2095 cm^{-1} (Rh–H), 1725 cm^{-1} (formic acid), and 1620, 1567, 1361, and 1331 cm^{-1} (Figure 4c). The intensities of the absorptions at 1620 and 1331 cm^{-1} (associated with **7**) were markedly pressure dependent, being barely detectable below 200 psi and increasing in intensity at higher pressures; release of the H_2/CO_2 pressure caused rapid disappearance of these bands whereas those at 1567 and 1361 cm^{-1} (of **6**) persisted for several hours.

In principle, the reaction of a transition metal hydride with CO_2 can produce two possible insertion products, a formato complex (mono- or bidentate) or a metallo carboxylic acid species (eq 4).

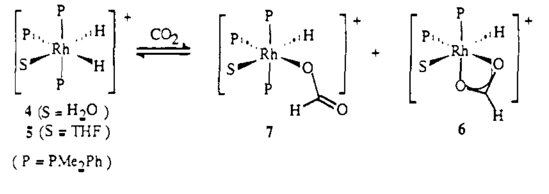


(4)

The available IR data base of metal formato complexes[14] and our subsequent NMR experiments (vide infra) permit assignment of the new absorptions at 1567 and 1361 cm^{-1} to $\nu(CO_2)_{asym}$ and $\nu(CO_2)_{sym}$ vibrations of a bidentate formato complex **6** and the 1620- and 1331-cm^{-1} absorptions to the $\nu(CO_2)_{asym}$ and $\nu(CO_2)_{sym}$ stretching vibrations of a monodentate formato complex **7**. The alternative metallo carboxylic acid, which could be expected to have a carbonyl absorption band in the same region,[19] was eliminated on the basis of ^{13}C NMR experiments (vide infra).

NMR experiments following the addition of CO_2 to hydride complexes **3–5** allowed further characterization of these putative formato derivatives. After treatment of the wet THF solution of **3** and **4** with 200 psi of CO_2, the $^{31}P\{^{1}H\}$ NMR spectrum (Figure 7) revealed the continued presence of **3** but the nearly complete disappearance of **4**. A new doublet resonance assigned to **6** was found at 29.0 ppm (J_{Rh-P} = 135.4 Hz), which appeared as a doublet of doublets (J_{Rh-P} = 135.4 Hz, J_{H-P} = 9.7 Hz) in the selectively decoupled $^{31}P\{^{1}H, (CH_3)_2PPh\}$ NMR spectrum. These features are indicative of a complex which contains only one hydride ligand and a single phosphine magnetic environment. Under the same conditions, the ^{1}H NMR spectrum indicated the disappearance of the Rh–H resonances of **4** and their replacement with a single hydride resonance assigned to **6** at −19.1 ppm (broad m).

In order to further verify the formato formulation for **6**, the $^{13}C\{^{1}H\}$ NMR spectrum of a solution of **3**/**4** following pressurization with ca. 150 psi of $^{13}CO_2$ was obtained. In addition to the resonance for $^{13}CO_2$ at 124.9 ppm, a new intense absorption at 170.3 ppm appeared, assigned to bidentate complex **6** (Figure 8). In the ^{1}H-coupled ^{13}C NMR spectrum (Figure 8 inset), this latter resonance was cleanly split into a doublet with a ^{13}C–H coupling constant of 204.6 Hz. This result indicates that the carbon producing the 170.3 ppm absorption has a single, directly bonded H, only consistent with a formate ligand. On the basis of these ^{1}H, $^{31}P\{^{1}H\}$, and ^{13}C NMR spectra as well as the IR spectroscopic analysis, we conclude that the reaction between rhodium hydride complex **4** and CO_2 results in the generation of a bidentate formato complex $[HRh(H_2O)(PMe_2Ph)_2(\eta^2\text{-}OCHO)]^+$ (**6**) and a monodentate formato complex $[HRh(H_2O)_{1,2}(PMe_2Ph)_{3,2}(\eta^1\text{-}OCHO)]^+$ (**7**). The latter was detectable only under high pressure (>200 psi) of CO_2 by IR analysis (eq 5). Pressure limitations of the



(5)

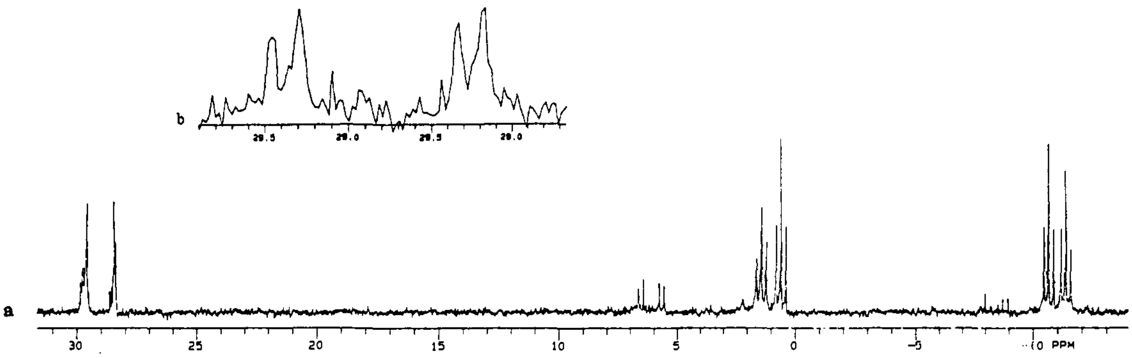


Figure 7. (a) $^{31}P\{^1H\}$ NMR spectrum of the reaction of rhodium hydrides **3** and **4** with CO_2 (200 psi). (b) Inset: expansion of the low-field region of the $^{31}P\{^1H, CH_3)_2PPh\}$ NMR spectrum of the same solution.

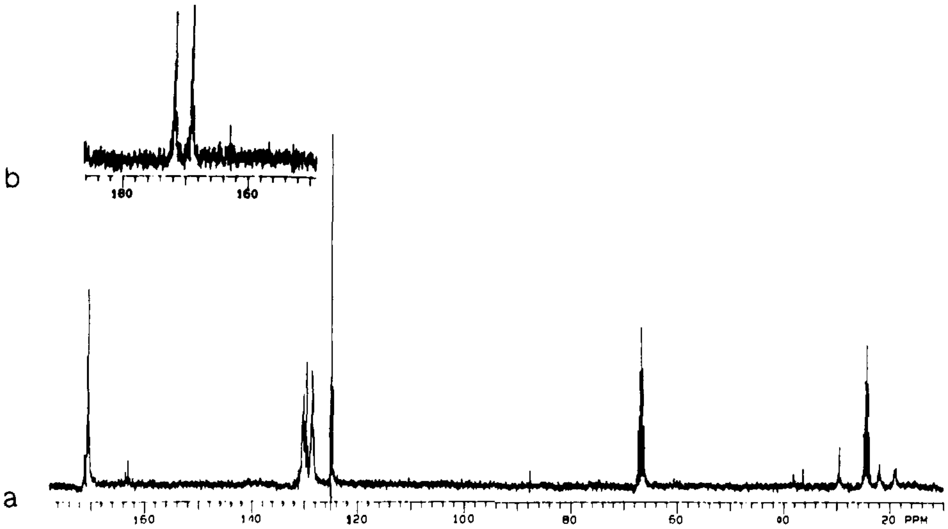


Figure 8. (a) $^{13}C\{^1H\}$ NMR spectrum after reaction of rhodium hydrides **3** and **4** with $^{13}CO_2$ (ca. 150 psi) in THF-d_8. (b) Inset: proton-coupled ^{13}C NMR spectrum of solution from (a) in 150–180 ppm region.

commercially available NMR tubes prevented NMR studies at higher pressures.

In order to probe further the origin of the catalytic rate acceleration effect by H_2O, in situ IR and NMR studies were conducted of the interaction of rhodium hydrides **3** and **5** (L = THF) with CO_2 in the absence of added H_2O. IR monitoring of a solution of complexes **3** and **5** in dry THF under 700 psi of CO_2 revealed that formato complexes **6′** and **7′** (L = THF) were also generated in this system but at a significantly slower rate, requiring ca. 25 h to produce the same amount of formic acid produced within 5 h in the presence of added water. The $^{31}P\{^1H\}$ NMR spectrum of the same reaction mixture in THF-d_8 under 200 psi of CO_2 showed the gradual development of a broad doublet resonance at 28.9 ppm after 24 h assigned to **6′** (S = THF).

Formic Acid Decomposition Catalyzed by 3 and 4. Treatment of a THF solution containing rhodium dihydride complexes **3** and **4** with 90% formic acid resulted in slow gas evolution from the solution. In situ IR monitoring of the reaction revealed that the 1725-cm^{-1} band of formic acid gradually diminished while the 2334-cm^{-1} band of free CO_2 and that of the bidentate formato complex **6** (at 1567 cm^{-1}) increased (Figure 9); the putative monodentate formato complex **7** was not detected under these conditions nor were free carbon monoxide or CO complexes. Consequently, the rhodium hydride species **4** (and possibly **3**) catalyzes the reduction of CO_2 to formic acid as well as the reverse reaction, its decomposition to CO_2 and H_2.

Discussion

Recent studies in this laboratory have established the reactivity of $(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}CO_2)$ (**1**) with the acidic metal hydrides $HCo(CO)_4$ and $H_2Fe(CO)_4$;[12] weaker acids such as $CpMo(CO)_3H$ and Cp_2MoH_2 were unreactive. The failure of the rhodium hydrides $[H_2Rh(PMe_2Ph)_3S]^+$ and $[H_2Rh(PMe_2Ph)_4]^+$ to react with **1** may reflect a weaker acidity for these species. The pK_a values for these complexes apparently have not been determined, but their deprotonation by Et_3N to form $HRhL_3$ has been demonstrated.[16]

The activity of the present system for CO_2 hydrogenation, particularly with added water, is comparable to the most active of those reported by the Inoue[8a] and Khan[8b] groups. We note that although small quantities of water accelerate formic acid production in the present system, it is not an essential component as is the case with the neutral phosphine complexes tested by the Japanese group. The high selectivity for formic acid in the present Rh-catalyzed reactions may be contrasted with the case of the $RuCl_3/Na_2EDTA$ system, which produces substantial amounts of formaldehyde and CO as well.[8b] The inhibition of CO_2 reduction by added PMe_2Ph could be derived from a number of effects on the catalytic cycle. One certain contributor, on the basis of the in situ IR and NMR results, is that added phosphine causes conversion of $[H_2Rh(PMe_2Ph)_3(S)]^+$ (**4**) to $[H_2Rh(PMe_2Ph)_4]^+$ (**3**), which is unreactive toward CO_2 insertion.

Kinetic studies using the initial-rate method show that the catalytic production of formic acid is apparently first order each in **2** (after prehydrogenation), in H_2, and in CO_2 in the range 50–300 psi. The first-order rate dependency on precatalyst concentration is supportive of a mononuclear active catalyst or catalysts (as opposed to a cluster). Without the H_2 preactivation period, formic acid is still produced catalytically but non-first-order behavior is observed. The origin of the induction period is not clear, since H_2 reacts rapidly with **2**[16] to release norbornane, even at 1 atm. Perhaps the active solvato complexes **4** and **5**, detected in the spectroscopic studies, are only gradually formed during this period, an issue which we have not yet addressed. The first-order dependence on both H_2 and CO_2 concentrations is consistent with a two-substrate catalytic mechanism operating below saturating concentrations of the substrates.[20] The apparent simplicity of

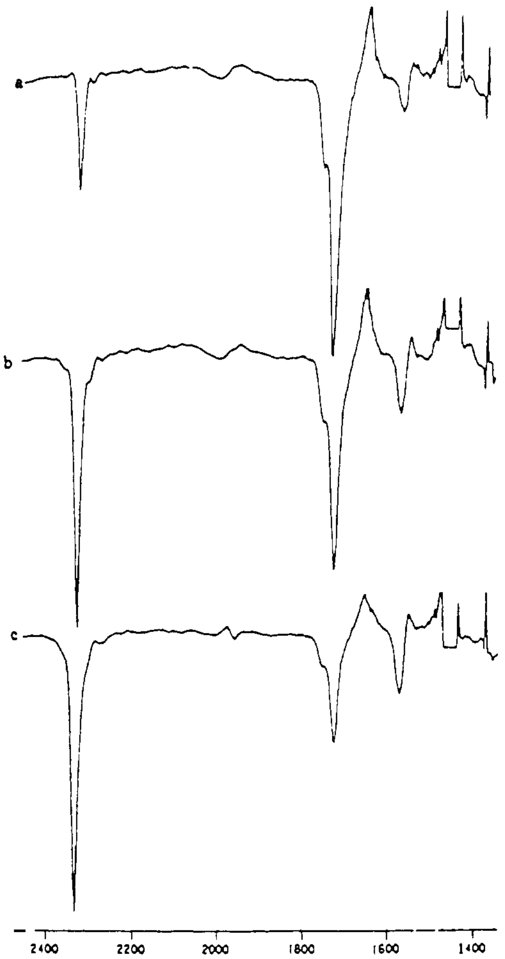


Figure 9. IR spectra showing decomposition of formic acid by **3** and **4** in THF: (a) 0.33 h; (b) 1.0 h; (c) 2.0 h.

the kinetic expression, however, should be viewed with some caution because of the mixture of rhodium complexes present. More extensive kinetic studies are planned to elucidate in greater detail the mechanism of the catalysis.

Our spectroscopic studies show that whereas $[Rh(NBD)(PMe_2Ph)_3]^+$ (**2**) is unreactive toward CO_2 at 700 psi, H_2 (200–700 psi) reacts readily with **2** to give primarily $[H_2Rh(PMe_2Ph)_3(S)]^+$ (**4**, S = H_2O; **5**, S = THF) along with a lesser amount of $[H_2Rh(PMe_2Ph)_4]^+$ (**3**) (eq 3). Small amounts of an unidentified black precipitate and of the tentatively identified $[RhH_2(PMe_2Ph)_2S_2]^+$ are likely relevant to the phosphine imbalance posed by the generation of **3**–**5** from **2**, particularly if the precipitate is Rh metal or a Rh–phosphine cluster. Tetrakis complex **3** has been identified previously,[15] but the tris(phosphine) solvates **4** and **5** appear to be the first spectroscopically characterized examples of this type.[30] Such species could play a significant role in catalytic hydrogenations of other substrates by cationic rhodium–phosphine complexes. The formation of aquo complex **4** under conditions where THF is in huge excess (i.e. as solvent) suggests that this species is more stable than the THF adduct **5**. The origin of the differing stabilities of **4** and **5** is uncertain and may reflect a composite of steric and electronic (e.g. basicity, hard/soft character) factors.

Among the three rhodium hydride species identified in this study, two undergo insertion of CO_2. The reactions of **4** and **5** ($[H_2Rh(PMe_2Ph)_3(S)]^+$; **4**, S = H_2O; **5**, S = THF) with CO_2 provide the first examples of CO_2 insertion of a cationic metal hydride. The accumulated IR and NMR spectroscopic data clearly establish the generation of at least one and probably two formato species in these reactions. At lower CO_2 pressures (used for NMR experiments) only one insertion product is detected, namely $[HRh(S)(PMe_2Ph)_2(\eta^2\text{-}OCHO)]^+$ (**6**), which has IR absorptions at 1567 and 1361 cm^{-1} and a ^{13}C NMR resonance at 170.3 ppm. These IR absorption positions are typical of the $\nu(CO_2)_{asym}$ and $\nu(CO_2)_{sym}$ vibrations of bidentate formato complexes.[14] The ^{13}C NMR chemical shift and especially the doublet pattern exhibited in the proton-coupled spectrum of **6** secure the formato (rather than metallo carboxylic acid) assignment; the ^{13}C–H coupling constant of 204.6 Hz is in the range typical of organic formates[22] and is virtually identical to that reported for the bidentate formato derivative $(diphos)_2Re(O_2CH)$.[14g]

The additional species **7** observed by IR spectroscopy under higher pressures of CO_2 is formulated as a formato derivative as well, $[HRh(S)_{1,2}(PMe_2Ph)_{3,2}(\eta^1\text{-}OCHO)]^+$, although on the basis of less direct evidence. The position of $\nu(CO_2)_{asym}$ for **7** (1620 cm^{-1}) and the $\Delta\nu$ between $\nu(CO_2)_{asym}$ and $\nu(CO_2)_{sym}$ (289 cm^{-1}) are typical of monodentate formato complexes.[14] The concentration dependence of **7** on the pressure of CO_2 indicates that it readily decarboxylates (i.e. insertion of CO_2 is readily reversible). Similarly, only **6** is detected in the decomposition of formic acid by **3** and **4**. Although reasonable, it is not clear whether the mono- and bidentate complexes **7** and **6** are in equilibrium. The back-reaction **6** → **7** is certainly slow, considering the rapid disappearance of **7** and the longevity of **6** after release of the CO_2/H_2 pressure from the **6**, **7** mixture. It seems likely that the monodentate species **7** is a precursor to **6**, accompanied by L or S dissociation.

Two other reasonable formulations for **7**, however, cannot be ruled out on the basis of available data. An isomeric metallo carboxylic acid species (Rh–COOH) could account for the observed C=O bands at 1620 and 1331 cm^{-1}, but three pieces of circumstantial/negative evidence favor the formato assignment: (1) Almost all of the reported metallo carboxylic acid complexes[21] have lower frequency C=O absorption bands than **7**. (2) Given the fact that metallo carboxylic acid complexes are typically produced by H_2O or OH^- addition to metal carbonyls, the same species should have been formed when **2** or **3**–**5** were treated with CO/H_2O—but this was not observed. (3) In every well-documented case to date, insertion of CO_2 into a M–H bond has produced a metal formate.[14] Alternatively, one could envision that **7** is a bis(formate) complex, e.g. $[RhP_{2,3}(\eta^1\text{-}O_2CH)(\eta^2\text{-}O_2CH)(S)_{1,0}]^+$, derived from insertion of CO_2 into the mono(formato) complex **6**. If this were the case, however, one should observe production of **7** *at the expense of* **6** under high CO_2 pressure and potentially a second-order dependence of the catalytic rate on the CO_2 pressure, neither of which was found. Additional studies designed to unequivocally identify **7** are planned.

The attenuated reactivity of tetrakis complex $[H_2Rh(PMe_2Ph)_4]^+$ (**3**) toward CO_2 is noteworthy. Complex **3** is probably the most hydridic (and least acidic) of the three, but the slow dissociation of its ligands[16] could be a contributing factor to its unreactivity if precoordination of CO_2 facilitates its insertion. We point out, however, that Darensbourg and co-workers have demonstrated that CO_2 insertion into $(CO)_5MH^-$ does not require CO predissociation.[14a,c] It is interesting to contrast the reactions of hydride complexes **4** and **5** with CO_2 to those of the neutral $HRh(PR_3)_3$ complexes investigated by Otsuka, Ibers, and co-workers.[23] The latter react with CO_2 to produce bidentate *bicarbonato* complexes, $H_2Rh(PR_3)_2(O_2COH)$ [ν(OCO) 1587 and 1338 cm^{-1}].

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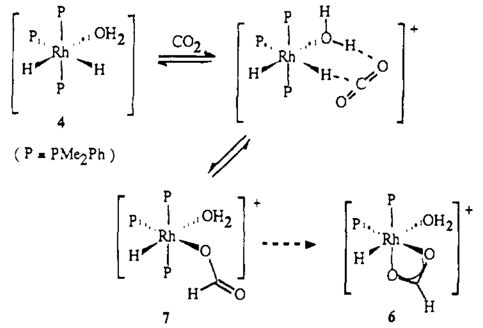
[20] Rudolph, F. B.; Fromm, H. J. *Contemporary Enzyme Kinetics and Mechanism*; Purich, D. L., Ed.; Academic Press: New York, 1983; Chapter 3, pp 53–73.

[21] Partin, J. A.; Richmond, M. G. *J. Organomet. Chem.* **1990**, *396*, 339. Lee, S. W.; Tucker, W. D.; Richmond, M. G. *Inorg. Chem.* **1990**, *29*, 3053. Sweet, J. R.; Graham, W. A. G. *Organometallics* **1982**, *1*, 982. Deeming, A. J.; Shaw, B. L. *J. Chem. Soc. A.* **1969**, 443. Appleton, T. G.; Bennett, M. A. *J. Organomet. Chem.* **1973**, *55*, C88. Grice, N.; Kao, S. C.; Pettit, R. *J. Am. Chem. Soc.* **1979**, *101*, 1627. Catellani, M.; Halpern, J. *Inorg. Chem.* **1980**, *19*, 566.

[22] Levy, G. C.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*; Wiley: New York, 1972.

[23] Yoshida, T.; Thorn, D. L.; Okano, T.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 4212.

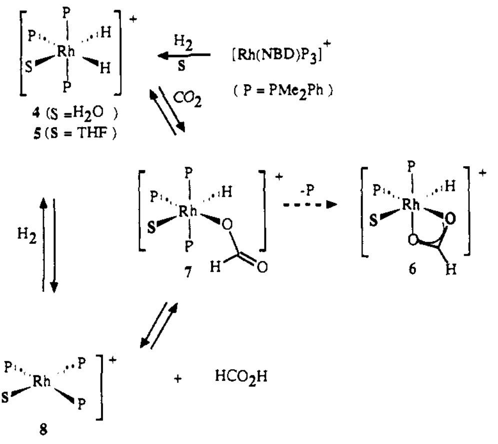
Scheme I. Possible Origin of Increased Rate of CO_2 Insertion into Aquo Complex **4**



The mechanistic details of the CO_2 insertion reaction itself have not yet been investigated in depth. However, an accelerating effect of H_2O in this process has been discovered. The aquo complex $[H_2Rh(PMe_2Ph)_3(H_2O)]^+$ (**4**), produced under "wet" conditions, reacts with CO_2 significantly faster than does the THF adduct **5**. Since the amount of water added (0.4%) is probably too small to cause a significant change in bulk solvent properties or in CO_2 solubility, a more specific molecular effect is likely to be operative. The most obvious explanation would invoke a more facile ligand dissociation (i.e. greater lability) of H_2O, mediating the subsequent coordination and insertion of CO_2. However, the apparently greater association constant of H_2O compared to THF (based on the preponderance of **4** over **5** in slightly wet THF) suggests that a different effect may be involved. Admittedly speculative, we propose that the transition state for insertion could be stabilized by an H-bonding interaction between the coordinated H_2O molecule (of increased acidity) and an oxygen of the approaching CO_2 (Scheme I). Such an interaction would polarize the CO_2 fragment, enhancing its electrophilicity at carbon and its susceptibility to hydride transfer from Rh. A similar facilitating role for coordinated water in the action of the enzyme carbonic anhydrase (promoting insertion of CO_2 into a Zn–OH bond) has been supported by crystallographic studies.[24] Acceleration by H_2O of the hydrogenation of ketones catalyzed by **2**[18b] as well as of the hydrogenation of CO_2 to formic acid catalyzed by various neutral metal phosphine complexes[8a] has been noted, but the origin of the effect was not probed experimentally. It is also possible, in the presence of water, that the $H_2CO_3/HCO_3^-/CO_3^{2-}$ equilibrium could play some role in the present system.[23] While this possibility cannot be discounted at present, the in situ spectroscopic studies provided no evidence of such species (or metal derivatives) under the reaction conditions.

A few other observations are of relevance in defining the primary mechanistic pathway for catalysis of CO_2 hydrogenation by **2**. Since formic acid could be produced by CO hydration, the question arises whether (reverse) water gas shift catalysis in the present system could generate CO which is subsequently hydrated. Although the evidence is negative, we found no indication for simultaneous water gas shift catalysis—free CO was not detected spectroscopically nor was formic acid produced when **2** was pressurized with CO in wet THF. In apparent contrast, it is interesting to point out that $Rh(CO)(PPh_3)_2Cl$ is produced in the reaction of Wilkinson's complex with H_2 and CO_2[25] and that $HRh(PR_3)_3$ (R = ^iPr, cyclohexyl) catalyzes the water gas shift reaction.[23] This latter fact provides strong evidence against the involvement (by proton loss) of neutral monohydride species in the present catalytic system. Secondly, both formato complexes **6** and **7** can be detected under catalytic conditions by IR spectroscopy. Finally, we have found that the hydride complexes **4** and **5** catalyze formic acid decomposition, producing CO_2 (and presumably H_2) and the bidentate formato complex **6**; the nondetection of the monodentate species **7** is understandable, given its ready decarboxylation at low CO_2 pressures. Presumably, formic acid decomposition proceeds via reversible dihydrogen elimination from **4** and **5**, oxidative addition to the coordinatively unsaturated RhP_3S^+ intermediate producing **6** and **7**, and decarboxylation. Together these results demonstrate the presence of the formato derivative(s) in both the forward and reverse reactions and under catalytic conditions.

Scheme II. Proposed Mechanism for Hydrogenation of CO_2 Catalyzed by **2**



In the formulation of a mechanism for the catalytic hydrogenation of CO_2 by **2**, the following key experimental observations should be accommodated: (1) the kinetics, which are first order each in **2** (following pretreatment with H_2), in H_2, and in CO_2; (2) inhibition of CO_2 hydrogenation by added PMe_2Ph; (3) the facile reaction of **2** with H_2 and its unreactivity toward CO_2; (4) detection of formato derivatives **6** and **7** under catalytic conditions, in the direct reaction of dihydrides **4** and **5** with CO_2, and during formic acid decomposition by **4** and **5**; and (5) the catalytic rate enhancement by water. We propose the catalytic cycle shown in Scheme II to account for these features. The addition of H_2 to complex **2** in the presence of H_2O (with hydrogenation of norbornadiene to norbornane) leads to the formation of rhodium dihydride complexes **4** and **5**, which serve as the active catalyst species. Subsequent CO_2 insertion into the metal hydride bond in **4** and **5** results in the generation of monodentate **7** and bidentate **6** formato complexes. Reductive elimination of formic acid from **7** produces a coordinatively unsaturated rhodium species, e.g. **8**, which undergoes rapid oxidative addition of dihydrogen to regenerate the rhodium hydride complexes **4** and **5**, completing the catalytic cycle.

The observed kinetic behavior is consistent with either the CO_2 insertion step (e.g. **4**, **5** to **7**) or the reductive elimination step (**7** or **8**) being rate-limiting. However, the presence of significant concentrations of the formato complexes under catalytic conditions points to reductive elimination as the slow step. The conclusion is further supported by the observation that **6** and **7** are detected (by IR spectroscopy) in significant concentrations *prior to* the production of appreciable quantities of formic acid. Rate-limiting reductive elimination has been observed in a number of octahedral Rh(III) systems.[26] Further kinetic studies are needed to determine the various rate and equilibrium constants so as to verify this hypothesis. It seems likely that the monodentate formato species **7** is initially produced in the CO_2 insertion step, since ligand dissociation from a six-coordinate species is not required (as is the case for generation of bidentate **6**), and that **7** is the primary species which undergoes reductive elimination to produce formic acid. In fact, the relative stability of bidentate **6** (e.g. after H_2/CO_2 release) suggests that it may be an unproductive "shunt" in the catalytic cycle. Of course, it is virtually impossible *to prove* that species detected under reaction conditions (e.g. **6** or **7**) are true intermediates (i.e. product precursors), but the combined weight of the experimental evidence and prior chemical precedent supports an important role, particularly for monodentate formato species **7**.

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(24) Allen, L. C. *Catalytic Activation of Carbon Dioxide*; Ayers, W. M., Ed.; ACS Symposium Series 363; American Chemical Society: Washington, DC, 1988; Chapter 7, pp 91-101.

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

As noted earlier, the phosphine inhibition effect probably arises from generation of the inactive tetrakis complex $[H_2Rh(PMe_2Ph)_4]^+$ (**3**). Additionally, PMe_2Ph also could block other steps in the cycle by replacing a weakly coordinated solvent ligand or by inhibiting reductive elimination of formic acid from **7** (if prior PMe_2Ph dissociation is required[26]). The effect of water on the CO_2 insertion step has been discussed previously, but since this step does not appear to be rate-limiting, other roles may be operative. For example, the transition state for reductive elimination of formic acid could be stabilized by H-bonding from H_2O to the incipient HCO_2H.

Conclusions

This study has provided the first detailed insight into the mechanism of homogeneous catalytic hydrogenation of carbon dioxide to formic acid. The addition of H_2 to $[Rh(NBD)(PMe_2Ph)_3]BF_4$ (**2**) generates rhodium dihydride complexes $[H_2Rh(PMe_2Ph)_3(S)]$ (**4**, **5**; S = H_2O, THF), which are active catalysts for the hydrogenation of CO_2 to formic acid as well as for the decomposition of formic acid to CO_2 and H_2. In situ IR and NMR experiments have revealed that monodentate **7** and bidentate **6** formato complexes are generated under catalytic conditions. Combined kinetic and spectroscopic results suggest that reductive elimination of formic acid from **7** is the rate-limiting step in the catalytic cycle. The present system offers a rare opportunity to probe in detail the mechanistic, activity, and selectivity determinants in a catalytic process involving carbon dioxide. Future efforts are planned to examine the influence of phosphine structure on catalytic activity and to conduct more complete kinetic and spectroscopic studies.

Experimental Section

General Materials and Procedures. All reactions and manipulations were conducted under the indicated gas using standard Schlenk line and drybox techniques. THF was distilled under nitrogen from sodium benzophenone. Carbon dioxide (Linde anaerobic grade, purity >99.99%) and hydrogen (commercial grade, purity >99.95%) were used in the experiments without further purification. $[Rh(NBD)(PMe_2Ph)_3]BF_4$ (**2**) was prepared in two steps by the literature method and had appropriate spectroscopic properties.[27,28] ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian XL-300 NMR spectrometer; ^1H and ^{13}C resonances are referenced to Me_4Si at 0.00 ppm; ^{31}P resonances are referenced to external 85% phosphoric acid. Infrared spectra were collected on a Perkin-Elmer 1420 spectrometer or a Bio-Rad FTS-7 FTIR spectrometer.

Preparative-scale hydrogenation reactions were performed in a Parr 4770 150-mL stainless-steel autoclave fitted with a dip tube for withdrawing liquid samples. Kinetic studies were conducted in a Parr 4561 (300-mL) stainless-steel autoclave equipped with a Parr 4831 temperature controller and a direct-drive stirrer; sample solutions were placed in a glass liner within the autoclave. High-pressure IR experiments were conducted in a specially constructed IR cell fitted with ZnS windows modeled after the "spectraclave" described by King and King.[29] High-pressure NMR experiments were conducted in Wilmad 522-PV high-pressure NMR tubes.

Interaction of $[H_2Rh(PMe_2Ph)_3S]BF_4$/$[H_2Rh(PMe_2Ph)_4]BF_4$ with $Cp_2Mo(\eta^2\text{-}CO_2)$ (1). A mixture consisting of 10 mL of THF and 0.10 g (0.14 mmol) of $[Rh(PMe_2Ph)_3(NBD)]BF_4$ was stirred in a side-arm round-bottom flask under 1 atm of H_2 at room temperature for 1 h. The resulting solution was then cooled to −78 °C and treated with a solution of $Cp_2Mo(\eta^2\text{-}CO_2)$[13a] (0.055 g, 0.20 mmol) in 20 mL of THF. Then the resulting mixture was allowed to warm to −20 °C and maintained at this temperature under a H_2 atmosphere for 3 days. IR analysis showed only unreacted **1** and $Cp_2Mo(CO_3)$.[13a]

Preparative-Scale Hydrogenation of CO_2 to Formic Acid. In the autoclave were placed a magnetic stirring bar and a solution of **2** (50 mg, 0.072 mmol) in 50 mL of THF (dry or with 0.4–3% H_2O added). After attachment of the head, the system was flushed three times with hydrogen, then charged with 700 psi each of carbon dioxide and hydrogen, and stirred magnetically at room temperature. Reaction progress was monitored by IR spectroscopy using the 1725-cm^{-1} carbonyl absorption of formic acid. The concentration of formic acid was calculated by comparison with spectra produced from standard formic acid solutions. In runs utilizing catalyst preactivation, the system was first flushed three times with H_2 and then stirred under 700 psi of H_2 for 3–6 h. After release of hydrogen, the system was pressurized with CO_2 (700 psi) and then again with H_2 (700 psi).

In one run, the reactor was charged with 50 mg of **2** (0.072 mmol), 50 mL of THF, and 30 mg of PMe_2Ph (0.22 mmol). After pressurization with CO_2 (750 psi) and H_2 (750 psi), the reaction mixture was heated to 40 °C. IR monitoring over 3 days failed to detect significant quantities of formic acid.

CO Hydration/Water Gas Shift Reaction Catalysis Activity of 3 and 4. The autoclave was charged with 50 mg (0.72 mmol) of **2**, 1 mL of H_2O, 50 mL of THF, and 400 psi of H_2. After the reaction mixture was stirred at room temperature for 6 h, the H_2 pressure was released and the autoclave was recharged with 500 psi of CO. After 3 days of stirring, IR analysis failed to detect any formic acid; a weak absorption at 1920 cm^{-1}, suggestive of a CO complex, was observed.

Kinetics Experiments. The stainless-steel autoclave containing the indicated amount of complex **2**, 50 mL of THF, and, for "wet" runs, 0.2 mL of H_2O was charged with 400 psi of H_2 and stirred at room temperature for 6 h. After this period, the hydrogen pressure in the autoclave was released. The system was then warmed to 40 °C and charged with the indicated pressure of CO_2 followed by H_2; stirring initiated the reaction. Liquid samples were withdrawn at 5–10-min intervals and were analyzed by IR spectroscopy for formic acid using the 1725-cm^{-1} absorption. After a set of data was collected, a plot of formic acid concentration vs time was made using the computer program Cricket Graph. The plots contained a linear portion in the initial stages (<10% conversion). The slope of the linear portion of the curve provides the initial rate of reaction.

Formic Acid Decomposition Catalyzed by 3 and 4. A THF solution containing dihydride complexes **3** and **4** was generated in the high-pressure IR reactor cell by treating **2** (50 mg) in 2 mL of THF (with 1% H_2O added) with 300 psi of H_2 for 3–6 h. Following release of the H_2 pressure, 100 μL of 90% formic acid was injected, the solution was agitated, and the reaction solution was then monitored by IR spectroscopy.

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Registry No. 2, 141198-72-3; **3**, 141198-73-4; **4**, 141198-75-6; **5**, 141198-77-8; 6, 141198-79-0; **6′**, 141198-81-4; **7**, 141198-83-6; **7′**, 141198-85-8; CO_2, 124-38-9; H_2O, 7732-18-5; $[RhH_2(PMe_2Ph)_2S_2]BF_4$ (S = THF), 141198-87-0; $[RhH_2(PMe_2Ph)_2S_2]BF_4$ (S = H_2O), 141198-88-1; $Cp_2Mo(\eta^2\text{-}CO_2)$, 96040-81-2; formic acid, 64-18-6.

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(26) Milstein, D. *Acc. Chem. Res.* **1984**, *17*, 221. Milstein, D.; Fultz, W. C.; Calabrese, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 1336. Chan, A. S. C.; Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 838.

(27) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 3089.

(28) Denise, B.; Pannetier, G. *J. Organomet. Chem.* **1978**, *148*, 155.

(29) King, R. B.; King, A. D., Jr.; Iqbal, M. Z.; Frazier, C. C. *J. Am. Chem. Soc.* **1978**, *100*, 1687.

(30) Solution NMR data for $[(triphos)RhH_2(S)]^z$ have been reported: Bianchini, C.; Meli, A.; Laschi, F.; Ramirez, J. A.; Zanello, P.; Vacca, A. *Inorg. Chem.* **1988**, *27*, 4429. Ott, J. Ph.D. Dissertation No. 8000, ETH, Zurich, Switzerland, 1986.