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Review

Recent advances in the homogeneous hydrogenation of carbon dioxide

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Contents

Abstract

Homogeneous hydrogenation of carbon dioxide continues to attract interest in the hope of finding active and selective catalysts for the production of valuable organics based on this cheap and abundant carbon source. This review covers advances published or in press since 1995. The survey of the field shows that while very active catalysts and co-catalysts have been discovered in this period for the production of formic acid and its derivatives, there has been only preliminary development of homogeneous catalysts for the production of other oxygenates (e.g. methanol, CO) and C_n-compounds ($n > 1$).

Keywords: Carbon dioxide; Hydrogenation; Formic acid; Formamides; Homogeneous catalysis

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Abbreviations: acac, acetylacetonato; AMS, accessible molecular surface; Cl_2bpy, 6,6′-dichloro-2,2′-bipyridine; COD, 1,5-cyclooctadiene; DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene; DEA, diethanolamine; DFT, density functional theory; DHphen, 4,7-dihydroxy-1,10-phenanthroline; DMF, dimethylformamide; DMI, 1,3-dimethyl-2-imidazolidinone; dcpb, 1,4-bis(dicyclohexylphosphino)butane; dcpe, 1,2-bis(dicyclohexylphosphino)ethane; dippe, 1,2-bis(diisopropylphosphino)ethane; dppb, 1,4-bis(diphenylphosphino)butane; dppe, 1,2-bis(diphenylphosphino)ethane; dppp, 1,3-bis(diphenylphosphino)propane; dppm, 1,1-bis(diphenylphosphino)methane; EDTA-H, protonated ethylenediaminetetraacetic acid; hfacac, 1,1,1,5,5,5-hexafluoroacetylacetonate; MEA, monoethanolamine; NMP, *N*-methylpyrrolidine; nbd, norbornadiene; PEG or PEO, poly(ethylene glycol) or poly(ethylene oxide); PTA, 1,3,5-triaza-7-phosphaadamantane; $scCO_2$, supercritical carbon dioxide; TEA, triethanolamine; TOF, turnover frequency (TON per h); tos, *p*-toluenesulfonate; TON, turnover number (mole product per mole catalyst); Tp, tris(pyrazolyl)borate; TPPMS, sodium triphenylphosphine monosulfonate; TPPTS, sodium triphenylphosphine trisulfonate

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1. Introduction

It has been almost a decade since the field of homogeneously-catalyzed CO_2 hydrogenation has been reviewed by one of us [1] and by Leitner [2]. Advances that have been reported since then include the discovery of new catalysts and more effective alcoholic co-catalysts, increases in mechanistic understanding, the greater use of alternative media, and the development of methods for the preparation of formamides other than DMF by CO_2 hydrogenation. The authors have therefore prepared this review which covers advances published or in press since 1995, in addition to a more comprehensive review of the topic of aqueous-phase hydrogenation of CO_2 or carbonates. Recent advances in the homogeneously-catalyzed hydrogenation of carbon dioxide to formic acid, formate esters, formamides, CO, methanol and other products are reviewed. Unanswered questions still remain even in the relatively well understood case of reduction to formic acid, including the role of the water or alcohol co-catalysts found to be helpful in many systems, and the kinetic role, if any, of added amine.

2. Hydrogenation of CO_2 and carbonates in water

2.1. General considerations on the use of water as solvent

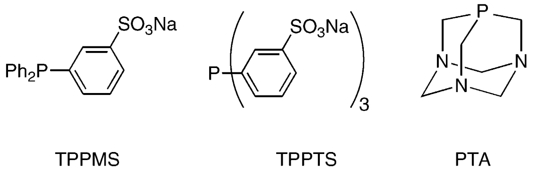
The highest volume process involving carbon dioxide as a raw material is its reduction and utilization as a C1 building block in green plant photosynthesis which takes place in a bulk aqueous environment. Several attempts have been made to achieve the homogeneous hydrogenation of CO_2 in aqueous solutions. The possible primary products of this reaction are formic acid, formaldehyde, methanol, and methane, however, in general the exclusive formation of formic acid was observed (Eq. (1)):

$$CO_2 + H_2 \rightleftharpoons HCO_2H \qquad (1)$$

It seems plausible to use water as the solvent for this reaction, because when all the reactants and the product are hydrated the standard free energy is slightly negative, $\Delta G^\circ_{298} = -4\,\text{kJ mol}^{-1}$. In contrast, the reaction between gaseous H_2 and CO_2 yielding liquid HCO_2H is accompanied by a free energy change of $\Delta G^\circ_{298} = +33\,\text{kJ mol}^{-1}$. Electrolytic dissociation of aqueous formic acid or its reaction with bases make the hydrogenation of CO_2 even more favorable. Nevertheless, it should be remembered that in order to achieve reasonable rates and conversions, many of the reactions are run at elevated temperatures and that favors the decomposition of formic acid.

In aqueous solutions one also has to consider the CO_2/bicarbonate/carbonate equilibrium (Eq. (2)):

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3{}^- + H^+ \rightleftharpoons CO_3{}^{2-} + 2H^+ \qquad (2)$$



Scheme 1. Structures of selected water-soluble phosphines.

Through this equilibrium the actual reactive species may change with changes in the pH, temperature and CO_2 pressure. The actual pH of the aqueous solutions under CO_2 pressure can be precisely determined either from the ^{13}C NMR intensities of the separate resonances of CO_2 and $HCO_3{}^-$ (acidic solutions, slow exchange) or from the position of the ^{13}C NMR signal (basic solutions, fast exchange between $HCO_3{}^-$ and $CO_3{}^{2-}$) [3].

In addition to its bulk solvation effects, water may also participate in the catalytic process on a more intimate molecular level. Indeed, it has been found in several cases that small amounts of water accelerated the hydrogenation of CO_2 in organic solvents. In general, these effects are explained by the interaction of CO_2 and coordinated H_2O which would facilitate either the coordination of CO_2 or the hydride transfer to its carbon center from the catalyst. Examples of such "water effects", together with the suggested mechanisms describing the possible role of H_2O can be found in references [1,4] and in later sections of this review.

Homogeneous catalysis in aqueous solutions needs water-soluble catalysts. In the hydrogenation of CO_2, rhodium- and ruthenium-based complexes predominate with the following water-soluble phosphine ligands [4]: mono- and trisulfonated triphenylphosphine (TPPMS and TPPTS, respectively, Scheme 1), $P(CH_2OH)_3$, $P(CH_2CH_2CH_2OH)_3$, $P(CH_2CH_2CN)_3$, and $P(CH_2)_6N_3$ (1,3,5-triaza-7-phosphaadamantane, PTA, Scheme 1).

The most important properties of aqueous catalytic systems for carbon dioxide hydrogenation are collected in Table 1, together with recent data for the same reaction studied in organic solvents.

2.2. Hydrogenation of CO_2 in water–amine mixtures

Leitner's group [10,11] has used $RhCl(TPPTS)_3$, as well as the in situ prepared rhodium-based catalysts $[RhCl(COD)_2]_2$/TPPTS and $[RhH(COD)]_4$/TPPTS (P:Rh = 2.6:1 in both cases) for the hydrogenation of CO_2 in aqueous solutions of amines, NEt_3 and $HNMe_2$, or aminoalkanols $(HOCH_2CH_2)_xNH_{3-x}$ ($x = 1$, 2 or 3: mono-, di- and triethanolamine, respectively). Typically, the reactions were run with $H_2:CO_2 = 1:1$, total initial pressure 40 bar, [Rh] = 2–6 mM, [amine] = 1.2–4.0 M at $T = 23$–$81\,^\circ C$. Initial turnover frequencies were as high as $7260\,h^{-1}$ at 81 °C (Table 1). The use of the two alkylamines equally led to complete conversions (i.e. 1 mol of HCO_2H per mole of amine). However, $HNMe_2$ was found superior to NEt_3 due

Table 1
A comparison of catalytic systems for the hydrogenation of CO_2 to formic acid

Catalyst precursor	Solvent	Additives	$p(H_2, CO_2)$[a] (atm)	T (°C)	t (h)	TON	TOF[b] (h^{-1})	Ref.
Rhodium								
$[RhCl(COD)]_2$ + dppb	DMSO	NEt_3	20, 20	RT	22	1150	52	[5]
$[RhCl(COD)]_2$ + dippe	DMSO	NEt_3	40 total	24	18	205	11	[6]
$[RhH(COD)]_4$ + dppb	DMSO	NEt_3	40 total	RT	18	2200	122	[7]
$[RhH(COD)]_4$ + dppb	DMSO	NEt_3	40 total	RT	0.8	312	390	[7]
$RhCl(PPh_3)_3$	MeOH	PPh_3, NEt_3	20, 40	25	20	2700	125	[8]
$RhCl(PPh_3)_3$	C_6H_6	Na_2CO_3	60, 55	100	3	173	58	[9]
$RhCl(TPPTS)_3$	H_2O	$NHMe_2$	20, 20	RT	12	3439	287	[10]
$RhCl(TPPTS)_3$	H_2O	$NHMe_2$	20, 20	81	0.5		7260	[10]
$RhCl(TPPTS)_3$	H_2O	$NHMe_2$	20, 20	23			1364	[11]
$[RhCl(\eta^2\text{-P-O})_2]BPh_4$	MeOH	NEt_3	25, 25	55	4.2	420	100	[12]
Rh(hfacac)(dcpb)	DMSO	NEt_3	20, 20	25	–	–	1335	[13]
$[Rh(nbd)(PMe_2Ph)_3]BF_4$	THF	H_2O	48, 48	40	48	128	3	[14]
$RhCl_3$ + PPh_3	H_2O	$NHMe_2$	10, 10	50	10	2150	215	[15]
Ruthenium								
$Ru_2(CO)_5(dppm)_2$	Acetone	NEt_3	38, 38	RT	1	207	207	[16]
$Ru_2(CO)_5(dppm)_2$	Acetone	NEt_3	38, 38	RT	21	2160	103	[16]
$RuCl_3$, PPh_3	EtOH	NEt_3, H_2O	60, 60	60	5	200	40	[17]
$RuH_2(PPh_3)_4$	C_6H_6	NEt_3, H_2O	25, 25	RT	20	87	4	[18]
$RuH_2(PPh_3)_4$	C_6H_6	Na_2CO_3	25, 25	100	4	169	42	[19]
$RuH_2(PMe_3)_4$	$scCO_2$	NEt_3, H_2O	85, 120	50	1	1400	1400	[20]
$RuCl_2(PMe_3)_4$	$scCO_2$	NEt_3, H_2O	80, 140	50	47	7200	153	[21]
$RuCl(OAc)(PMe_3)_4$	$scCO_2$	NEt_3/C_6F_5OH	70, 120	50	0.3	31667	95000	[22]
$TpRuH(PPh_3)(CH_3CN)$	THF	NEt_3, H_2O	25, 25	100	16	760	48	[23]
$[Ru(Cl_2bpy)_2(H_2O)_2][O_3SCF_3]_2$	EtOH	NEt_3	30, 30	150	8	5000	625	[24]
$[(C_5H_4(CH_2)_3NMe_2)Ru(dppm)]BF_4$	THF	None	40, 40	80	16	8	0.5	[25]
$[RuCl_2(CO)_2]_n$	H_2O, *i*PrOH	NEt_3	81, 27	80	0.3	400	1300	[26]
K[RuCl(EDTA-H)]	H_2O	–	3, 17	40	0.5	na	250	[27]
$[RuCl_2(TPPMS)_2]_2$	H_2O	$NaHCO_3$	60, 35	80	0.03	320	9600	[28]
$[RuCl(C_6Me_6)(DHphen)]Cl$	H_2O	KOH	30, 30	120	24	15400	642	[29]
$CpRu(CO)(\mu\text{-dppm})Mo(CO)_2Cp$	C_6H_6	NEt_3	30, 30	120	45	43	1	[30]
Palladium								
$Pd(dppe)_2$	C_6H_6	NEt_3/H_2O	25, 25	110	20	62	3	[18]
$Pd(dppe)_2$	C_6H_6	NaOH	24, 24	RT	20	17	0.9	[31]
$PdCl_2$	H_2O	KOH	110, na	160	3	1580	530	[32]
$PdCl_2(PPh_3)_2$	C_6H_6	NEt_3, H_2O	50, 50	RT	na	15	na	[33]
Other metals								
$Ni(dppe)_2$	C_6H_6	NEt_3, H_2O	25, 25	RT	20	7	0.4	[18]
$NiCl_2(dcpe)$	DMSO	DBU	40, 160	50	216	4400	20	[34]
$[Cp^*IrCl(DHphen)]Cl$	H_2O	KOH	30, 30	120	10	21000	2100	[29]

[a] In some cases, the pressure of CO_2 was not given and was calculated from the total stated pressure minus the pressure of H_2.
[b] The TOF values are not directly comparable to each other because some are at complete conversion and some are at partial conversion. They can, however, give an order of magnitude indication. Initial TOF values will be even higher.

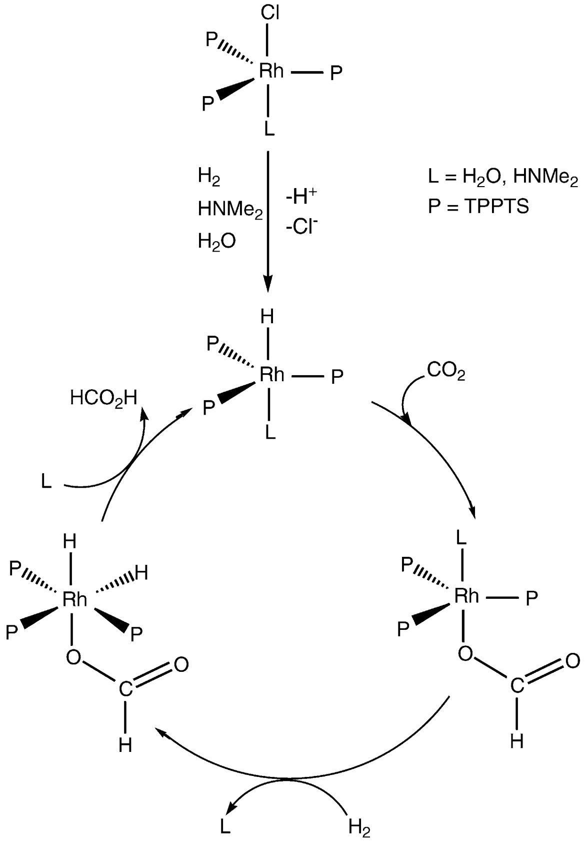
Table 2
Hydrogenation of CO_2 in aqueous solution of various amines with a $RhCl(TPPTS)_3$ catalyst [11]

Amine	TOF (h^{-1})	$[HCO_2H]/[amine]$
NEt_3	1364	0.99
$HNMe_2$	1364	0.99
MEA	98	0.65
DEA	48	0.14
TEA	22	0.04

Conditions: [Rh] = 2.02 mM, H_2:CO_2 = 1:1, p_{total} = 40 bar, T = 23 °C, [amine] = 3.53 M. MEA, DEA, and TEA stand for mono-, di- and tri-ethanolamine, respectively.

to its higher solubility in water providing homogeneous conditions in a wide concentration range. The ethanolamines proved less suitable bases in that their use provided slower reactions and lower final $[HCO_2H]/[amine]$ ratios (Table 2).

The sole product of the reaction was HCO_2H (as the respective ammonium formate salt). No reaction was observed in the absence of a nitrogeneous base, and in these aqueous systems the final concentration of formic acid never exceeded that of the added amine (Table 1). This is in contrast to nonaqueous systems (DMSO/NEt_3 or supercritical CO_2/NEt_3) where HCO_2H/NEt_3 product ratios of 1.6–1.8 could be obtained. In the basic aqueous solutions there was no decomposition of the product formate back to H_2 and



Scheme 2. Suggested mechanism of the hydrogenation of CO_2 catalyzed by $RhCl(TPPTS)_3$ in aqueous solutions of amines [11].

CO_2 when the pressure was decreased from 40 to 1 bar, clearly an advantageous feature with respect to the further workup and product isolation.

The rate of the $RhCl(TPPTS)_3$-catalyzed reaction showed a linear dependence on the concentration of the catalyst and on the partial pressure of H_2 and a saturation-type dependence on the partial pressure of CO_2. Added TPPTS decreased the rate considerably. An overall activation energy of $25\,kJ\,mol^{-1}$ was determined.

Based on these kinetic features and on the results of ^1H and ^{31}P NMR spectroscopic measurements the mechanism depicted in Scheme 2 was suggested. In the absence of dimethylamine, $RhCl(TPPTS)_3$ was shown to react with H_2 yielding the expected $RhH_2Cl(TPPTS)_3$ and the cationic $[RhH_2(TPPTS)_3]Cl$ dihydrides. However, the key intermediate in this mechanism is the monohydridorhodium complex, $RhH(TPPTS)_3L$ ($L = H_2O$ or $HNMe_2$) which forms only in the presence of $HNMe_2$. Therefore $HNMe_2$ is not only a sink for HCO_2H but also plays an active role in the formation of the catalytically active rhodium species. At the time of the investigations, no direct NMR evidence could be obtained for $RhH(TPPTS)_3L$ [11]. Somewhat later the analogous monohydrido complex $RhH(TPPMS)_3(H_2O)$, formed in strongly basic aqueous solutions, was unambiguously characterized by Joó et al. [35].

Further steps of the catalytic cycle involve the insertion of CO_2 into the Rh–H bond giving rise to the formation of a monodentate formato-Rh complex, oxidative addition of H_2 and reductive elimination of HCO_2H. Theoretical studies called attention to the possibility of σ-bond metathesis involving a coordinated dihydrogen and the η^1-O_2CH ligand [36].

Karakhanov et al. [15] investigated the hydrogenation of CO_2 in aqueous solution using Rh/PPh_3 catalyst prepared in situ by the reaction of $RhCl_3$ and PPh_3 in the presence of various solubilizing agents. These agents included cetylpyridinium chloride, cetyltrimethylammonium bromide, sodium dodecyl sulfate, ethoxylated β-cyclodextrin and poly(ethylene oxide), PEO, with an average molecular weight of 35,000 g/mol. Ethoxylated β-cyclodextrin and PEO were found to be far superior to the other three surfactants and poly(ethylene oxide) was used in most of the experiments. Carbon dioxide hydrogenations were run in the presence of an added base, such as NEt_3, $HNEt_2$, $HNMe_2$, $MeNHCH_2CH_2OH$, and Na_2CO_3; the highest reaction rates were obtained with $HNMe_2$. Typical reaction conditions: $[Rh] = 2\,mM$, $[PPh_3] = 6\,mM$, $[PEO] = 6\,mM$, $[base] = 3.5\,M$, $p(H_2) = p(CO_2) = 10\,bar$, $T = 20$–$155\,^\circ C$. Although the molar concentration of PEO is small, such a reaction mixture contains 210 g/L poly(ethylene oxide), which certainly alters the solvent properties relative to neat water.

The major product of the reaction was HCO_2H, although when using $HNMe_2$ or $HNEt_2$ as the base, small amounts of dimethyl- or diethylformamide, respectively, were also obtained. The rate of the formation of HCO_2H showed a sharp maximum as a function of the amine concentration, peaking at $[HNEt_2]/[H_2O] = 0.2$, while that of the formamide increased steadily but slightly. A similar sharp maximum was observed in the concentration of HCO_2H as a function of the poly(ethylene oxide) concentration at $[PEO] = 6\,mM$. An important feature of the reaction is that at 50 °C and under the conditions mentioned above a total turnover number of 2150 was obtained in 10 h, which corresponds to a final $[HCO_2H]/[amine]$ ratio of 1.23. The same ratio at 155 °C dropped to 0.43. Conversely, hydrogenation of CO_2 in the presence of $HNEt_2$ at 50 °C led to a $[HCO_2H]/[amine]$ ratio of 0.51 and this increased to 1.34 at 155 °C. Thus, in this system it is possible to obtain higher than stoichiometric quantitites of formic acid (relative to the amine used), albeit the $[HCO_2H]/[amine]$ ratios do not reach the 1.6–1.8 observed in purely organic solvents or in $scCO_2$.

The authors did not discuss the possible composition of the catalyst and, indeed, the data presented in the paper do not allow far-reaching conclusions in this respect. It is known [4] that in aqueous systems, especially in the presence of micellar agents or cyclodextrin derivatives the reduction of Rh^{3+} by phosphines can give rise to the formation of stabilized colloids which are highly active hydrogenation catalysts. Conversely, it was also shown that $RhCl_3$ reacts with neat poly(ethylene glycol) with the formation of $Rh(PEG)_x$

and the latter complex can be used for the hydroformylation of various olefins [37]. Further studies are required to clarify the details of this interesting catalytic system for CO_2 hydrogenations.

Ikariya's group studied the effect of water on the synthesis of dimethylformamide (DMF) in $scCO_2$ (Eq. (3)) using $RuCl_2(PMe_3)_4$ as catalyst. They have observed [38] that after certain conversions the water formed in the reaction condenses into a separate aqueous phase in the originally homogeneous system and this leads to a sharp drop in the rate of the catalytic process. The problem was circumvented by the use of water-soluble catalysts such as $RuCl_2[PH(CH_2OH)_2]_2[P(CH_2OH)_3]_2$. After the phase separation the reactions proceeded further in a water/$scCO_2$ biphasic system in which the aqueous phase contained the catalyst and the amine and/or ammonium carbonates. The comparison of $RuCl_2(PMe_3)_4$ and $RuCl_2[PH(CH_2OH)_2]_2[P(CH_2OH)_3]_2$ revealed that the latter is a robust catalyst capable of 10,000 turnovers in 48 h, while the former needed 64 h for a TON of 9600 (1.6 mmol Ru, 100 °C, $[HNMe_2]$:[Ru] = 10,000:1, $p(H_2) = 84$–86 bar, total initial pressure 216–220 bar; $HNMe_2$ was used as liquid $[H_2NMe_2]^+[OCONMe_2]^-$). The water-soluble catalyst retained its high activity even in systems with a $[H_2O]$:[amine] ratio of 2:1 (TON = 6200 in 4 h). Under the same conditions $RuCl_2(PMe_3)_4$ showed only a modest performance (TON = 710 in 4 h). $RuCl_2[PH(CH_2OH)_2]_2[P(CH_2OH)_3]_2$ outperformed $RuCl_2(PMe_3)_4$ also in the synthesis of methyl formate (Eq. (4)) with a TON of 1400 compared to 200 under comparable conditions.

$$CO_2 + H_2 + HNMe_2 \rightarrow HCONMe_2 + H_2O \qquad (3)$$

$$CO_2 + H_2 + CH_3OH \rightarrow HCO_2CH_3 + H_2O \qquad (4)$$

In another series of experiments the catalysts were prepared in situ from $[RuCl_2(COD)]_n$ and several water-soluble phosphines. Under the conditions mentioned above, the catalysts formed with the hydroxyalkylphosphines $P(CH_2OH)_3$ and $P(CH_2CH_2CH_2OH)_3$ showed high activity for DMF production, characterized by TONs of 7000 and 5500, respectively, in 16 h. In contrast, the use of the aromatic phosphines TPPTS and TPPMS led to the formation of less active catalysts (TONs of 1900 and 1100 in 16 h).

2.3. *Hydrogenation of CO_2 in amine-free solutions*

Joó's group has made extensive studies [3,28,39–44] of the hydrogenation of CO_2 in amine-free aqueous solutions. In acidic solutions (including unbuffered water under CO_2 pressure) the reactions were very slow. On the other hand, in several cases high rates were observed around pH 8 so the actual substrate of the catalytic hydrogenation could be established as HCO_3^- rather than CO_2 (Eq. (5)).

$$HCO_3^- + H_2 \rightleftharpoons HCO_2^- + H_2O \qquad (5)$$

Table 3
Catalytic activity of various Ru(II) complexes in the hydrogenation of sodium bicarbonate in aqueous solutions

Catalyst precursor	$p(H_2,CO_2)$ (atm)	T (°C)	TOF_{max} (h^{-1})	Ref.
$RuCl_2(PTA)_4$	60, 60	80	807	[3]
$[RuCl_2(TPPMS)_2]_2$	60, 35	80	9600	[28]
$RuCl_3(NO)(TPPTS)_2$	30, 10	70	400	[41]
$RuCl_3(NO)(TPPMS)_2$	30, 10	70	210	[41]
$RuCl_2(\eta^6$-*p*-cymene)(PTA)	100, 0	70	287	[42]
$[RuCl_2(\eta^6-C_6H_6)]_2$/4PTA	100, 0	80	409	[42]
$RhCl(TPPMS)_3$	37, 3	24	204	[43]
$RhCl(PTA)_3$	50, 50	50	162	[44]

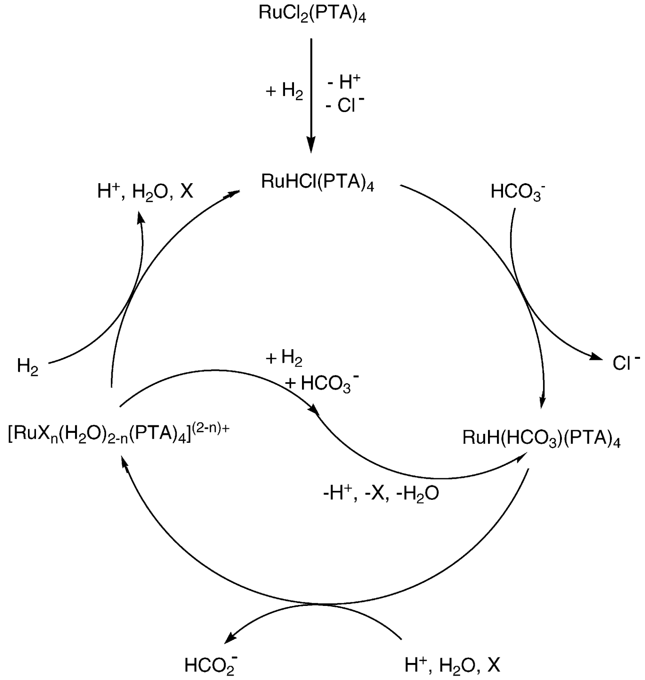
Conditions: [M] = [Ru] or [Rh] = 1.0–2.6 mM, $[PR_3]_{total}$/[M] = 2–7, $[NaHCO_3]$ = 0.2–1.0 M.

No other products than formate were detected in these reactions. In most cases there was no significant formate decomposition under the alkaline conditions provided by $NaHCO_3$ and $NaHCO_2$ so the hydrogenations could run close to completion. The catalysts studied and the highest turnover frequencies reported are shown in Table 3.

In general, the activities of the Ru- and Rh-phosphine catalysts of Table 3 in the hydrogenation of aqueous sodium bicarbonate are comparable to the activities of the Rh-based catalysts discussed in Section 2.2 for hydrogenation of CO_2 in aqueous amine solutions. This contrasts with the findings of Leitner et al. [11] who determined a turnover frequency as low as 6 h^{-1} in the case of $RuCl_2(TPPTS)_3$ in aqueous $HNMe_2$ solution under CO_2 pressure.

The kinetics of the hydrogenation of $NaHCO_3$ with the $RuCl_2(PTA)_4$ complex was studied in detail [3]. The rate of formation of HCO_2^- showed a first order dependence on the concentration of the catalyst, leveled off with increasing $[NaHCO_3]$ and varied in a slightly nonlinear manner with H_2 pressure. Increasing CO_2 pressure (i.e. decreasing pH) led to a substantial increase in the rate of the reaction. While in strongly basic solutions (pH 10.5), the reaction rate was close to zero but at pH 5.9 a TOF of 70 h^{-1} was determined. However, in the absence of $NaHCO_3$ (i.e. in aqueous solutions of CO_2) the rate of hydrogenation was only 1.8 h^{-1}. Based on this pH dependence it was concluded that the real substrate of the catalytic hydrogenation was the bicarbonate anion.

Separate high pressure ^1H and ^{31}P NMR spectroscopic studies under conditions close to those of the catalytic reactions revealed the formation of various hydride species in the reaction of H_2 with $RuCl_2(PTA)_4$ or with $[Ru(H_2O)_6](tos)_2$ + nPTA mixtures (tos = *p*-toluenesulfonate, $n = 2$–6). At pH 12, in the absence of added PTA the hydrogenation of $RuCl_2(PTA)_4$ afforded the neutral dihydride $RuH_2(PTA)_4$ as the only detectable species. Conversely, in acidic solutions (pH 2) the major hydride species was $[RuH(PTA)_4X]^{q+}$ (X = H_2O, $q = 1$ or X = Cl^-, $q = 0$). When $[Ru(H_2O)_6](tos)_2$ was hydrogenated in the presence of five PTA, formation of $[RuH(PTA)_5]^+$ was also detected; however it is unlikely to serve a catalytic role in the reactions run with $RuCl_2(PTA)_4$



Scheme 3. Possible mechanism of the hydrogenation of bicarbonate catalyzed by $RuCl_2(PTA)_4$ in aqueous solution [3]: X = Cl^-, HCO_3^-, n = 1 or 2.

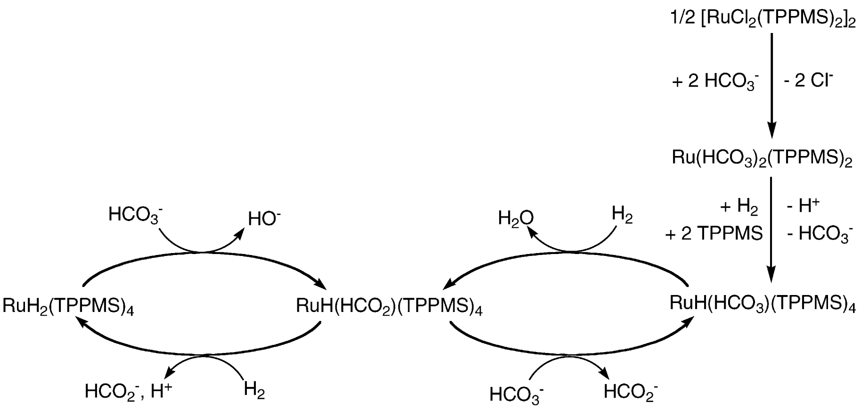
in the absence of added PTA. These NMR studies also showed no detectable phosphine dissociation from the respective hydrides. Because there was negligible catalysis in strongly basic solutions, catalysis by $RuH_2(PTA)_4$ can also be excluded, leaving $[RuH(PTA)_4X]^{q+}$ as the most likely catalytic species. Indeed, the increased reaction rates at higher CO_2 pressures could be explained with the increasing proportion of this monohydride species in acidic solutions. The suggested reaction mechanism is shown in Scheme 3.

The overall activation barrier in the hydrogenation of CO_2 with $RuCl_2(PTA)_4$ was found to be 86 kJ mol^{-1}. This is an unusually high value in comparison with the activation energies determined for $RhCl(TPPTS)_3$ (25 kJ mol^{-1} [11]) and for $K[Ru^{III}(EDTA\text{-}H)Cl]\cdot 2H_2O$ (31 kJ mol^{-1} [27]), and probably reflects the activation requirements in the slow hydride formation step in the reaction of the coordinatively saturated $RuCl_2(PTA)_4$ and H_2.

The hydrogenation of bicarbonate with the $[RuCl_2(TPPMS)_2]_2$ catalyst (precursor) was found to be similar except that this complex reacted more readily with H_2 than does $RuCl_2(PTA)_4$ and gave faster HCO_3^- hydrogenation to HCO_2^- under comparable conditions [28]. The reaction was accelerated by added TPPMS and as a function of the phosphine concentration the reaction rate showed a sharp break at $[TPPMS]_{total}/[Ru] = 4$, with only a minor rate increase with further phosphine addition. This was interpreted as showing the catalytic role of a tetrakisphosphino-species. The reaction of $[RuCl_2(TPPMS)_2]_2$ with H_2 in water had been thoroughly studied earlier, and was shown to yield (in ligand excess) $RuHCl(TPPMS)_3$ (below pH 5) and $RuH_2(TPPMS)_4$ (above pH 8) [45]. Taking the pH of the aqueous $NaHCO_3$ solutions the participation of $RuH_2(TPPMS)_4$ in the catalytic cycle is more likely. Indeed, this species was observed by NMR spectroscopic measurements in the reaction mixtures after complete conversion of bicarbonate to formate.

Reaction of $RuCl_2(TPPMS)_2$ with $NaHCO_3$ in water under argon or nitrogen afforded a sparingly soluble yellow compound which analyzed for $Ru(HCO_3)_2(TPPMS)_2$ [28]. This complex cleanly dissolved under hydrogen pressure and in stoichiometric hydrogenations yielded HCO_2^-.

Based on all these findings the overall mechanism depicted in Scheme 4 was suggested. The key species in this scheme is the hydrido-bicarbonato-ruthenium(II) complex $RuH(HCO_3)(TPPMS)_4$ (with four phosphine ligands as suggested by the kinetic measurements). As yet this species has not been observed experimentally. Its reaction with H_2 gives $RuH(HCO_2)(TPPMS)_4$ and replacement of formate by bicarbonate in the latter complex gives back $RuH(HCO_3)(TPPMS)_4$ initiating a new catalytic cycle. $RuH(HCO_2)(TPPMS)_3$ had already been detected in solu-



Scheme 4. Suggested mechanism of the hydrogenation of bicarbonate catalyzed by $[RuCl_2(TPPMS)_2]_2$ in aqueous solution [28].

tion [46], and $RuH(HCO_2)(PPh_3)_3$ had been isolated and characterized by single crystal X-ray diffraction [47,48]. Alternatively, the reaction of $RuH(HCO_2)(TPPMS)_4$ would lead to $RuH_2(TPPMS)_4$ (observed in the reaction mixtures at full conversion) and the reaction of this dihydride with HCO_3^- would afford HCO_2^- in an intermolecular hydrogen transfer step. According to these ideas, the isolated $Ru(HCO_3)_2(TPPMS)_2$ complex is not directly involved in the catalytic cycle(s). This suggestion is consistent with the reaction rate being first order with respect to the catalyst concentration, the hydrogen pressure and the concentration of $NaHCO_3$ in the low concentration regime (0.1 M). At high $NaHCO_3$ concentrations (0.5 M) a pronounced substrate inhibition was observed, which could be explained by the increased stability of $Ru(HCO_3)_2(TPPMS)_2$ against hydrogenation in the presence of a large excess of HCO_3^-.

When the reactions were run in the presence of CO_2 a very high rate increase was observed (at $p(H_2) = 60$ bar, $p(CO_2) = 35$ bar at 80 °C, a 0.3 M $NaHCO_3$ solution was hydrogenated with a turnover frequency of $9600\,h^{-1}$). It is tempting to speculate that increased CO_2 pressures lower the pH of the reaction mixtures so much that $RuHX(TPPMS)_{3,4}$ ($X = Cl^-$ or H_2O) could form in substantial amounts. Replacement of X by HCO_3^- would provide a faster entry into the catalytic cycle in Scheme 4 than the reaction of H_2 with $Ru(HCO_3)_2(TPPMS)_2$. Nevertheless, up till now no experimental evidence for such a pathway has been reported.

The nitrosyl complexes $RuCl_3(NO)(TPPMS)_2$ and $RuCl_3(NO)(TPPTS)_2$ were also studied as water-soluble catalysts for carbon dioxide/bicarbonate hydrogenation [41] based on the expectation that polarization of the Ru–H bonds by the effect of the NO ligand in the intermediate hydrides would lead to increased catalyst activities. In aqueous solutions of pH 6.0 (phosphate buffer) under 100 bar H_2, the complexes were, indeed, converted quantitatively to $RuH(NO)(L)_3$ (L = TPPMS or TPPTS). Catalysis of the hydrogenation of bicarbonate to formate was also observed with these complexes, with turnover frequencies in the 200–400 h^{-1} range which is lower than those obtained with $RuCl_2(TPPMS)_2$ but still fairly high among the known ruthenium-phosphine catalysts (Table 2). The catalytic activity showed a maximum as a function of the pH with the highest values obtained at pH 6.8. In more basic solutions the catalysts were deactivated by the formation of the nitro-complexes $RuCl_3(NO_2)(TPPMS)_2$ and $RuCl_3(NO_2)(TPPTS)_2$; this deactivation set an upper pH-limit for the hydrogenation of CO_2/bicarbonate with these complexes in aqueous solution at around pH 7.

$[RuCl_2(\eta^6\text{-}C_6H_6)]_2$ and $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ reacted with PTA under hydrogen pressure to yield the half-sandwich hydrido complexes $[RuH(\eta^6\text{-}C_6H_6)(PTA)_2]^+$ and $[RuH(\eta^6\text{-}p\text{-cymene})(PTA)_2]^+$ which catalyzed the hydrogenation of bicarbonate with fairly high turnover frequencies (Table 2) [42]. It was suggested that ion-pairing between the cationic catalyst and HCO_3^-, assisted by a hydrogen bonding interaction between bicarbonate and the nitrogen atom of one of the PTA ligands contributed to the high catalytic activity. It was also observed that further reactions of these complexes at $T = 60\,°C$ and $p(H_2) = 100$ bar lead to the slow formation of $[RuHCl(PTA)_4]$, $[RuH(H_2O)(PTA)_4)]^+$, $[RuH_2(PTA)_4]$ and $[RuH(PTA)_5]^+$, especially in the cases with added phosphine ($[PTA]_{total}/[Ru] > 2$). Thus, the loss of the η^6-arene ligand slowly transforms the catalysts into the species known from the $RuCl_2(PTA)_4$-catalyzed reactions, and for that reason the water-soluble arene–Ru(II)–phosphine complexes were not further investigated in the aqueous hydrogenation of CO_2.

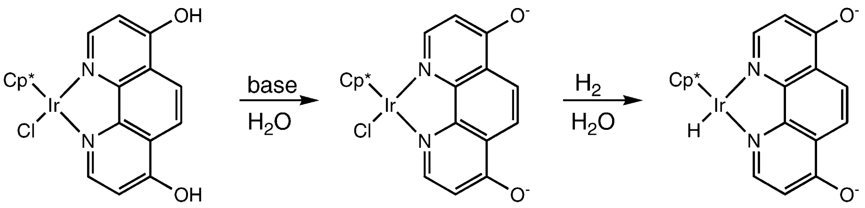
Pruchnik et al. studied the hydrogenation of CO_2 with catalysts prepared from $Rh_2(OAc)_4$ and PTA or other water-soluble small phosphines such as $P(CH_2OH)_3$ and $P(CH_2CH_2CN)_3$ [49]. The major product of the reaction was CO with a TOF of $75\,h^{-1}$, however, very interestingly, a few percent of methane was also detected (Eq. (6)). While the formation of CO is a known process (the reverse water gas shift reaction [50]), the hydrogenation of CO_2 to CH_4 is quite unusual in homogeneously-catalyzed reactions. Further investigation of this catalytic system could provide an important insight into the mechanism of CO_2 hydrogenation into products other than HCO_2H and CO.

$$CO_2 + H_2 \xrightarrow[70\,°C, H_2O\ 1\,bar, CO_2/H_2=1/1]{[Rh_2(OAc)_4]+6PTA} \underset{major}{CO} + \underset{minor}{CH_4} \qquad (6)$$

Pruchnik et al. have patented a process for the removal of carbon oxides from gases and for the manufacture of hydrocarbons, alcohols, ethylene glycol, glycerol and formic acid [51]. The process comprises the hydrogenation of CO and/or CO_2 with hydrogen in aqueous acid solutions in the presence of iridium cluster compounds $Ir_4(CO)_8(PR_3)_3$, PR_3 = diphenyl(2-pyridyl)phosphine, phenylbis(2-pyridyl)phosphine, tris(2-pyridyl)phosphine or rhodium complexes $Rh(acac)(CO)(PR_3)$, PR_3 = phenylbis(2-pyridyl)phosphine. No follow-up study of these catalytic systems has been reported.

Other catalysts for the hydrogenation of CO_2/bicarbonate include $RhCl(TPPMS)_3$ [43] and $RhCl(PTA)_3$ [44] (Table 2). It was also mentioned in the literature that the water-soluble cationic hexahydrido-ruthenium cluster $[Ru_4H_6(\eta^6\text{-}C_6H_6)_4]^{2+}$ was found to catalyze the hydrogenation of CO_2 to HCO_2H with no amine additive being required [52].

Very recently Himeda et al. [29,53] have reported very active catalyst precursors [Cp*IrCl(DHphen)]Cl and $[RuCl(C_6Me_6)(DHphen)]Cl$ containing 4,7-dihydroxy-1,10-phenanthroline (DHphen) as a ligand (Scheme 5, Cp* = C_5Me_5). In basic solution, the DHphen ligand is deprotonated, making it more electron donating. The authors suggested that this factor was responsible for the particularly high activities observed for CO_2 hydrogenation in 1 M KOH, which were as high as TON 21,000 and initial TOF 36,400 h^{-1} for the Ir complex at 120 °C.



Scheme 5. Observed transformations of the Himeda iridium catalyst in aqueous phase.

2.4. *Hydrogenation of calcium carbonate in aqueous suspensions*

The successful realization of bicarbonate hydrogenation made possible the hydrogenation of calcium carbonate. Under CO_2 pressure part of $CaCO_3$ goes into aqueous solution as calcium bicarbonate which then reacts with H_2 under the action of water-soluble catalysts; the overall process is shown in Eq. (7). This reaction produces a useful chemical: calcium formate is used in animal nutrition and leather tanning.

$$CaCO_3 + CO_2 + 2H_2 \rightleftharpoons Ca(HCO_2)_2 + H_2O \tag{7}$$

$RhCl(TPPMS)_3$ [39,54], $RuCl_2(TPPMS)_2$ [28,39] and $RuCl_2(PTA)_4$ [39] were all shown to be active for the hydrogenation of $CaCO_3$ with CO_2/H_2 mixtures. Typically the reactions were run with a suspension of 100–200 mg $CaCO_3$ in 2–10 mL water, 1 mM catalyst, $p(CO_2) = 20$ bar, $p(H_2) = 20$–80 bar in the temperature range of 20–70 °C. Under such conditions the highest TOF observed with $RhCl(TPPMS)_3$, $RuCl_2(TPPMS)_2$ and $RuCl_2(PTA)_4$ were 26.6, 18.7 and 2.5 h^{-1}, respectively.

One important property which is different in the hydrogenation of calcium carbonate relative to that of $NaHCO_3$ is the pH of the aqueous reaction medium. Under the acidic conditions due to carbonic acid formed under CO_2 pressure the decomposition of formate is fast and the equilibrium conversions of $CaCO_3$ and CO_2 can be well below 100% depending on the temperature. Detailed studies with the $RhCl(TPPMS)_3$ catalyst have shown that formate decomposition becomes negligible at or below 20 °C. At such low temperatures $CaCO_3$ could be completely hydrogenated to $Ca(HCO_2)_2$, although in rather slow reactions (TOF below 10 h^{-1}).

Perhaps the most important observation concerning the hydrogenation of $CaCO_3$ with the $RhCl(TPPMS)_3$ catalyst precursor is that the final formate concentration can substantially exceed the stoichiometric concentration defined by Eq. (7) [54]. For example, hydrogenation of 1 mmol $CaCO_3$ under 20 bar CO_2 and 80 bar H_2 at 24 °C gave 3.21 mmol HCO_2^- corresponding to 160% of the stoichiometric yield. Of the 3.21 mmol formate only 1.0 mmol had its carbon source in $CaCO_3$ and that means an efficient use of CO_2 from the gas phase.

3. Hydrogenation of CO_2 to formic acid in nonaqueous solvents

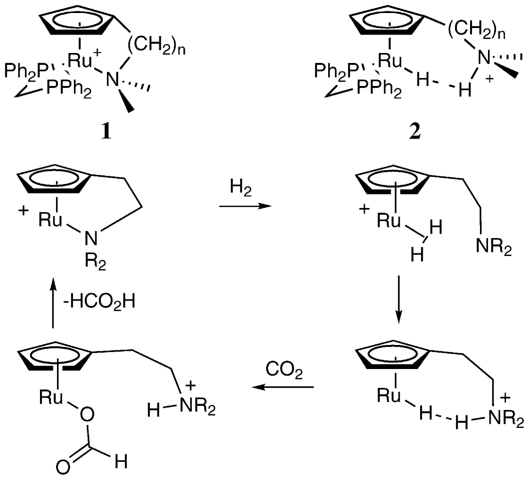
3.1. *Catalysis by ruthenium complexes bearing pendant amines*

Placement of a basic amine group on a pendant arm of a ligand has been investigated by Lau's group as a strategy for promoting the hydrogenation of CO_2 [25]. The tethered amine could influence the heterolytic activation of H_2 by replacing the external base. Alternatively or additionally, the protonated amine group could influence the CO_2 insertion step by hydrogen bonding to the CO_2 oxygen atoms. Complex 1 ($n = 2$ or 3) was found to catalyze the hydrogenation of CO_2 in the absence of added base, but the yield was very low (TON = 8) even after 16 h. One wonders if the catalytic activity would have been much higher in the presence of an added external base such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). High pressure $^{31}P\{^1H\}$ NMR spectroscopy showed that the only detectable metal complex in solution during the catalysis was complex 2, which contains a hydride–proton hydrogen bond. The fact that no formate species is detected suggests that either CO_2 insertion into the Ru–H bond is rate limiting or that no such insertion takes place in the mechanism. Because the authors observed, in a separate experiment, that CS_2 readily inserts into the Ru–H bond of complex 2, giving a dithioformate complex, and that reaction of 1 with formic acid gave 2, they proposed a mechanism involving CO_2 insertion (Scheme 6).

Hybrid density functional calculations by Matsubara [55,56] evaluated the effect of the protonated tethered amine in two possible pathways for the CO_2 insertion step of Scheme 6. In one pathway (path B of Scheme 7), CO_2 inserts after coordination to a site liberated by phosphine dissociation. In the other pathway (path A), CO_2 inserts without prior coordination. They found that the proton on the tether hydrogen-bonds to the O atoms of the CO_2, increasing the electrophilicity of the CO_2 carbon and lowering the energy of the transition state in path A only. As a result, path A was found to be more favorable for this complex.

3.2. *Catalysis by ruthenium trimethylphosphine complexes*

As described in the previous review [1], the Noyori's group reported the highly active catalyst precursors

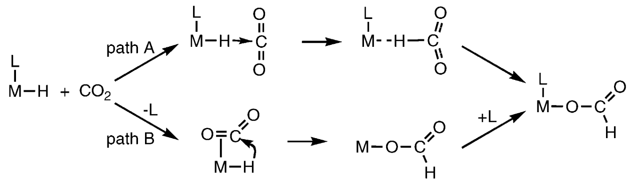


Scheme 6. A proposed mechanism involving a protonated tether.

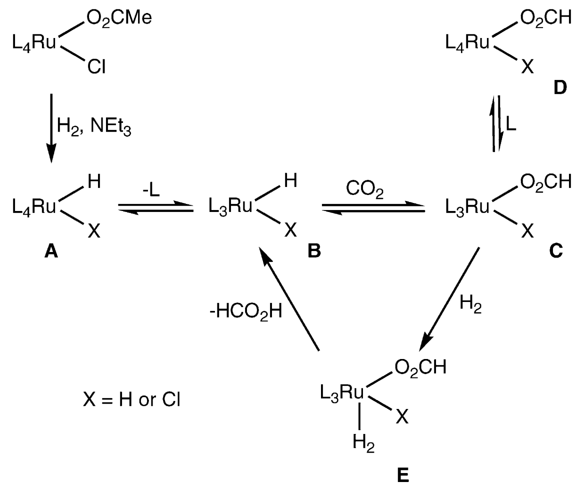
$RuXY(PMe_3)_4$ (X, Y = H, Cl, or acetate) for the hydrogenation of supercritical CO_2 [20,21,57–62]. It was not clear at the time, however, why the reaction was found to be more rapid in supercritical CO_2 than in several common organic solvents. In order to address this question, the Jessop group [63] more recently investigated the kinetics of the CO_2 hydrogenation, using the $RuCl(OAc)(PMe_3)_4$ precursor, which has the advantages of having the high activity and negligible induction period of the $RuH_2(PMe_3)_4$ precursor but having the greater ease of handling of the $RuCl_2(PMe_3)_4$ complex. The kinetic studies were performed in liquid NEt_3 and at subcritical CO_2 pressures because unavoidable phase behaviour changes interfere with kinetic studies at supercritical conditions. The results showed that the hydrogenation is first order in both H_2 and CO_2, consistent with a CO_2-insertion mechanism as originally proposed (Scheme 8).

Curiously, addition of the inert gas CHF_3 to the reaction mixture during the reaction catalyzed by $RuCl(OAc)(PMe_3)_4$ was found to increase the rate of the reaction, while ethane decreased the rate; the cause of the effect is believed to be the alteration of the solvent properties (mass transport, H_2 solubility, and dielectric constant) by the dissolution of these gases in the liquid solvent [63].

The above mechanism (Scheme 8, where X = H) was evaluated by Musashi and Sakaki [36], using ab initio calculations on the model catalyst $RuH_2(PH_3)_4$. They predicted that the CO_2 insertion (A to D) must proceed by ligand dissociation before CO_2 insertion, and that the hydrogenolysis step (E to B) must proceed by a six-membered transition state (Scheme 9).

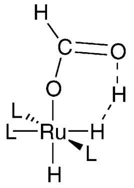


Scheme 7. Alternative pathways for CO_2 insertion into a metal–hydride bond.

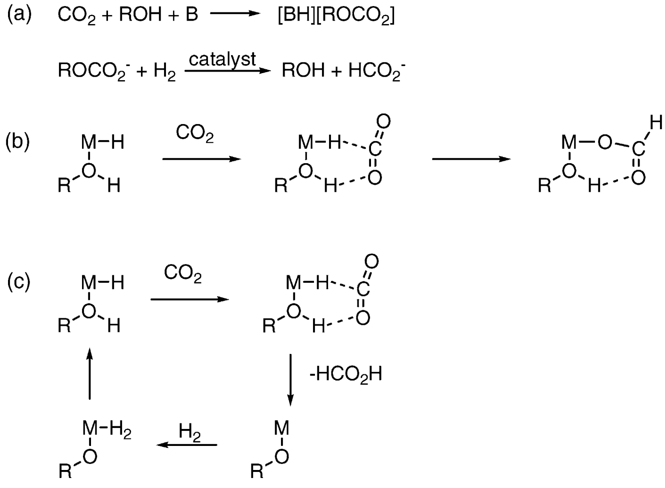


Scheme 8. The neutral mechanism for CO_2 hydrogenation by RuHX $(PMe_3)_4$ and related complexes.

Alcohols, as well as water, were found to promote the reaction, in concert with the $RuCl(OAc)(PMe_3)_4$ catalyst precursor. Water and methanol were already known to be reasonably effective [21,63], but alcohols having sufficient acidity to protonate the amine, such as pentafluorophenol, 3,5-bis(trifluoromethyl)phenol, 2,4-dinitrophenol, and even triflic acid were found by Jessop's group to be significantly more effective at promoting the hydrogenation [22]. Acidic promoters having non-coordinating conjugate bases were not effective, including HBF_4 and 2,6-di-*tert*-butylphenol. The fact that only trace quantities of the alcoholic promoters are required suggests that they act not by modifying the solvent but by some direct involvement in the mechanism. Several possibilities have been considered, including the possibilities (Scheme 10) that (a) the reaction proceeds not by hydrogenation of CO_2 directly but rather by the hydrogenation of an alkylcarbonate anion; (b) the alcohol helps to bind the CO_2 while it is being inserted into the M–H bond; and (c) the CO_2 is being hydrogenated by a concerted ionic hydrogenation as postulated by Noyori for ketone hydrogenation. The first of these was discredited by the observation that an isolated alkylcarbonate salt could not be hydrogenated by H_2 in the presence of the $RuCl(OAc)(PMe_3)_4$ catalyst precursor [22]. The other two mechanisms in Scheme 10 were more difficult to evaluate. The role of alcohol remained enigmatic.



Scheme 9. A six-membered transition state for hydrogenolysis.



Scheme 10. Three possible explanations for involvement of alcohol in the CO_2 hydrogenation.

The choice of amine also was found to have a significant effect on the rate of CO_2 hydrogenation by these Ru complexes (as was found for the Rh system by Leitner and co-workers [64]). While most studies used NEt_3, Munshi et al. [22] found that a significant increase in rate could be obtained by using DBU as the base. Insoluble bases are ineffective [21,22]. The effectiveness of DBU may be related to the ability of DBU to trap CO_2 as a stable 1:1 adduct [65,66].

The mechanism shown in Scheme 8 has several weaknesses. It explains neither the effect of alcohol promoter nor the effect of base. It is inconsistent with the fact that a 20-equivalent excess of added PMe_3 fails to slow the reaction [21]. Musashi and Sakaki's [36] ab initio calculations showed that the CO_2 insertion into the Ru–H bond requires prior coordination of the CO_2 molecule in a site made available by the dissocation of a ligand.

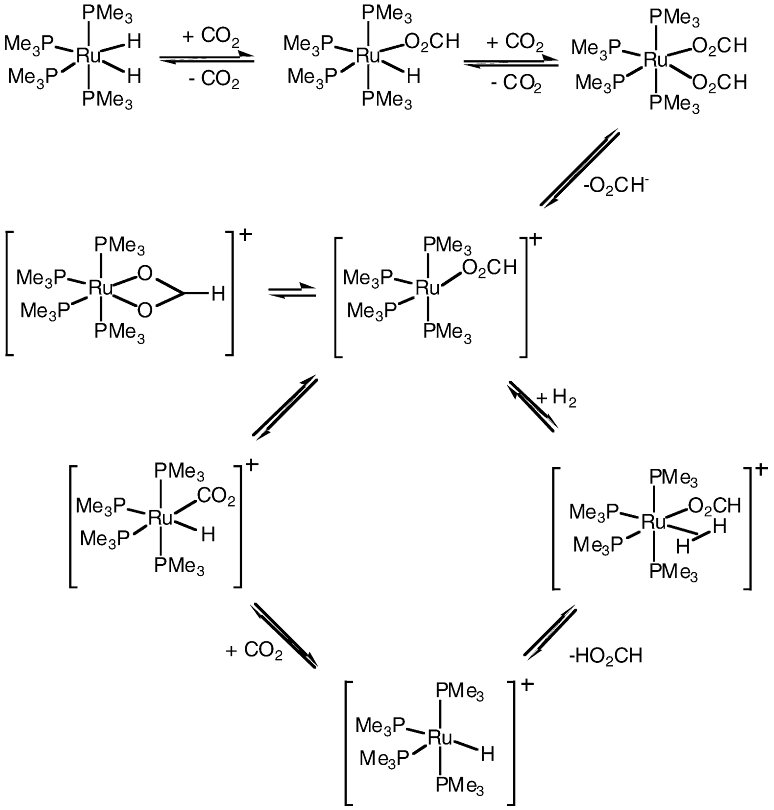
The groups of Linehan and Jessop combined to use high pressure NMR spectroscopy to re-evaluate the mechanism for the reaction catalyzed by $RuXY(PMe_3)_4$ and the role of the alcohol. First [22], they eliminated the possibility that the reaction proceeds by hydrogenation of an alkyl carbonate ($ROC(O)O^-$) formed by the reaction of ROH with CO_2; the complex $RuCl(OAc)(PMe_3)_4$ was found to be completely ineffective for the hydrogenation of the isolated carbonate $[DBUH][O_2COMe]$. They also found that $RuCl(OAc)(PMe_3)_4$ does indeed readily lose one PMe_3 ligand in solution, but the resulting isolable complex $RuCl(\eta^2\text{-}OAc)(PMe_3)_3$ is not as effective a catalyst as the original [67]. Most interestingly, however, they found that added *o*-cresol or methanol causes the conversion of $RuCl(OAc)(PMe_3)_4$ to $[Ru(\eta^2\text{-}OAc)(PMe_3)_4]Cl$, but *tert*-butanol and 2,6-di-*tert*-butylphenol had little or no effect. This trend among the alcohols exactly matches the trend in the effectiveness of the alcohols to promote the hydrogenation of CO_2, suggesting that the promotion effect and the conversion of the complex to $[Ru(\eta^2\text{-}OAc)(PMe_3)_4]Cl$ are related. Further, the isolated catalyst precursor $[Ru(\eta^2\text{-}OAc)(PMe_3)_4]BAr_4$ (Ar = C_6H_5 or $C_6H_3(m\text{-}CF_3)_2$) catalyzes the hydrogenation of CO_2 as rapidly as does $RuCl(OAc)(PMe_3)_4$ and without the need for an acidic alcohol as a promoter. This evidence, along with in situ NMR detection of a number of species, led the researchers to propose that a role of the alcohol is to promote the liberation of an anionic ligand to generate a cationic species. A cationic mechanism, involving generation of an active site not by dissociation of a phosphine but by dissociation of an anionic ligand, is consistent with this hypothesis and the spectroscopic and kinetic evidence (Scheme 11).

3.3. Catalysis by other ruthenium complexes

Other Ru(II) complexes found to be active for the hydrogenation of CO_2 include $TpRuH(PPh_3)(MeCN)$, $CpRu(CO)(\mu\text{-}dppm)Mo(CO)_2Cp$, *cis*-$[Ru(Cl_2bpy)_2(H_2O)_2](O_3SCF_3)_2$, all reported by Lau's group (Tp = tris(pyrazolyl) borate, dppm = $Ph_2PCH_2PPh_2$, Cl_2bpy = 6,6′-dichloro-2,2′-bipyridine). The last of these three has produced the greater yield of formic acid, up to 5000 TON after 8 h, albeit at the very high temperature of 150 °C [24]. The Ru/Mo heterobimetallic complex had low activity for CO_2 hydrogenation [30]. The first complex was studied in some detail [23]. Like many other catalysts for this reaction [14,18,21,22], it was found to afford higher rates in the presence of water. High pressure NMR showed that the complex is converted to $TpRuH(H_2)(PPh_3)$, $TpRu(O_2CH)(MeCN)(PPh_3)$ and more slowly to $TpRuH(CO)(PPh_3)$ at 80 °C in dry THF-d8 under CO_2 and H_2 pressure. In the absence of H_2, $TpRuH(PPh_3)(MeCN)$ was converted into two formate complexes of unknown structure; the authors suggested the hydrated formate structures shown in the proposed mechanism (Scheme 12).

Density functional theory calculations by Yin et al. [23] evaluated the proposed mechanism in Scheme 12. The mechanism is a simple CO_2 insertion followed by hydrogenolysis mechanism, albeit modified to include stabilizing effects of water molecules. The hydrogen bonding with the water molecule lowered the transition state energy from 134 to 109 kJ/mol, although even this energy seems too high considering that the reaction is extremely rapid. As an alternative mechanism, the authors suggested a possible concerted ionic hydrogenation adapted from Noyori's mechanism for ketone hydrogenation by Ru(II) hydride amine complexes (cf. Scheme 10c), but no detailed calculations were performed to evaluate that possibility.

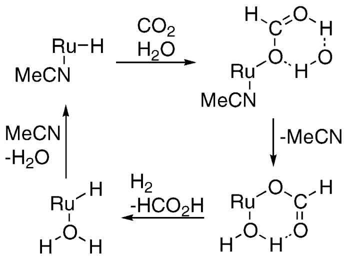
The diruthenium complex $Ru_2(CO)_5(dppm)_2$ was found by Puddephatt's group [16] to be active for CO_2 hydrogenation. Turnover frequencies as high as $207\,h^{-1}$ in the first hour and total yields of 2160 TON were obtained at room temperature. Unfortunately, kinetic studies were not possible, but an NMR spectroscopic study of the reverse reaction,



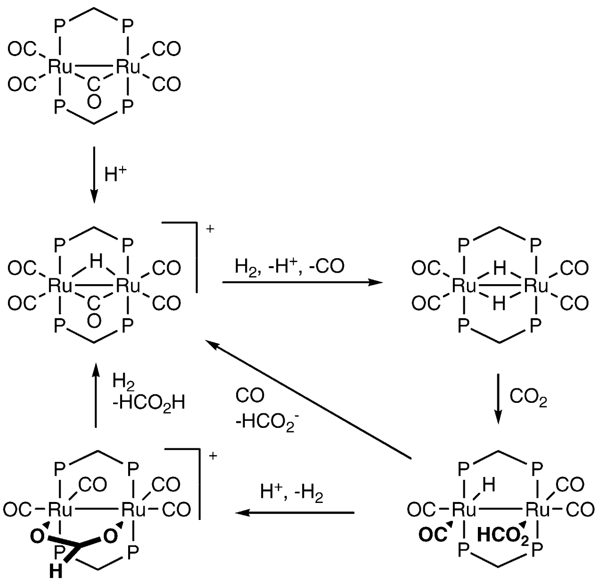
Scheme 11. The cationic mechanism for CO_2 hydrogenation by $RuH_2(PMe_3)_4$ and related catalyst precursors $RuXY(PMe_3)_4$ (X, Y = H, Cl, OAc).

the decomposition of formic acid, detected the presence of five complexes, all shown in Scheme 13. The structure of the hydrido formate species (bottom right) was uncertain. During the forward (hydrogenation) reaction, only the left three species were detected spectroscopically. The detected species could be linked together to form a proposed mechanism.

Zhang et al. [17] in China used $RuCl_3$ and PPh_3 together to form an in situ catalyst in $EtOH:H_2O$ (5:1) solvent with NEt_3 base at 60 °C. The Ru-containing product after catalysis was $RuH_2(CO)(PPh_3)_3$, indicating that CO formation or at least decarbonylation of formic acid or ethanol had taken place. Addition of free CO gas poisoned the catalyst, producing catalytically inactive $Ru(CO)_3(PPh_3)_2$. A mechanism qualitatively similar to Scheme 8 (with X = H and L_4 = $(CO)(PPh_3)_3$) was proposed, but with the important difference that the CO_2 was proposed to insert into the Ru–H



Scheme 12. Possible mechanism for the hydrogenation of CO_2 catalyzed by $TpRuH(PPh_3)(MeCN)$ [23]. The Tp and PPh_3 ligands are omitted for clarity. All steps are likely to be reversible, but forward direction only is shown.



Scheme 13. Possible mechanism for the hydrogenation of CO_2 catalyzed by $Ru_2(CO)_5(dppm)_2$ [16]. All steps are likely to be reversible, but forward direction only is shown.

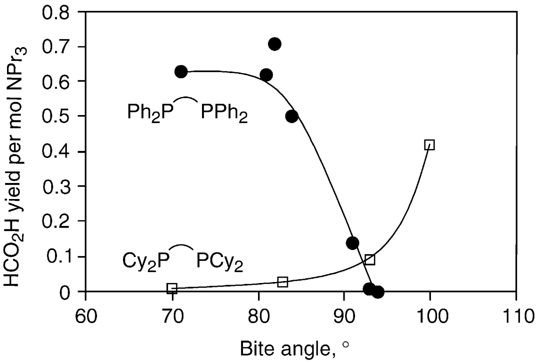


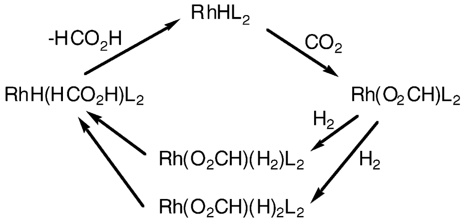
Fig. 1. Dependence of the formic acid yield in the first hour of reaction on the bite angle of the diphosphine ligand. The catalyst was formed in situ from $[RuCl_2(C_6H_6)]_2$ and two equivalents of the diphosphine (reprinted with permission from Tai et al., Inorg. Chem. 41 (2002) 1606, copyright 2002 American Chemical Society [68]).

bond without prior dissociation of a ligand (i.e. going from A to D directly in the scheme).

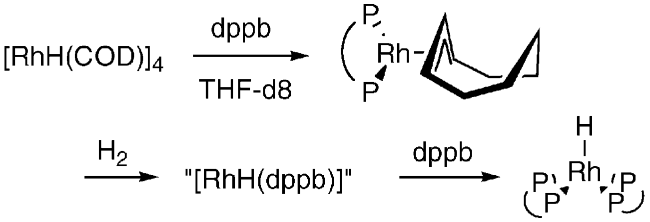
In situ catalyst formation was used by Tai et al. [68] to compare the effectiveness of Ru(II) catalysts with 44 different phosphine ligands, in an approach reminiscent of Leitner's studies with $[RhCl(cod)]_2$ (see Section 3.5). Each combination contained the Ru(II) precursor $[RuCl_2(C_6H_6)]_2$ and either three equivalents of a monophosphine (PR_3) or two equivalents of a diphosphine, all in 0.5 mL each of MeOH and N^nPr_3. Overall, the monophosphines showed no correlation whatsoever with the basicity of the phosphine, suggesting that electronic factors do not dominate. In a subset of the monophosphines, the trialkylphosphines, the activity of the catalyst was inversely dependent on the cone angle of the phosphine, with PMe_3 being by far the most active. The only other monophosphines with comparable activity were PMe_2Ph and $P(C_6H_4pF)_3$. Among the diphosphines, a rather unusual interplay of electronic and bite angle effects was observed (Fig. 1). For the bis(diphenylphosphino) compounds, higher bite angle ligands generated inferior catalysts while for the bis(dicyclohexylphosphino) compounds, the higher bite angle ligands were superior. The reason for the apparently contradictory trends is not known. The most active diphosphine-containing catalysts were those containing $Ph_2P(CH_2)_nPPh_2$ ($n = 1$ or 2) or *cis*- or *trans*-$Ph_2PCH{=}CHPPh_2$ (the last of these being incapable of chelating).

3.4. Catalysis by [RhH(diphosphine)]

The combination of $[RhH(COD)]_4$ and dppb was found by Leitner et al. [7] to generate an extremely active catalyst, presumably [RhH(dppb)]. NMR studies in THF-d8 revealed some details of the reaction pathway from the COD complex to a phosphine hydride complex (Eq. (8)). The slow reaction with H_2 in this sequence was believed to be the reason for the induction period observed in some solvents.

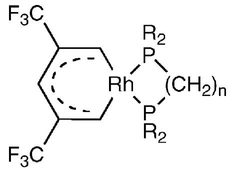


Scheme 14. Mechanisms evaluated for hydrogenation by RhH(dppb) or $RhH(PH_3)_2$.



(8)

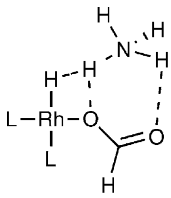
Leitner's group [13,69] described a new series of Rh(I) precursors (structure **3**, $n = 2, 3,$ or 4, R = Ph, Cy, or ^{i}Pr), the most active being that containing the dcpb ligand (R = Cy, $n = 4$). That precursor catalyzed the reaction at a rate of 1335 h^{-1} at only 25 °C. A general relationship between the P–Rh–P bite angle, the catalytic rate, and the ^{103}Rh NMR chemical shift was observed; the larger the bite angle the greater the chemical shift and the greater the rate of catalysis. However, a more accurate correlation was found between the rate and the accessible molecular surface (AMS) calculated for the Rh(diphosphine) fragment; the smaller the AMS the greater the rate. A kinetic study of the system (with dppb, R = Ph, $n = 4$) showed that the rate dependence was first order in Rh, roughly first order in CO_2 pressure, and saturation kinetics in H_2 pressure, consistent with a mechanism involving sequential reactions of the active catalyst (probably RhH(dppb)) with CO_2 and then H_2 followed by a rate limiting step releasing formic acid (e.g. the cycle shown in Scheme 14) [64].



3

Ab initio MP2 calculations were used by Hutschka et al. [64,70] to evaluate two versions of the proposed mechanism of hydrogenation of CO_2 by RhH(dppb). The two evaluated mechanisms (Scheme 14) both involve CO_2 insertion into the Rh–H bond of $RhHL_2$ (L_2 = dppb in the experiments, $2PH_3$ in the calculations) but differ in the step involving H_2. One pathway proceeds by oxidative addition of H_2, giving a dihydride, followed by reductive elimination of formic acid. The other pathway proceeds by coordination of H_2, giving a molecular hydrogen complex, followed by "sigma bond metathesis” or transfer of a proton to the formate by a four-centred transition state. The calculations showed that the dihydride was thermodynamically more stable than the molecular hydrogen complex but that the reductive elimination had a much larger activation energy than the sigma bond metathesis. The authors thus concluded that the more likely mechanism was the metathesis route.

Further calculations by the same group explored the role of external base on the metathesis step of this mechanism [71]. A base-assisted proton transfer mechanism, through an intermediate of structure **4**, was found to be energetically more facile than the unimolecular pathway (structure **5**). The assistance of base in such a step may be one reason for the dependence of the rate of hydrogenation on the concentration and choice of amine in many such catalytic systems. Although the trialkylamines that are usually used as bases are not capable of hydrogen-bonding to the carbonyl of the formate ligand as shown in structure **4**, they are still expected to lower the barrier. Another potential reason for the effect of base is assistance of external base in the rate-limiting dissociation of formic acid later in the catalytic cycle.



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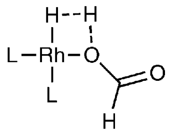
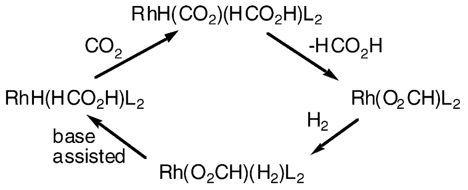


5

The elimination of the formic acid from $RhH(HCO_2H)L_2$, regenerating $RhHL_2$, completes the catalytic cycle, but this step was calculated to be highly endothermic [64,70,72]. It was found, experimentally and by calculation, to be the rate determining step. Density functional calculations by Pomelli et al. [72] showed that an associative mechanism, involving coordination of CO_2 before HCO_2H dissociation, had a far lower barrier and was therefore a more likely mechanism than the dissociative mechanism shown in Scheme 14. The overall mechanism, combining the lowest-energy routes according to the papers of Pomelli et al. and Hutschka et al., is shown in Scheme 15.

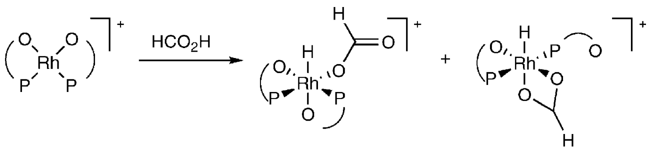
3.5. Catalysis by other Rh complexes

Using in situ combinations of phosphines and $[RhCl(cod)]_2$ in DMSO solution, Graf and Leitner evaluated the effect of the phosphine choice on catalytic activity [73]. Among the triarylphosphines, those with intermediate basicity, such as $P(C_6H_4pMe)_3$, had the highest activity. *ortho*-Substituted triarylphosphines were inferior. Among the diphosphines, dppb was the most active, while in the series $R_2PCH_2CH_2PR_2$ (R = alkyl) the activity increased with increasing steric bulk of the R group.



Scheme 15. Optimized mechanism for hydrogenation by “$RhHL_2$”.

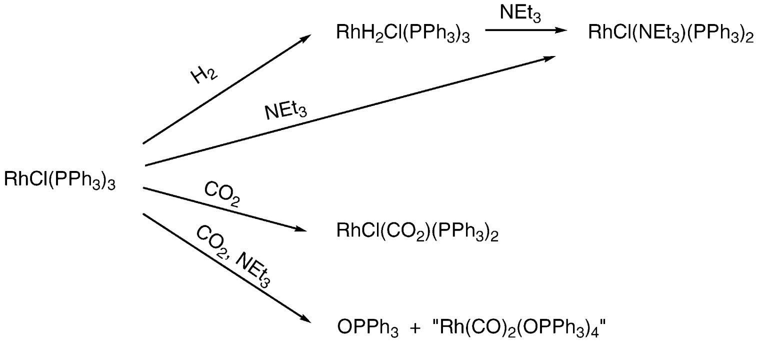
Lindner et al. [12] speculated that a particularly active catalyst precursor would contain a mixture of phosphine and weaker ligands, so that active sites would be readily available. The chelating hemilabile ligand $Cy_2PCH_2CH_2OMe$, here referred to as P-O, was used in the catalyst precursors $RhCl(\eta^2\text{-P-O})(\eta^1\text{-P-O})$ and $[RhCl(\eta^2\text{-P-O})_2]BPh_4$. Only the latter was active, giving formic acid in up to $100\,h^{-1}$. Stoichiometric experiments showed that the complex reacts with formic acid to give isomeric formato species (eq. 9) which could, conceivably, be part of the catalytic cycle.



(9)

The effectiveness of Wilkinson’s catalyst, $RhCl(PPh_3)_3$, as a catalyst precursor for CO_2 hydrogenation was first noticed by Inoue et al. in 1976 [18]. The use of this complex has recently been studied in more detail by Ezhova et al. [8] who found that the hydrogenation is strongly solvent dependent, giving high rates in DMSO and especially MeOH and essentially no reaction in solvents such as THF, benzene, heptane and water. The activity also increased if three equivalents of PPh_3 were added to the solution. A range of other Rh(I) catalyst precursors, with or without added phosphines, were less active. NMR spectroscopy was used to study a number of reactions of $RhCl(PPh_3)_3$ with individual components and combinations of reagents, as summarized in Scheme 16. During the actual hydrogenation of CO_2, the predominant detectable Rh-containing species was initially $RhH_2Cl(PPh_3)_3$ but was thereafter $RhCl(NEt_3)(PPh_3)_2$. The reduction of the latter complex to metallic Rh is inhibited by excess PPh_3.

A very recent computational study may explain why rhodium(III) complexes have received less attention than Rh(I) complexes as catalysts for CO_2 hydrogenation. The mechanisms in the present review include CO_2 insertions into Rh(I)–H or Ru(II)–H bonds only. A notable earlier example was Tsai and Nicholas’ $[Rh(diene)(PMe_2Ph)_3]BF_4$ precursor which is converted to $[RhH_2(PMe_2Ph)_3(solvent)]^+$ (solvent = THF or water) in situ; the proposed mechanism for catalysts involved CO_2 insertion into the Rh(III)–H bond [14]. Musashi and Sakaki [74] have now used DFT calculations to show that the barrier to CO_2 insertion into a metal–hydride bond increases



Scheme 16. Reactions between Wilkinson's catalyst and reagents involving in CO_2 hydrogenation [8].

in the order:

$$RhH(PH_3)_2 < RuH_2(PH_3)_3 < [RhH_2(PH_3)_2(OH_2)]^+ < [RhH_2(PH_3)_3]^+$$

This suggests that CO_2-insertion is more likely to be rate limiting, and the catalysis sluggish as a result, for Rh(III) than for Rh(I) or Ru(II). The trends in barriers to insertion are entirely electronic, and do not involve any steric or hydrogen-bonding interactions. The main reason for the trend is the greater M-formate bond strength in the Rh(I) and Ru(II) formates than the Rh(III) formates. The reason for the lower barrier in Rh(I) than Ru(II) is the stronger M–H bond in the Ru(II) complex.

For the Rh(III) complexes $[RhH_2(PH_3)_2(OH_2)]^+$ and $[RhH_2(PH_3)_3]^+$, Musashi and Sakaki's calculations [74] showed that subsequent steps in the catalytic cycle do not have barriers as large as the CO_2 insertion. The computational result that the water-containing complex should have a lower barrier for CO_2 insertion than does the water-free complex matches the experimental result that addition of water accelerates the reaction. Although it has been proposed in the past [14] that a water ligand promotes the reaction by hydrogen-bonding to stabilize the CO_2 during the insertion, the calculations show that the barrier-lowering effect of water as a ligand does not involve any hydrogen-bonding interactions.

3.6. Catalysis by complexes of other transition metals

There has been very little work on finding active catalysts containing metals from outside the platinum group. Inoue et al. in 1976 reported that $Ni(dppe)_2$ could catalyze the hydrogenation, giving formic acid in very low yield [18]. Yamaji [9,19] in 1981 tested three such metal complexes, $CoH_3(PPh_3)_3$, $CoCl_3(PPh_3)_3$ and $NiCl_2(PPh_3)_2$ for their activity for the hydrogenation of CO_2 at 100 °C and 42–50 bar pressure (1:1, H_2:CO_2), with Na_2CO_3 as the base. He found that they were inactive. Mo and Fe complexes have been found to be catalytically active for the decomposition of formic acid to CO_2 and H_2 [75,76] and would therefore likely be catalysts for the reverse.

Combinatorial methods have been used to test the activity of various combinations of metal salts with phosphine or amine ligands. Jessop's group [34] found that a surprising number of combinations had at least some activity for CO_2 hydrogenation, even with metals outside the platinum group. A few, including combinations of $FeCl_3$, $NiCl_2$, or $MoCl_3$ with dcpe, were investigated in more detail using more conventional techniques and found to have significant activity. The isolated complex $NiCl_2(dcpe)$ catalyzed the reaction at a rate of $20\,h^{-1}$ and to a yield of 4400 TON, certainly inferior to the results with Rh and Ru catalysts but respectable considering that the system has not been optimized.

4. Synthesis of formamides

At the time of the previous review, by far the most efficient method for preparing dimethylformamide (DMF), using a homogeneous catalyst and CO_2, was by reacting Me_2NH, H_2, and supercritical CO_2 using $RuCl_2(PMe_3)_4$ as catalyst (Eq. (10)). Not long afterward, this method was used to prepare DMF with a TON of 420,000 and with complete selectivity [21]. The reaction was found, by spectroscopic measurements of the reaction mixture at partial conversion, to proceed via CO_2 hydrogenation to the formate salt, followed by dehydration to the formamide. That method, however, was only efficient for producing dimethylformamide (DMF) from dimethylamine. The reaction was slow or completely failed if the method was used to prepare other dialkylformamides from the corresponding dialkylamines. Since then, the method has been improved by several groups, with the identification of another highly effective catalyst and the discovery of ways to extend the method to other formamides.

$$R_2NH + CO_2 + H_2 \xrightarrow{\text{catalyst}} [R_2NH_2][O_2CH] \rightarrow R_2NC(O)H + H_2O \qquad (10)$$

Baiker's group [77] discovered that $RuCl_2(dppm)_2$ and in particular $RuCl_2(dppe)_2$ are even more active than $RuCl_2(PMe_3)_4$, giving DMF with TON as high as 740,000 and TOF as high as $360{,}000\,h^{-1}$. While these results were obtained at supercritical pressures, TOF as high as 150,000 h^{-1} could be obtained even at subcritical pressures. The $RuCl_2(dppe)_2$ catalyst was also superior in catalyzing the synthesis of methyl formate from CO_2, H_2, and MeOH, giving a TOF of 830 h^{-1}, the highest yet reported for that reaction.

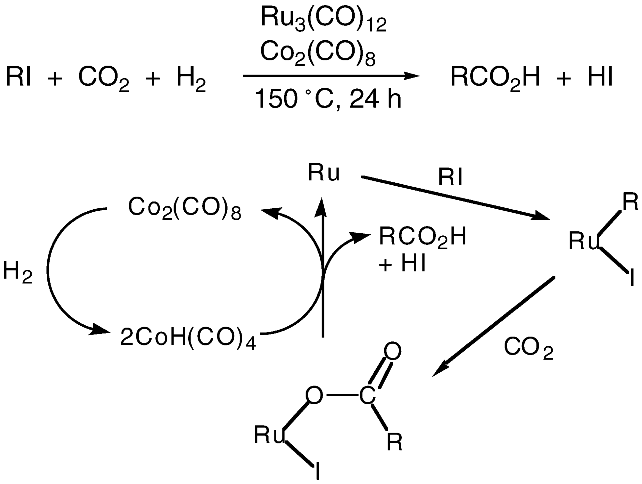
Heterogenized versions of Ru(II) catalyst precursors for the DMF synthesis have been reported by two groups. Sol–gel, silica- and aerogel-supported analogues of $RuCl_2(dppm)_2$, $RuCl_2(dppp)_2$, $RuCl_2(PMe_3)_4$ and related complexes were found by Baiker's group [78–81] to have both recyclability and very respectable turnover frequencies. Ikariya's group prepared a $RuCl_2(diphosphine)_2$ catalyst supported on a poly(styrene) poly(ethylene glycol) crosslinked graft copolymer resin [82].

Some work has been performed on extending the reaction to the formation of higher formamides. Liu et al. [83] showed that the $RuCl_2(dppe)_2$ catalyst could be used in ionic liquid for the synthesis of di-*n*-propylformamide from CO_2, H_2, and di-*n*-propylamine. The product could be extracted from the ionic liquid with supercritical CO_2 and the catalyst/ionic liquid solution recycled. This reaction would have been difficult in a monophasic $scCO_2$ system because the dipropylamine starting material would have precipitated as a solid insoluble carbamate. Preliminary experiments in the Jessop's group have shown that liquid polymers can also serve as the liquid phase for the production of such formamides [84]. Jessop's group has also extended the original solvent-free method to the conversion of aniline to formanilide (Eq. (11)) [85]. Aniline is a particularly difficult amine because it is not a strong enough base to promote the hydrogenation of CO_2 to formic acid, a necessary first step in the preparation of the formamide. However, addition of a stoichiometric quantity of DBU rectifies this problem and allows formanilide to be prepared in 72% isolated yield. Because the DBU is not consumed in the reaction, it could presumably be recycled, although this was not attempted.

$$\begin{aligned} &PhH + CO_2 + H_2 + DBU \\ &\quad \xrightarrow[100\,^{\circ}C]{RuCl_2(PMe_3)_4} [DBUH][O_2CH] + PhNH_2 \\ &\quad \rightarrow PhNH_2NC(O)H + H_2O + DBU \end{aligned} \tag{11}$$

5. Synthesis of other products

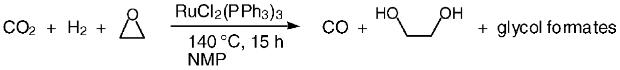
Carboxylic acids have been prepared from methyl iodides, CO_2 and H_2 (Eq. (12), formation of [BH]I assumed). Fukuoka et al. [86] found that the hydrogenation with a 10:1 ratio of $Co_2(CO)_8$ and $Ru_3(CO)_{12}$ as catalysts gave up to 17 TON of acetic acid (with respect to the moles of Ru atoms). Similarly, benzoic acid and propanoic acid could be obtained in low yield from PhI and EtI, respectively. Byproducts from these reactions were CO from CO_2 hydrogenation and methane, benzene, or ethane from RI hydrogenation. It would be instructive to determine why these reactions formed alkanoic acids from alkyl halide while catalysts such as $RuCl_2(PPh_3)_4$ and carbonyl anions of Cr and W under similar conditions gave alkyl formates instead [87,88] (see section V of the earlier review [1]). Fukuoka et al. reported that addition of methyl formate to the reaction mixture did not increase the yield of acetic acid, which rules out the possibility that acetic acid forms by isomerization of methyl formate. Similarly, addition of CO did not increase the yield, so the reverse water-gas shift reaction is also an unlikely pathway. Thus a pathway involving CO_2 insertion was proposed (Scheme 17).



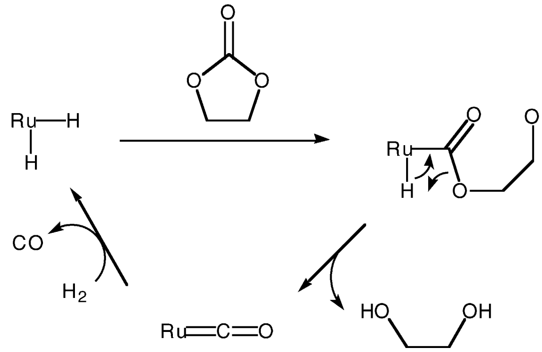
Scheme 17. Proposed mechanism for the preparation of carboxylic acids.

$$RI + CO_2 + H_2 \xrightarrow[150\,^{\circ}C, 24\,h]{Ru_3(CO)_{12}\ Co_2(CO)_8} RCO_2H + HI \tag{12}$$

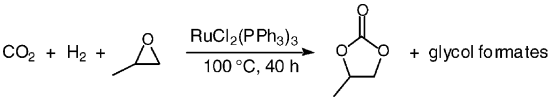
Reduction of CO_2 to CO is thermodynamically favourable only at elevated temperatures. The reaction is more favourable, even at lower temperatures, if there is a dehydrating reagent to drive the reaction by removing the water. Sasaki's group reported that in the presence of *N*-methylpyrrolidine (NMP) and ethylene oxide (which absorbs the water to give ethylene glycol), CO_2 is readily hydrogenated to CO in 71% yield (Eq. (13)), significantly higher than allowed in the absence of the dehydrating agent. An equimolar amount of ethylene glycol was produced, in addition to small quantities of ethylene glycol monoformate. Surprisingly, no ethylene carbonate was detected among the products, even though in the absence of amine, as reported by Koinuma et al. [89] many years ago, one obtains high yields of cyclic carbonate (Eq. (14)). Ethylene carbonate is, in fact, detected in the early stages of reaction (13), but it soon disappears, suggesting that the pathway for CO formation is hydrogenation of the cyclic carbonate (Scheme 18).



(13)



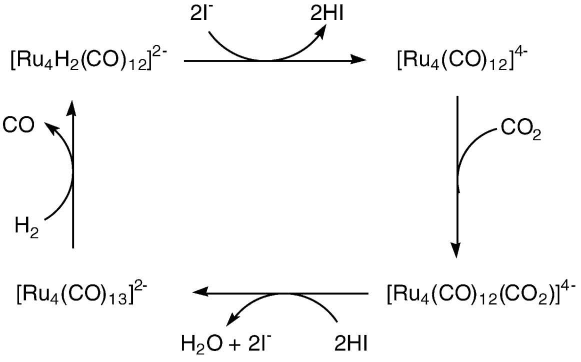
Scheme 18. Proposed mechanism for CO formation via hydrogenation of a cyclic carbonate.



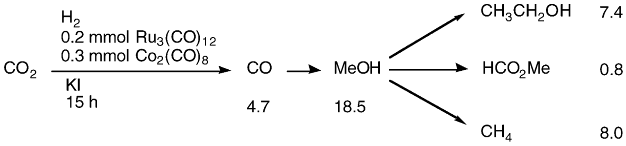
(14)

Methanol from CO_2 hydrogenation catalyzed by $Ru_3(CO)_{12}$/KI was reported by Sasaki's group [90] and described in the earlier review paper [1]. Those researchers published more details in a full paper in 1995 [91]. Monitoring the reaction at 240 °C revealed that the initial products are CO and then methanol, following which methane begins to form. In situ IR spectroscopy detected several species, including $[HRu_3(CO)_{11}]^-$, $[RuI_3(CO)_3]^-$, $[Ru_4H_3(CO)_{12}]^-$ and $[Ru_4H_2(CO)_{12}]^{2-}$. A mechanism for the reduction of CO_2 to CO was proposed (Scheme 19). The subsequent reduction of CO to methanol is believed to proceed by Dombek's mechanism [92], but the details of that rather complicated mechanism fall outside the scope of this review.

Hydrogenation of CO_2 to C2 products is obviously an important potential route to the synthesis of larger organic products from waste CO_2. Sasaki's group have reported the reduction of CO_2 to ethanol catalyzed by $Ru_3(CO)_{12}$/$Co_2(CO)_8$/KI [93]. Monitoring the reaction at 200 °C showed that after the formation of methanol via CO, the other products begin to form (Scheme 20, with mmol yield of each product shown). The optimum solvent was 1,3-dimethyl-2-imidazolidinone (DMI). The Ru complex $Ru_3(CO)_{12}$ is believed to be primarily responsible for the reduction of CO_2 to MeOH, while the $Co_2(CO)_8$ is responsible for the methanol homologation with CO.



Scheme 19. Proposed mechanism for the hydrogenation of CO_2 to CO.



Scheme 20. The hydrogenation of CO_2 to ethanol and other products.

The homologation step with the same two catalysts was studied in a later paper [94]. Hydrogenation of CO_2 in the presence of methanol and LiI in DMI converted 32% of the methanol to ethanol (16 TON with respect to $Co_2(CO)_8$). The proposed pathway is reduction of CO_2 to CO followed by homologation of methanol by CO. Note that the presence of iodide anion is crucial; $Ru_3(CO)_{12}$ converts MeOH, CO_2 and H_2 to methyl formate in the absence of iodide [95] but to ethanol in the presence of iodide [94].

6. Conclusions

In summary, highly efficient homogeneous catalysts are now known for the hydrogenation of CO_2 to formic acid and derivatives such as formamides. Active catalysts have been found for CO_2 hydrogenation in water, organic solvents, supercritical CO_2 and ionic liquids. The range of formamides that can be produced in high yield has been expanded greatly. However, there are still no high activity and selectivity homogeneous catalysts for the reduction of CO_2 to methyl formate, acetic acid, methanol, ethanol and methane.

Aqueous-phase hydrogenation of CO_2, bicarbonate or carbonate has been shown to produce formate salts in very high rates, with TOF as high as 9600 h^{-1} at 80 °C and 1364 h^{-1} at room temperature. It is particularly intriguing that in several cases the rate of the hydrogenation of aqueous bicarbonate is dramatically increased by increased CO_2 pressures even though CO_2 itself is only slowly hydrogenated in aqueous solutions. At present it is unknown whether this effect is due entirely to the pH changes caused by higher concentrations of dissolved CO_2 or whether carbon dioxide itself is also involved in the hydrogenation of $HCO_3{}^-$. Further mechanistic work is needed to achieve a better understanding of this phenomenon. Isolated examples of the hydrogenation of CO_2 in aqueous solutions to products other than formate, i.e. CO, CH_4, glycols, etc. do exist, however up till now no detailed studies have been made in order to establish the specific reasons and conditions and the role of the aqueous environment (if any) for such product distributions.

Ruthenium(II) complexes have received a great deal of scrutiny in nonaqueous solvents as well. Ruthenium-containing catalysts bearing ligands with amine functional groups at the end of pendant arms were found to be catalytically active in the absence of added base, but the catalytic activity was found to be low. Other Ru(II) precursors have been identified and some of these have been studied by in situ spectroscopy and/or computational methods. In particular, the extremely active Ru(II) trimethylphosphine complexes have been extensively investigated. A kinetic study showed that the rate is first order in both H_2 and CO_2, which explains the benefit of $scCO_2$ as a solvent. The mechanism is not as clear, however. A spectroscopic study suggested, but not unequivocally, a cationic mechanism in which an empty site is made available by halide loss rather than phosphine loss. In this system, the role of added alcohol and base in the mechanism is unclear, but the trends in the effectiveness of various alcohols in promoting the hydrogenation matches the trend in the ability of the alcohol to promote formation of cationic Ru complexes. The question of the role of alcohol and amine in the mechanism deserves further study in this and several other systems.

Rh(I) catalysts of the form Rh(H)(diphosphine) have been made from a variety of precursors, and the steric requirements have been mapped out. Again in these systems, there are questions of the role of base, with some speculation offered. Other Rh(I) precursors have been identified, but none with rates as high as those which generate RhH(diphosphine) catalysts.

There has been very little work on catalysis by complexes not containing either Ru or Rh. A quick survey has shown that many have at least some activity, but the best, $NiCl_2$(dcpe), still has yields and rates well below those of Ru and Rh.

It is difficult to make comparisons of activity based upon the data collected in this article, because all of the catalyst precursors have been tested at very different conditions. If one makes a very rough correction for the different pressures and temperatures by assuming that all the rates are first order in both H_2 and CO_2 pressures and that rates always double when the temperature rises by 10 °C, then we can compare the precursors. By this admittedly rough comparison, the most active catalyst precursors for formic acid production are $RhCl(TPPTS)_3$, Rh(hfacac)(dcpb) and $RuCl(OAc)(PMe_3)_4$, in decreasing order of corrected TOF, although these three are very close in activity. It is particularly striking that the most active of these is the aqueous-phase catalyst, which might not have been expected a priori based on mass transfer rates.

Further progress has also been made in the synthesis of formamides, a reaction which at the time of the previous review was restricted primarily to the synthesis of dimethylformamide. Methods have now been found to prepare other dialkylformamides and even to prepare phenylformamide (formanilide) from CO_2 and aniline. The rate of production of DMF has also been significantly increased by the identification of a new Ru(II) precursor.

Other products, such as methanol, ethanol, and methane remain more difficult to prepare by the homogeneous hydrogenation of CO_2, and there is still no homogeneously-catalysed synthesis of oxalic acid by CO_2 hydrogenation.

Acknowledgements

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References

[1] P.G. Jessop, T. Ikariya, R. Noyori, Chem. Rev. 95 (1995) 259.
[2] W. Leitner, Angew. Chem. Int. Ed. Engl. 34 (1995) 2207.
[3] G. Laurenczy, F. Joó, L. Nádasdi, Inorg. Chem. 39 (2000) 5083, and supporting material.
[4] F. Joó, Aqueous Organometallic Catalysis, Kluwer Academic Publishers, Dordrecht, 2001.
[5] E. Graf, W. Leitner, J. Chem. Soc. Chem. Commun. (1992) 623.
[6] T. Burgemeister, F. Kastner, W. Leitner, Angew. Chem. Int. Ed. Engl. 32 (1993) 739.
[7] W. Leitner, E. Dinjus, F. Gaßner, J. Organomet. Chem. 475 (1994) 257.
[8] N.N. Ezhova, N.V. Kolesnichenko, A.V. Bulygin, E.V. Slivinskii, S. Han, Russ. Chem. Bull. Int. Ed. 51 (2002) 2165.
[9] T. Yamaji, Teijin Ltd., Japan Kokai Tokkyo Koho Pat. 166.146 (1981).
[10] F. Gassner, W. Leitner, J. Chem. Soc. Chem. Commun. (1993) 1465.
[11] W. Leitner, E. Dinjus, F. Gassner, in: B. Cornils, W.A. Herrmann (Eds.), Aqueous-Phase Organometallic Catalysis, Wiley-VCH, Weinheim, 1998, p. 486.
[12] E. Lindner, B. Keppeler, P. Wegner, Inorg. Chim. Acta 258 (1997) 97.
[13] R. Fornika, H. Görls, B. Seemann, W. Leitner, J. Chem. Soc. Chem. Commun. (1995) 1479.
[14] J.-C. Tsai, K.M. Nicholas, J. Am. Chem. Soc. 114 (1992) 5117.
[15] E.A. Karakhanov, S.V. Egazar'yants, S.V. Kardashev, A.L. Maksimov, S.S. Minos'yants, A.D. Sedykh, Petroleum Chem. 41 (2001) 268;
E.A. Karakhanov, S.V. Egazar'yants, S.V. Kardashev, A.L. Maksimov, S.S. Minos'yants, A.D. Sedykh, Neftekhimiya 41 (2001) 293.
[16] Y. Gao, J.K. Kuncheria, H.A. Jenkins, R.J. Puddephatt, G.P.A. Yap, J. Chem. Soc., Dalton Trans. (2000) 3212.
[17] J.Z. Zhang, Z. Li, H. Wang, C.Y. Wang, J. Mol. Catal. A: Chem. 112 (1996) 9.
[18] Y. Inoue, H. Izumida, Y. Sasaki, H. Hashimoto, Chem. Lett. (1976) 863.
[19] T. Yamaji, Teijin Ltd., Japan Kokai Tokkyo Koho Pat. 140.948 (1981).
[20] P.G. Jessop, T. Ikariya, R. Noyori, Nature 368 (1994) 231.
[21] P.G. Jessop, Y. Hsiao, T. Ikariya, R. Noyori, J. Am. Chem. Soc. 118 (1996) 344.
[22] P. Munshi, A.D. Main, J. Linehan, C.C. Tai, P.G. Jessop, J. Am. Chem. Soc. 124 (2002) 7963.
[23] C. Yin, Z. Xu, S.-Y. Yang, S.M. Ng, K.Y. Wong, Z. Lin, C.P. Lau, Organometallics 20 (2001) 1216.
[24] C.P. Lau, Y.Z. Chen, J. Mol. Catal. A: Chem. 101 (1995) 33.
[25] H.S. Chu, C.P. Lau, K.Y. Wong, Organometallics 17 (1998) 2768.
[26] D.J. Drury, J.E. Hamlin, BP Chemicals Ltd., European Patent Appl. 0.095.321 (1983).
[27] M.M.T. Khan, S.B. Halligudi, S. Shukla, J. Mol. Catal. 57 (1989) 47.
[28] J. Elek, L. Nádasdi, G. Papp, G. Laurenczy, F. Joó, Appl. Catal. A: Gen. 255 (2003) 59.

[29] Y. Himeda, N. Onozawa-Komatsuzaki, H. Sugihara, H. Arakawa, K. Kasuga, Proceedings of the 50th Symposium on Organometallic Chemistry, Osaka, Japan, 2003.

[30] M.L. Man, Z. Zhou, S.M. Ng, C.P. Lau, J. Chem. Soc., Dalton Trans. (2003) 3727.

[31] H. Hashimoto, S. Inoue, Japan Pat. 07.612 (1978).

[32] K. Kudo, N. Sugita, Y. Takezaki, Nihon Kagaku Kaishi (1977) 302.

[33] M. Sakamoto, I. Shimizu, A. Yamamoto, Organometallics 13 (1994) 407.

[34] C.C. Tai, T. Chang, B. Roller, P.G. Jessop, Inorg. Chem. 42 (2003) 7340.

[35] F. Joó, J. Kovács, A.C. Bényei, L. Nádasdi, G. Laurenczy, Chem. Eur. J. 7 (2001) 193.

[36] Y. Musashi, S. Sakaki, J. Am. Chem. Soc. 122 (2000) 3867.

[37] T. Borrmann, H.W. Roesky, U. Ritter, J. Mol. Catal. A: Chem. 153 (2000) 31.

[38] Y. Kayaki, T. Suzuki, T. Ikariya, Chem. Lett. (2001) 1016.

[39] F. Joó, G. Laurenczy, L. Nádasdi, J. Elek, Chem. Commun. (1999) 971.

[40] G. Laurenczy, F. Joó, L. Nádasdi, High Pressure Res. 18 (2000) 251.

[41] Á. Kathó, Z. Opre, G. Laurenczy, F. Joó, J. Mol. Catal. A: Chem. 204–205 (2003) 143.

[42] H. Horváth, G. Laurenczy, Á. Kathó, J. Organometal. Chem. 689 (2004) 1036.

[43] F. Joó, G. Laurenczy, P. Karady, J. Elek, L. Nadasdi, R. Roulet, Appl. Organometal. Chem. 14 (2000) 857.

[44] L. Nádasdi, A. Ormos, G. Laurenczy, F. Joó, Proceedings of the International Symposium on Homogeneous Catalysis, vol. 13, Tarragona, Spain, 2002, p. 78.

[45] F. Joó, J. Kovács, A.C. Bényei, Á. Kathó, Angew. Chem. Int. Ed. 37 (1998) 969.

[46] A. Bényei, F. Joó, J. Mol. Catal. 58 (1990) 151.

[47] S. Komiya, A. Yamamoto, J. Organomet. Chem. 46 (1972) C58.

[48] I.S. Kolomnikov, A.I. Gusev, G.G. Aleksandrov, T.S. Lobeeva, Y.T. Struchkov, M.E. Vol'pin, J. Organometal. Chem. 59 (1973) 349.

[49] F.P. Pruchnik, P. Smolenski, I. Raksa, Polish J. Chem. 69 (1995) 5.

[50] K. Tominaga, Y. Sasaki, K. Hagihara, T. Watanabe, M. Saito, Chem. Lett. (1994) 1391.

[51] F. Pruchnik, K. Wajda-Hermanowicz, G. Kluczewska, M. Zuber, P. Smolenski, Uniwersytet Wroclawski, Poland, Pol. Pat. 175908 B1 (1999).

[52] G. Süss-Fink, Proceedings of the International Conference, Eurohydrides, Dijon, 2000, p. OC14.

[53] Y. Himeda, N. Onozawa-Komatsuzaki, H. Sugihara, H. Arakawa, K. Kasuga, Organometallics 23 (2004) 1480.

[54] I. Jószai, F. Joó, Proceedings of the 28th International Conference on Solution Chemistry, Debrecen, 2003, p. 183.

[55] T. Matsubara, Organometallics 20 (2001) 19.

[56] T. Matsubara, K. Hirao, Organometallics 20 (2001) 5759.

[57] T. Ikariya, P.G. Jessop, R. Noyori, ERATO, Japan Tokkai Pat. 5-274721 (1993).

[58] P.G. Jessop, Y. Hsiao, T. Ikariya, R. Noyori, J. Am. Chem. Soc. 116 (1994) 8851.

[59] T. Ikariya, P.G. Jessop, R. Noyori, ERATO, Japan Tokkai Pat. 6-125,401 (1994).

[60] T. Ikariya, P.G. Jessop, Y. Hsiao, R. Noyori, ERATO, Japan Tokkai Pat. 6-125,402 (1994).

[61] P.G. Jessop, Y. Hsiao, T. Ikariya, R. Noyori, J. Chem. Soc. Chem. Commun. (1995) 707.

[62] T. Ikariya, Y. Hsiao, P.G. Jessop, R. Noyori, Research Development Corporation of Japan, Eur. Patent Appl. 0 652 202 A1 (1995).

[63] C.A. Thomas, R.J. Bonilla, Y. Huang, P.G. Jessop, Can. J. Chem. 79 (2001) 719.

[64] F. Hutschka, A. Dedieu, M. Eichberger, R. Fornika, W. Leitner, J. Am. Chem. Soc. 119 (1997) 4432.

[65] M. Iwatani, K. Kudo, N. Sugita, Y. Takezaki, Sekiyu Gakkaishi 21 (1978) 290.

[66] E.R. Pérez, M.O. da Silva, V.C. Costa, U.P. Rodrigues-Filho, D.W. Franco, Tetrahedron Lett. 43 (2002) 4091.

[67] A.D. Getty, C.C. Tai, J. Linehan, P.G. Jessop, M.M. Olmstead, A.L. Rheingold, 2003, submitted for publication.

[68] C.C. Tai, J. Pitts, A.D. Main, J. Linehan, P. Munshi, P.G. Jessop, Inorg. Chem. 41 (2002) 1606.

[69] K. Angermund, W. Baumann, E. Dinjus, R. Fornika, H. Gorls, M. Kessler, C. Kruger, W. Leitner, F. Lutz, Chem. Eur. J. 3 (1997) 755.

[70] F. Hutschka, A. Dedieu, W. Leitner, Angew. Chem. Int. Ed. Engl. 34 (1995) 1742.

[71] F. Hutschka, A. Dedieu, J. Chem. Soc., Dalton Trans. (1997) 1899.

[72] C.S. Pomelli, J. Tomasi, M. Sola, Organometallics 17 (1998) 3164.

[73] E. Graf, W. Leitner, Chem. Ber. 129 (1996) 91.

[74] Y. Musashi, S. Sakaki, J. Am. Chem. Soc. 124 (2002) 7588.

[75] J.H. Shin, D.G. Churchill, G. Parkin, J. Organomet. Chem. 642 (2002) 9.

[76] C. Bianchini, M. Peruzzini, A. Polo, A. Vacca, F. Zanobini, Gazz. Chim. Ital. 121 (1991) 543.

[77] O. Kröcher, R.A. Köppel, A. Baiker, Chem. Commun. (1997) 453.

[78] O. Kröcher, R.A. Köppel, A. Baiker, Chem. Commun. (1996) 1497.

[79] O. Kröcher, R.A. Koppel, M. Froba, A. Baiker, J. Catal. 178 (1998) 284.

[80] L. Schmid, M. Rohr, A. Baiker, Chem. Commun. (1999) 2303.

[81] L. Schmid, A. Baiker, Stud. Surf. Sci. Catal. 130 (2000) 557.

[82] Y. Kayaki, Y. Shimokawatoko, T. Ikariya, Adv. Synth. Catal. 345 (2003) 175.

[83] F.C. Liu, M.B. Abrams, R.T. Baker, W. Tumas, Chem. Commun. (2001) 433.

[84] D.J. Heldebrant, S.M. Walsh, P.G. Jessop, 2004, unpublished material.

[85] P. Munshi, D. Heldebrant, E. McKoon, P.A. Kelly, C.-C. Tai, P.G. Jessop, Tetrahedron Lett. 44 (2003) 2725.

[86] A. Fukuoka, N. Gotoh, N. Kobayashi, M. Hirano, S. Komiya, Chem. Lett. (1995) 567.

[87] I.S. Kolomnikov, T.S. Lobeeva, M.E. Vol'pin, Izv. Akad. Nauk SSSR, Ser. Khim. (1972) 2329.

[88] D.J. Darensbourg, C. Ovalles, J. Am. Chem. Soc. 109 (1987) 3330.

[89] H. Koinuma, H. Kato, H. Hirai, Chem. Lett. (1977) 517.

[90] K. Tominaga, Y. Sasaki, M. Kawai, T. Watanabe, M. Saito, J. Chem. Soc. Chem. Commun. (1993) 629.

[91] K. Tominaga, Y. Sasaki, T. Watanabe, M. Saito, Bull. Chem. Soc. Jpn. 68 (1995) 2837.

[92] B.D. Dombek, J. Organometal. Chem. 250 (1983) 467.

[93] K.-I. Tominaga, Y. Sasaki, M. Saito, K. Hagihara, T. Watanabe, J. Mol. Catal. 89 (1994) 51.

[94] K.-I. Tominaga, Y. Sasaki, T. Watanabe, M. Saito, in: T. Inui, M. Anpo, K. Izui, S. Yanagida, T. Yamaguchi (Eds.), Advances in Chemical Conversions for Mitigating Carbon Dioxide, Elsevier, Amsterdam, 1998, p. 495.

[95] D.J. Darensbourg, C. Ovalles, M. Pala, J. Am. Chem. Soc. 105 (1983) 5937.