

Chapter 2

Transformation of CO₂ to Formic Acid or Formate with Homogeneous Catalysts

Abstract Homogeneous hydrogenation of carbon dioxide to formic acid or formate has attracted much attention due to its high performance. Various metals including noble metals and nonprecious metals combined with different ligands have been investigated. The catalytic mechanism and catalyst design principle are described in detail. Recently developed CO₂ hydroboration and hydrosilylation to formate are also covered.

Keywords CO₂ hydrogenation • CO₂ hydroboration • CO₂ hydrosilylation
Formic acid • Catalyst design • Electronic effect • Pendent-base effect

Formic acid is widely used as preservative, insecticide, and industrial material for synthetic processes. It can be used directly in FA fuel cells to provide electricity. Most recently, it is recognized as one of the most promising hydrogen storage materials, especially for portable power application, because of its many advantages: (1) nontoxic and biodegradable, (2) liquid at ambient conditions, (3) easy to store and transport, (4) has relatively high hydrogen content (4.4 wt%), and (5) highly sustainable and renewable. The interconversion of H₂/CO₂ and FA/formate occurs highly selectively under relatively mild conditions.

The hydrogenation of CO₂ to formic acid or formate dates back to 1976. The pioneering work by Inoue et al., using triphenylphosphine (PPh₃) complexes of Ru, Rh, and Ir, opened the avenue for homogeneous catalytic hydrogenation of CO₂ to formic acid [1]. However, their research did not attract considerable attention until the 1990s, in which the interest on CO₂ conversion to formate was revived. The catalysts were extended to a variety of transition metals, such as Pd, Ni, and Fe. In addition to phosphorous ligands, *C,N*- and *N,N*-chelated ligands, *N*-heterocyclic carbene (NHC) ligands, and pincer ligands were also developed. The solvent effect has also been widely investigated. Highly polar solvents, such as MeOH, DMSO, and DMF, are demonstrated to be favorable for the transformation [2]. Noyori and Jessop et al. used supercritical carbon dioxide (scCO₂) as reactant and solvent and obtained high activity [3, 4]. Recently, water has achieved great success in a wide variety of applications [5].

Carbon dioxide is a cheap, safe, and abundant C1 building block [6]. Hydrogenation of CO₂ to formate/formic acid provides a sustainable method for

producing basic chemicals and fuels. Homogeneous hydrogenation of CO₂ to formate or formic acid has attracted increasing attention, and a number of reviews have summarized significant progress in the last two decades [6–11]. Table 2.1 lists the most efficient systems for this transformation. In this chapter, we will introduce the most recent development of CO₂ hydrogenation to FA/formate and highlight the most efficient catalytic systems and catalyst design principle.

2.1 CO₂ Hydrogenation Using Noble Metals

The work by Inoue et al. on homogeneous CO₂ hydrogenation to formic acid used a series of metal complexes with Ru, Rh, and Ir [1]. Following their work, a variety of noble metal complexes have been developed and exhibited remarkable activity.

2.1.1 Ruthenium Complexes

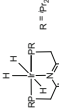
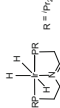
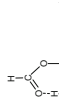
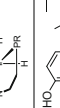
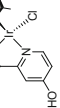
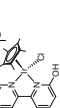
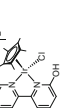
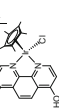
2.1.1.1 Ru Complexes with Phosphine Ligands

In 1994, Noyori and Jessop et al. explored a scCO₂ system for CO₂ hydrogenation with several merits [3]. scCO₂ can act as solvent and reactant, and hydrogen has high solubility in scCO₂. Therefore, scCO₂ is favorable for mass transport and heat transfer. RuH₂(PMe₃)₄ (**1**) and RuCl₂(PMe₃)₄ (**2**) afforded high initial rates of 1400 and 1040 h^{−1}, respectively, in the presence of Et₃N and MeOH at 50 °C. Subsequently, Jessop et al. utilized appropriate amine and alcohol adducts to accelerate the reaction rate, achieving a high TOF of 95,000 h^{−1} with RuCl(OAc)(PMe₃)₄ (**3**) in scCO₂ [4, 47].

Joó et al. performed extensive studies using phosphine ruthenium complexes including [RuCl₂(tppms)₂]₂ (**4**) (tppms: 3-sulfonatophenyldiphenylphosphine) and [RuCl₂(PTA)₂] (**5**) (PTA: 1,3,5-triaza-7-phosphaadamantane) (Fig. 2.1) in amine-free aqueous solutions [27, 28, 48–50]. A high TOF of 9600 h^{−1} was obtained with catalyst **4** at 9.5 MPa and 80 °C. Subsequently, reaction mechanisms were investigated in detail by Laurenczy and co-workers using ruthenium catalysts **5** [27, 51–53]. Beller and Laurenczy et al. reported moderate catalytic activity (TOF: 1259 h^{−1}) using in situ complex [RuCl₂(C₆H₆)₂]/dppm (**6**) (dppm: 1,2-bis(diphenylphosphino)methane) in aqueous NaHCO₃ under 8.5 MPa of H₂/CO₂ (5/3.5) at 70 °C [29]. Although this catalyst provided a high initial reaction rate, deactivation was observed after the first few hours.

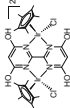
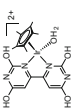
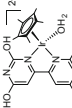
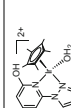
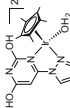
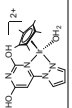
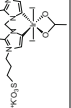
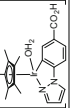
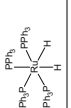
Leitner et al. developed a continuous-flow system for the hydrogenation of scCO₂ to produce pure formic acid in a single process unit [38]. They performed the reaction with a ruthenium precursor [Ru(cod)(methallyl)₂] (**7**) (cod: 1,5-cyclooctadiene; methallyl: CH₂C(CH₃)CH₂−) and ligand PBu₄tppms, using amine-free or amine-functionalized IL as the stationary phase at 50 °C under 10 MPa of H₂/CO₂ (1/1). Notably, they obtained high TON (1970) and TOF (>295 h^{−1}) values in a continuous-flow system using the amine-free IL EMIM

Table 2.1 Hydrogenation of CO₂ to formic acid/formate^{a,b}

Catalyst	Solvent	Additive	P(H ₂ /CO ₂)/ MPa	T/°C	Reaction time/h	TON	TOF ^c /h ⁻¹	Ref.
Ir complexes								
	H ₂ O/THF	KOH	4/4	200	2	300,000	150,000	[12, 13]
	H ₂ O/THF	KOH	4/4	120	48	3,500,000	73,000	[12, 13]
	H ₂ O	KOH	2.8/2.8	185	24	348,000	14,500	[14]
	H ₂ O	KOH	3/3	120	57	190,000	(42,000)	[15]
	H ₂ O	KHCO ₃	0.5/0.5	120	8	12,500	(25,200)	[16]
	H ₂ O	NaHCO ₃	0.05/0.05	25	33	330	(27)	[16]
	H ₂ O	KOH	3/3	120	48	222,000	(33,000)	[17]
	H ₂ O	KHCO ₃	0.05/0.05	25	336	7200	(65)	[18]

(continued)

Table 2.1 (continued)

Catalyst	Solvent	Additive	P(H ₂ /CO ₂)/MPa	T/°C	Reaction time/h	TON	TOF ^c /h ⁻¹	Ref.
	H ₂ O	KHCO ₃	2.5/2.5	80	2	79,000	(53,800)	[18]
	H ₂ O	KHCO ₃	1.5/1.5	80	8	34,000	(33,300)	[19]
	H ₂ O	KHCO ₃	0.05/0.05	25	24	190	65	[19]
	H ₂ O	KHCO ₃	0.5/0.5	50	1	388	388	[20]
	H ₂ O	KHCO ₃	0.5/0.5	50	1	440	440	[20]
	H ₂ O	KHCO ₃	0.5/0.5	50	1	637	637	[20]
	H ₂ O	KOH	3/3	200	75	190,000	2500	[21]
	H ₂ O	K ₂ CO ₃	1/1	25	15	100	6.8	[22]
Ru complexes								
	C ₆ H ₆	Et ₃ N/H ₂ O	2.5/2.5	rt	20	87	4	[1]

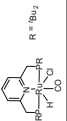
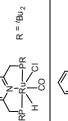
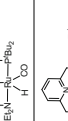
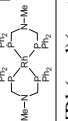
(continued)

Table 2.1 (continued)

Catalyst	Solvent	Additive	P(H ₂ /CO ₂)/ MPa	T/°C	Reaction time/h	TON	TOF ^c /h ⁻¹	Ref.
	scCO ₂	Et ₃ N	8.5/12	50	–	3700	1400	[3]
	scCO ₂	Et ₃ N	8.5/12	50	–	7200	1040	[3]
	scCO ₂	Et ₃ N/ C ₆ F ₅ OH	7/12	50	0.33	32,000	95,000	[4]
	scCO ₂	DBU/ C ₆ F ₅ OH	7/10	100	4	7625	1905	[23]
	scCO ₂	DBU/ C ₆ F ₅ OH	7/10	100	4	6630	1660	[23]
	DMSO	–	5/5	60	–	750		[24]
	EtOH	Et ₃ N	3/3	150	8	5000	625	[25]
K[RuCl(EDTA-H)]	H ₂ O	–	1.7/8.2	40	0.5	–	3750	[26]
	H ₂ O	NaHCO ₃	6/0	80	–	–	345	[27]
[RuCl2(tppm)s]₂]	H ₂ O	NaHCO ₃	6/3.5	80	0.03	–	9600	[28]
[RuCl2(C₆H₆)]/dppm	H ₂ O	NaHCO ₃	5/3.5	70	2	2520	1260	[29]
	toluene	DBU	70/70	100	4	1880		[30]

(continued)

Table 2.1 (continued)

Catalyst	Solvent	Additive	P(H ₂ /CO ₂)/ MPa	T/°C	Reaction time/h	TON	TOF ^c /h ⁻¹	Ref.
	DMF	DBU	2/2	70	2	38,600	–	[31]
	DMF	DBU	3/1	120			1,100,000	[31]
	Diglyme	K ₂ CO ₃	3/1	200	48	23,000	2200	[32]
	H ₂ O		37/3	70			21,500	[33]
Rh complexes								
[Rh(codCl)] ₂ /dppb	DMSO	Et ₃ N	2/2	rt	22	1150	30–47	[34]
RhCl(tppts) ₃	H ₂ O	NHMe ₂	2/2	81	0.5	–	7300	[9]
RhCl(tppts) ₃	H ₂ O	NHMe ₂	2/2	rt	12	3440	290	[9, 35]
RhCl(PPh ₃) ₃	DMSO	Et ₃ N	2/4	25	20	2500	125	[2]
[RhCl(tppms) ₃]/tppps	H ₂ O	HCO ₂ Na	1/1	50	20	120	–	[36]
	THF	Verkade's base	20/20	21	–	280	920	[37]
[Rh(cod)(methallyl) ₂]/ PBu ₄ /tppps	scCO ₂ /EMIM NTf ₂	Et ₃ N	5/5	50	20	310	630	[38]
[Rh(cod)(methallyl) ₂]/ PBu ₄ /tppps	scCO ₂ /EMIM NTf ₂	Et ₃ N/ EMIMCl	5/5	50	20	545	1090	[38]
			5/5	50	20	1970	>295	[38]

(continued)

Table 2.1 (continued)

Catalyst	Solvent	Additive	P(H ₂ /CO ₂)/ MPa	T/°C	Reaction time/h	TON	TOF ^c /h ⁻¹	Ref.
[Rh(cod)(methallyl) ₂]/ PBu ₄ /tppms	scCO ₂ /EMIM HCO ₂ (flow system)							
		KHCO ₃		100	72	3600		[39]
Non-precious metal complexes								
Ni(dppe) ₂	C ₆ H ₆	Et ₃ N/H ₂ O	2.5/2.5	rt	20	7	0.35	[1]
Fe(BF ₄) ₂ /PP ₃	MeOH	NaHCO ₃	6/0	80	20	610	30	[40]
Co(BF ₄) ₂ /PP ₃	MeOH	NaHCO ₃	6/0	120	20	3900	200	[41]
	H ₂ O/THF	NaOH	0.67/0.33	80	5	788	156	[42]
	THF	Verkade's base	0.05/0.05	21	<1	2000	3400	[43]
	MeCN		1/1	45	16	29,000	5700	[44]
	H ₂ O/THF	NaHCO ₃		25	72	188		[45]
	EtOH	DBU	1/1	25	72	1032		[45]
	C ₆ H ₆	DBU	1/1	100	16	35		[46]

^aInsignificant digits are rounded. ^bAbbreviations are the following: cod: 1,5-cyclooctadiene, dpbp: Ph₂P(CH₂)₄PPh₂, tppms: tris(3-sulfonophenyl)phosphine, tppms: 3-sulfonatophenyl(diphenyl)phosphine, PP₃: P(CH₂CH₂PPh₂)₃, dppm: 1,1-bis(diphenylphosphino)methane, dppe: 1,2-bis(diphenylphosphino)ethane, N'-N': pyridinylazolato, methyllyl: CH₂C(CH₃)CH₂-. ^cThe data in the parenthesis are initial TOFs

(HCO₂) (EMIM: 1-ethyl-3-methylimidazolium). The extraction rate of formic acid from the amine-functionalized ionic liquid was found to be the limiting factor under continuous-flow conditions.

A series of ruthenium(II) complexes [(N–N')RuCl(PMe₃)₃] (**8**) with PMe₃ and pyridinylazolato ligands (N–N', Fig. 2.1) bearing various electron-withdrawing and -donating substituents was investigated in the hydrogenation of CO₂ under supercritical conditions [54]. The triazolato system with an unsubstituted ligand was found to be superior (TON up to 4800) under relatively mild conditions. Under supercritical conditions, Thiel et al. reported that CO₂ hydrogenation catalyzed by simple ruthenium complexes with P(OMe)₃, P(OEt)₃, P(O^{*i*}Pr)₃, and P(OPh)₃ in the presence of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) and C₆F₅OH [23]. *trans*-[RuCl₂{P(OMe)₃}₄] offered high activity (TON = 6630, TOF = 1655 h^{–1}) similar to that of [RuCl₂(PMe₃)₄] (TON = 7625, TOF = 1905 h^{–1}) under the same experimental conditions.

Byers et al. studied the effect of inexpensive additives for CO₂ hydrogenation with RuCl₂(PPh₃)(*p*-cymene) (**9**) in DMSO or MeOH [55]. They suggested that the addition of inorganic additives, such as KHCO₃, KOAc, and KNO₃, improved catalytic activity by up to 510%. This study promoted the investigation of cheap additives to enhance CO₂ transformation.

Recently, Laurenczy et al. reported the direct hydrogenation of CO₂ to produce formic acid with [RuCl₂(PTA)₄] (**10**) in acidic media [24]. When H₂O was used as solvent, a formic acid solution of 0.2 M was obtained at pH 2.7 and 60 °C under 20 MPa H₂/CO₂ (3/1), corresponding to a TON of 74. When DMSO was used, formic acid concentration of 1.9 M was obtained at 60 °C under 10 MPa H₂/CO₂ (1/1) after 120 h. The catalyst is highly stable and can be recycled and reused multiple times without loss of activity. A total TON of 749 was achieved after the fourth cycle in recyclability tests. The most important merits of this system are direct FA production and without the need for basic additive and the requirement of acidification after reaction.

In 2016, Dang et al. investigated the steric and electronic effects of bidentate phosphine ligands in the Ru complexes **11–13** for the hydrogenation of CO₂ to formic acid by DFT calculations [56]. As shown in Scheme 2.1, the reaction undergoes three major steps: *cis-trans* isomerization of ruthenium dihydride complex, CO₂ insertion into the Ru–H bond, and H₂ insertion into the ruthenium formate ion to release HCOOH. The steric effect of the ligands slightly affected the reaction, and the electronic effect activated *cis-trans* isomerization and H₂ insertion.

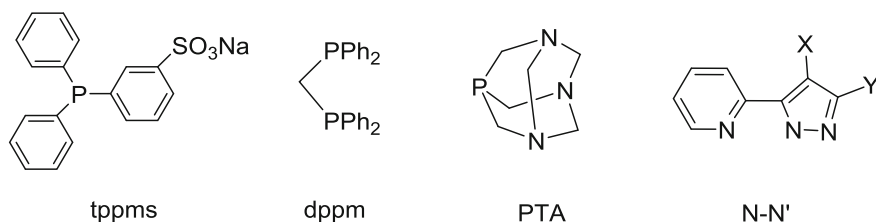
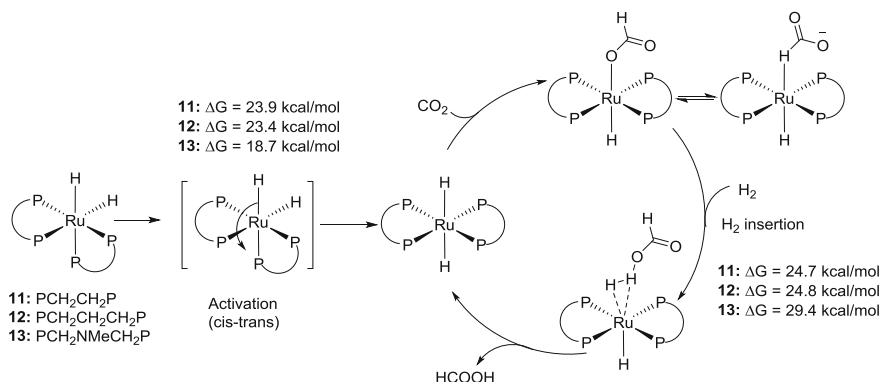


Fig. 2.1 Phosphine and *N,N*-bidentate ligands used in Ru complexes



Scheme 2.1 Overall process of Ru-catalyzed CO₂ hydrogenation. Redrawn based on Ref. [56]. Copyright (2016) Wiley-VCH GmbH & Co. KGaA, Weinheim

2.1.1.2 Ru Complexes with Pincer Ligands

Pincer complexes are demonstrated to activate small molecules, such as H₂ and CO₂, through metal–ligand cooperation [57]. The non-innocent nature of pincer ligands is crucial in the activation of CO₂ via an aromatization/de-aromatization mechanism [58, 59]. The crystal structures of CO₂ adducts **14** and **15** derived from Ru(PNP) complex **16** and Ru(PNN) complex **17** were reported by Milstein and Sanford, respectively (Fig. 2.2) [60, 61]. During hydrogenation, complex **16** reversibly converts to **15**. Complex **17** showed high activity in CO₂ hydrogenation and afforded a TON up to 23,000 and a TOF up to 2200 h⁻¹ at 200 °C for 48 h under 4 MPa H₂/CO₂ (3/1) in diglyme in the presence of K₂CO₃ [32].

In 2013, Pidko et al. reported the catalytic CO₂ hydrogenation with Ru–PNP pincer complexes **18–21** in the presence of DBU in THF. Complex **20** gave a high TOF of 14,500 h⁻¹ at 70 °C under 40 bar H₂/CO₂, whereas complex **21** exhibited better performance with a TOF of 21,500 h⁻¹ [33]. The authors revealed the effect of metal–ligand cooperation in catalytic CO₂ hydrogenation by in situ NMR spectroscopy and DFT calculations. Complex **20** produced from ligand-assisted CO₂ activation remained in an inactive state and inhibited the catalytic reaction. The addition of water restored the catalytic activity by providing a pathway toward the formation of active species (Scheme 2.2). Their group further investigated the reversible hydrogenation of CO₂ under mild conditions with Ru pincer complex **18** [31]. Using DBU as a base, complex **18** provided an unprecedented TOF as high as 1,100,000 h⁻¹ at 120 °C under 4 MPa H₂/CO₂ (3/1) in DMF. The catalytic mechanism of the Ru–PNP pincer complex in the presence of DBU was subsequently investigated using DFT calculations [62].

In 2016, Olah and Prakash et al. reported an environmentally friendly and direct approach for CO₂ capture by amines in aqueous media and in situ conversion to ammonium formate with Ru–PNP complexes **25** and **26** (Scheme 2.3) [63]. The amines in this process had a dual purpose of transforming CO₂ to ammonium

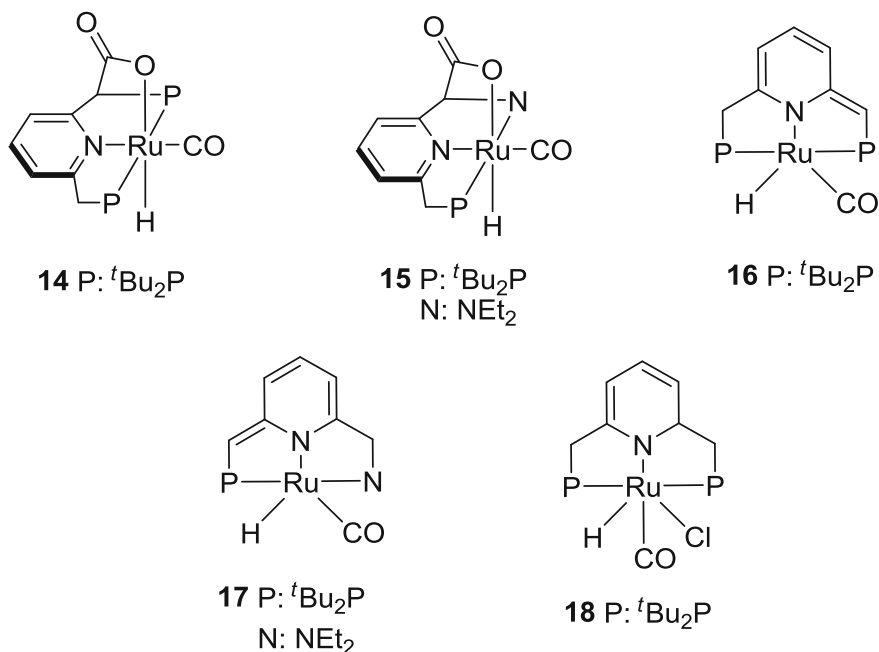
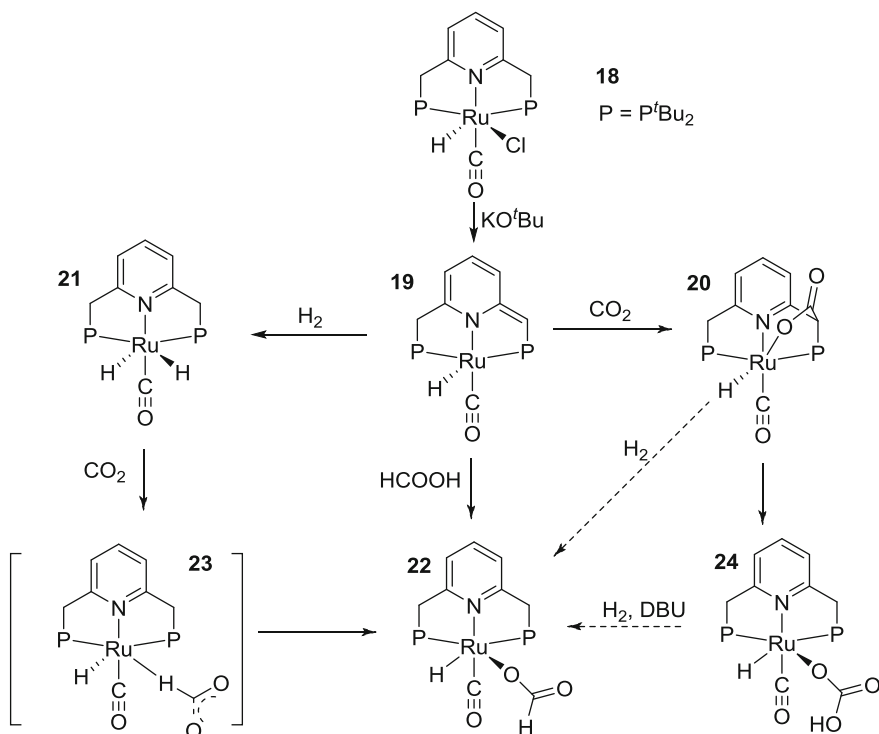


Fig. 2.2 Pincer Ru complexes for CO₂ hydrogenation

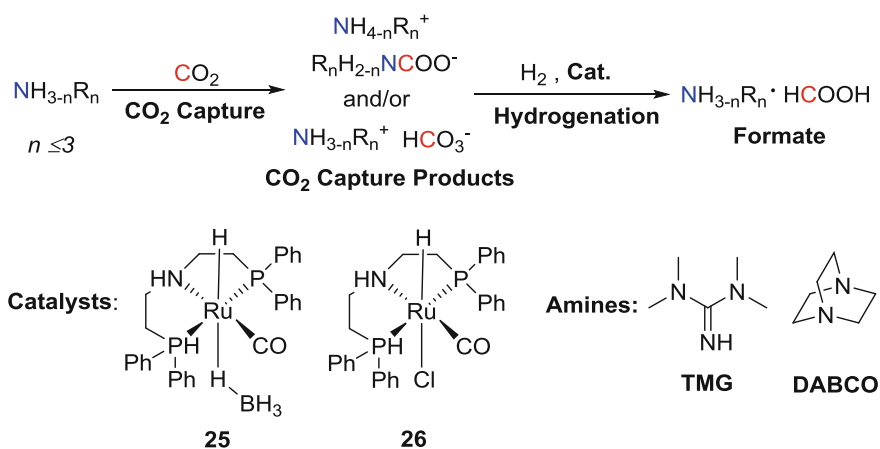
carbamate/bicarbonate/carbonate and stabilizing the formate product. Among the various amines tested, tetramethylguanidine (TMG) provided the highest yield of 95% and highest TON of 7375 for 20 h at 50 °C under 50 bar H₂ in the presence of complex **25**, while diazabicyclo[2.2.2]octane (DABCO) afforded the highest TOF (433 h⁻¹) under the same conditions. Catalyst recycling was also studied in a biphasic system consisting of 2-methyltetrahydrofuran and water. When catalyst **25** was used, an overall TON of >7000 for formate was obtained after five cycles, and the activity of the catalyst exhibited no significant decrease. This study presented an environmentally friendly and straightforward approach to produce formate from captured CO₂.

2.1.2 Rhodium Complexes

For CO₂ hydrogenation, phosphine ligands as σ -donors were demonstrated to be effective and applicable with metals, such as rhodium. In 1992, Tsai and Nicholas reported that a precatalyst [Rh(NBD)(PMe₂Ph)₃][BF₄] (**27**) (NBD: norbornadiene) can be converted to [H₂Rh(PMe₂Ph)₃(OH₂)]BF₄ (**28**) by the addition of H₂ in wet



Scheme 2.2 Experimentally observed transformations of Ru-PNP complexes in the presence of H₂ and CO₂. Redrawn based on Ref. [33]



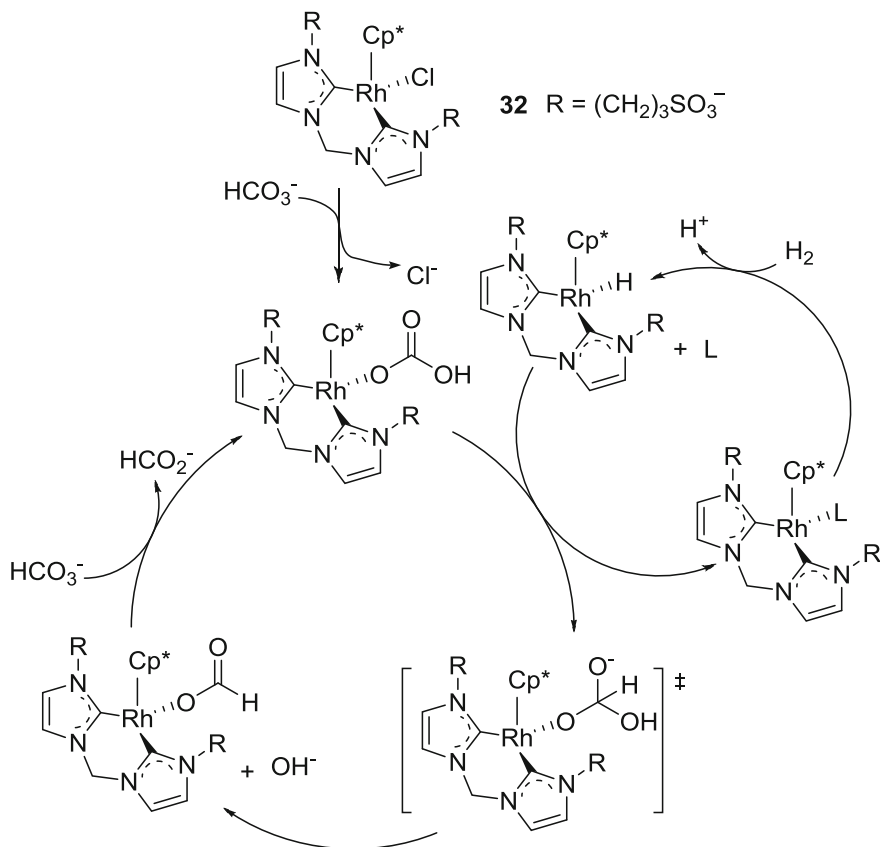
Scheme 2.3 CO₂ capture and conversion to ammonium formate

THF (4% H₂O) and produced formate more than twice as fast than that in dry THF [64]. The addition of a small amount of water was favorable for the catalytic activity of rhodium complex in CO₂ hydrogenation in THF. The authors speculated that H₂O molecule bound to a metal center could form a hydrogen bond with the oxygen atom of CO₂, improve electrophilicity of the carbon atom, and stabilize the transition state for CO₂ insertion. Kolesnichenko et al. studied the hydrogenation reaction catalyzed by Wilkinson's complex RhCl(PPh₃)₃ (**29**) in polar solvents (e.g., DMSO and MeOH), which afforded a TON of 2500 for 20 h at 25 °C under 6 MPa H₂/CO₂ (2/4) [2].

Most metal phosphine complexes are lipophilic, while introduction of polar groups, such as sulfonic acid, endows water solubility on the complexes. This improvement satisfied the catalytic CO₂ reduction in water. In 1993, a water-soluble rhodium catalyst RhCl(tppts)₃ (**30**) (tppts: tris(3-sulfonatophenyl)phosphine) was first reported by Leitner et al. for CO₂ hydrogenation in water. It gave a high TON of 3440 under relatively mild conditions (rt, 4 MPa H₂/CO₂ = 1/1) in the presence of HNMe₂ for 12 h [35].

Phosphines are usually "spectator" ligands. Mimicking the active site of [Fe–Fe]-hydrogenase, Kubiak et al. synthesized five [Rh(P₂N₂)₂]⁺ complexes and the corresponding rhodium hydrides with substituted cyclic diphosphine P₂N₂ (1,5-diaza-3,7-diphosphacyclooctane) [65]. They found that pendant amines introduced in the second coordination sphere were unable to deprotonate the strongly basic dihydride species. The effect of the P₂N₂ ligands was attributed to their electron-donating ability, which increased electron density at the metal center. [Rh(depe)₂]⁺ (depe: 1,2-bis(diethylphosphino)ethane) (**31**) was found to be the most active catalyst that gave a TON of 515 under 2 atm H₂/CO₂ (1/1) and 21 °C in THF in the presence of Verkade's base (2,8,9-triisobutyl-2,5,8,9-tetraaza-1-phosphabicyclo[3.3.3]undecane) for 1 h. The less hindered depe ligand is favorable for accessing the external base to the metal center to promote the oxidative addition of H₂.

NHC ligands are also strong electron donors. Very recently, Herrmann and Kühn et al. reported the hydrogenation of bicarbonate to formate using Rh catalyst **32** with water-soluble *bis*-NHC ligand under mild reaction conditions [39]. A high TON of 3600 was obtained with complex **32** under 50 bar H₂ in 2 mol/L KHCO₃ aqueous solution for 72 h at 100 °C. KHCO₃ showed better catalytic performance than NaHCO₃ as bicarbonate source because of the lower solubility of NaHCO₃ in water. The authors utilized DFT calculations to investigate the mechanism (Scheme 2.4). The mechanism was divided into three steps: first, the chloride ligand was replaced by bicarbonate; subsequently, bicarbonate was reduced to formate by reducing agents; and finally, formate was exchanged by bicarbonate. The rate-limiting step could be the reduction of the carbon atom. The authors suggested the involvement of another catalyst molecule, which provided an external hydride for the reduction of bicarbonate.



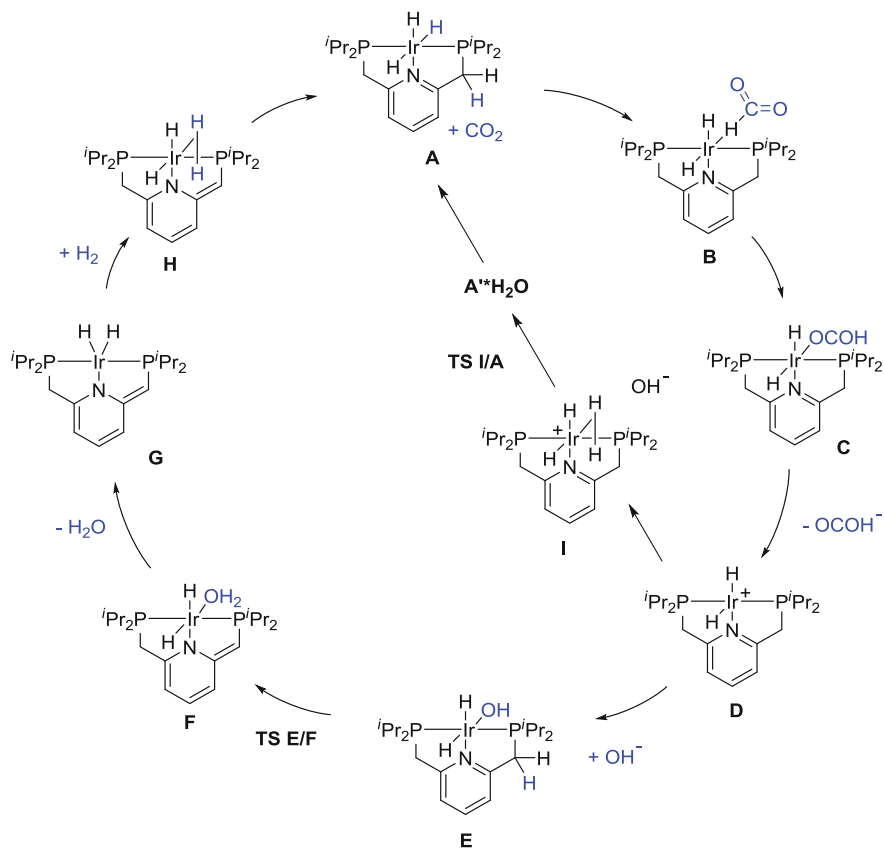
Scheme 2.4 Proposed overall mechanism for the reduction of bicarbonate to formate with sulfonated water-soluble complex **32**. Redrawn based on Ref. [39]. Copyright (2016) Wiley-VCH GmbH & Co. KGaA, Weinheim

2.1.3 Iridium Complexes

Compared with Ru and Rh complexes, Ir complexes have exhibited superior activity and recently attracted considerable attention. They also showed high stability and catalyzed reactions under high temperature, thereby providing higher outcomes.

2.1.3.1 Ir Complexes with Pincer Ligands

In 2009, Nozaki and co-workers developed an Ir trihydride complex $IrH_3(PNP)$ (**33**, Scheme 2.5) and achieved the highest activity for CO₂ hydrogenation. Given the low water solubility of the PNP complex, they chose THF as a cosolvent for



Scheme 2.5 Proposed mechanism for the hydrogenation of CO₂ by **33** based on Ref. [13]

homogeneous catalysis. Complex **33** (Fig. 2.3) showed an extraordinarily high TOF of 150,000 h⁻¹ at 200 °C and TON of 3,500,000 (48 h) at 120 °C under 8 MPa H₂/CO₂ (1/1) in H₂O/THF (5/1) [12, 13]. Soon after their study, the catalytic mechanisms of the PNP Ir complex were investigated with computational methods [13, 66, 67].

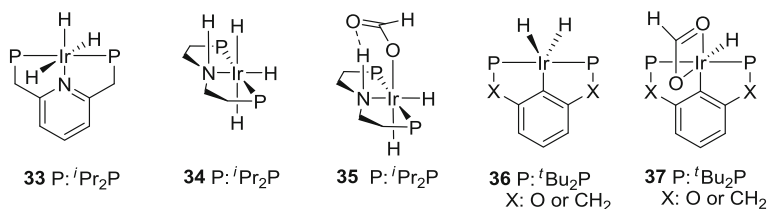
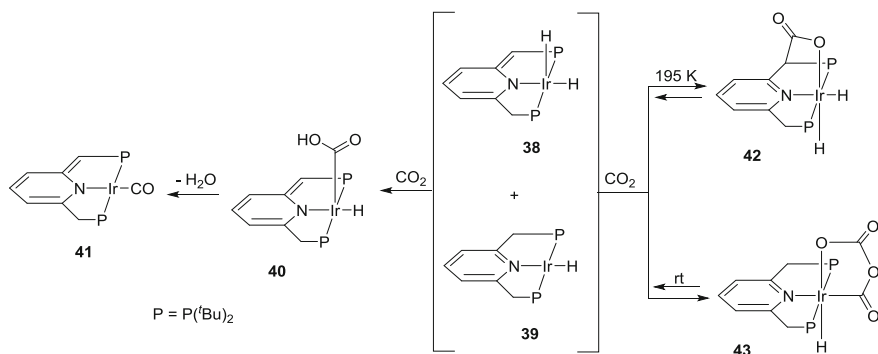


Fig. 2.3 Pincer Ir complexes for CO₂ hydrogenation in water

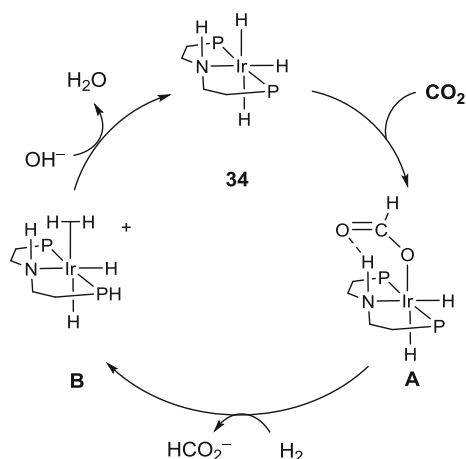


Scheme 2.6 Reaction pathway of complexes **38** and **39** with CO₂ to give complexes **40–43**. Reprinted with permission from Ref. [68]. Copyright (2016) American Chemical Society

Nozaki et al. carried out DFT calculations using pincer complex **33** as a catalyst [13]. Two competing reaction pathways were identified, and the rate-determining steps (RDSs) were determined to be deprotonative de-aromatization (via TS E/F) and hydrogenolysis (via TS I/A) (Scheme 2.5). The calculated free energy profiles provided an explanation for the effect of H₂ pressure, base, and solvent and were consistent with experimental data.

Feller and Milstein et al. presented a unique mode of stoichiometric CO₂ activation and reductive splitting based on metal–ligand cooperation [68]. The Ir pincer complexes **38** and **39** reacted with CO₂ to give intermediate **40**, which resulted in de-aromatized complex **41** by intramolecular dehydration with the assistance of H₂O molecule. Complexes **42** and **43** were formed reversibly by CO₂ binding to the ligand and metal (Scheme 2.6). DFT calculations revealed that thermodynamic products **42** and **43** were side products rather than intermediates. Their study helped us further understand the CO₂ activation mode of pincer complex through metal–ligand cooperation.

Scheme 2.7 Proposed mechanism for CO₂ hydrogenation using catalyst **34** with the displacement of formate by H₂ as the rate-determining step. Redrawn based on Ref. [14]. Copyright (2011) American Chemical Society



In 2011, Hazari and co-workers developed IrH₃(PNP) complex **34** bearing an N–H group, which formed stable complex **35** with CO₂ (Fig. 2.3) [14]. Their calculations indicated that CO₂ insertion was facilitated by an N–H–O hydrogen bond through an outer sphere interaction (Scheme 2.7). Complex **35** achieved a maximum TON of 348,000 and a high TOF of 18,780 h^{−1}. IrH₂(PCP) pincer complex **36** could form κ^2 -formato complex **37** by reaction with CO₂ (Fig. 2.3) [69]. Complexes **36** and **37** are efficient and selective catalysts for electrocatalytic reduction of CO₂ to formate in CH₃CN/H₂O.

2.1.3.2 Ir Complexes with *N,N*-Chelated Ligands

Compared with the widely used phosphine complexes, molecular complexes with *N,N*-chelated ligands have attracted less attention in the context of CO₂ hydrogenation [25, 70–73]. Recently, Himeda et al. have developed a series of *N,N*-chelated complexes [Cp^{*}Ir(DHPT)(OH₂)]²⁺ (DHPT: 4,7-dihydroxy-1,10-phenanthroline), [Cp^{*}Ir(nDHBP)(OH₂)]²⁺ (nDHBP: *n,n'*-dihydroxy-2,2'-bipyridine, *n* = 3, 4, 5, 6), [(Cp^{*}IrCl)₂(THBPM)]²⁺ (THBPM: 4,4',6,6'-tetrahydroxy-2,2'-bipyrimidine), and [Cp^{*}Ir(Nn)(OH₂)]²⁺ (*n* = 1–14, Fig. 2.4). Among these complexes, functionalized complex bearing OH group exhibited remarkable activity. The significant effect of the ligands is illustrated as follows:

Electronic effects. The studies by Jessop and Sakaki et al. indicated that complexes bearing strong electron-donating ligands have high activity in CO₂ hydrogenation [4, 74]. Inspired by their studies, Himeda's group developed a series of half-sandwich Ir complexes [Cp^{*}Ir(4,4'-R₂-bpy)Cl]⁺ (R = OH, OMe, Me, H) [17, 75–77]. The chloro ligand in these complexes can readily hydrolyze to form the corresponding aqua complexes [Cp^{*}Ir(4,4'-R₂-bpy)(OH₂)]²⁺ in the presence of water.

Among these catalysts, complexes bearing OH substituents show unique properties. The OH group ($\sigma_p^+ = -0.92$) is readily deprotonated to generate a considerably stronger oxyanion electron donor ($\sigma_p^+ = -2.30$) when the solution pH increases beyond 5–6 [76]. Tautomerism of the oxyanion form is observed. The conjugation effect makes the ligand highly electron donating (Scheme 2.8). These hydroxy-substituted diamine ligands are classified as “proton-responsive ligands” (Fig. 2.4) [78]. They are pH switchable and tunable in polarity and electron-donating ability, and thus, are capable of adjusting the catalytic activity and water solubility of the complexes.

Hammett constants (σ_p^+) are usually used to characterize the electron-donating ability of the substituents: the more negative the σ_p^+ values, the stronger their electron-donating ability. Figure 2.5 shows the correlation between the initial TOFs and the σ_p^+ values of the substituents for the [Cp^{*}Ir(4,4'-R₂-bpy)(OH₂)]SO₄ complexes. The activity of [Cp^{*}Ir(4DHBP)(OH₂)]SO₄ (4DHBP: 4,4'-dihydroxy-2,2'-bipyridine; Fig. 2.4) is over 1000 times higher than that of the unsubstituted analogue [Cp^{*}Ir(bpy)(OH₂)]SO₄ under the same conditions (80 °C, 1 MPa CO₂/

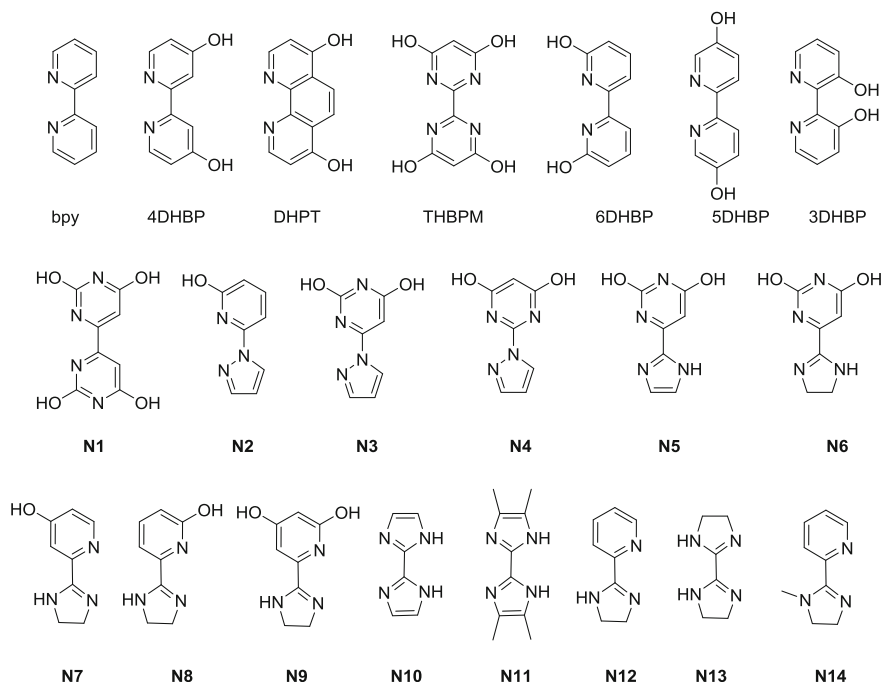
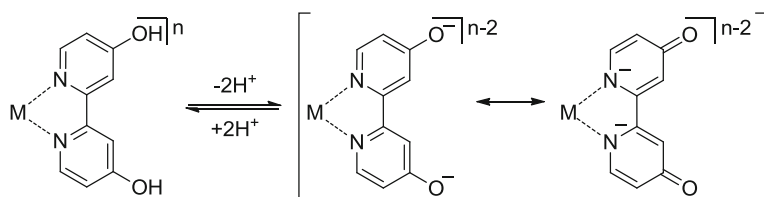


Fig. 2.4 Proton-responsive ligands used for CO₂ hydrogenation



Scheme 2.8 Acid–base equilibrium between hydroxy and oxyanion forms and resonance structures of oxyanion form

H₂ = 1). The significant improvement of the activity can be attributed to the strong electron-donating ability of the oxyanion. The catalytic activity of [Cp*Ir(6DHBP)(OH₂)]²⁺ and its analogues [Cp*Ir(6,6'-R₂-bpy)(OH₂)]SO₄ (R = OMe, Me, H) was also investigated [16]. As shown in the Hammett plots (Fig. 2.3), similar to the 4,4'-substituted analogues, stronger electron-donating substituents lead to higher reaction rates.

Most recently, Himeda et al. reported iridium catalysts with electron-donating imidazoline moieties as ligands for the hydrogenation of CO₂ to formate in aqueous solution. These complexes are considerably more effective than the imidazole

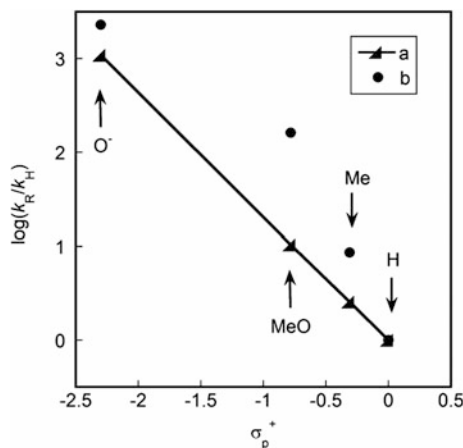


Fig. 2.5 Correlation between initial TOFs and σ_p^+ values of substituents (R) for the CO₂ hydrogenation catalyzed by (a) [Cp*Ir(4,4'-R₂-bpy)(OH₂)]SO₄ (R = OH, OMe, Me, H; triangles) and (b) [Cp*Ir(6,6'-R₂-bpy)(OH₂)]SO₄ (R = OH, OMe, Me, H; circles). Reaction conditions: 1 MPa of H₂/CO₂ (1/1), 80 °C; **a** 0.02–0.2 mM catalyst in 1 M KOH and **b** 0.01–0.2 mM catalyst in 1 M NaHCO₃. Reproduced from Ref. [16] with permission from the Royal Society of Chemistry

analogues [79]. The reaction rate (1290 h⁻¹) of the bisimidazoline complex [Cp*Ir(N13)(OH₂)]²⁺ was considerably higher than that (20 h⁻¹) of bisimidazole complex [Cp*Ir(N10)(OH₂)]²⁺ under 1 MPa at 50 °C. Under atmospheric pressure at room temperature, the bisimidazoline complexes exhibited a TOF of 43 h⁻¹, which is comparable to that of the most efficient dinuclear complex [(Cp*IrCl)₂(THBPM)]²⁺ (70 h⁻¹) [18]. The catalytic activity of the complex [Cp*Ir(N14)(OH₂)]²⁺ with an *N*-methylated imidazoline moiety was the same as that of the unsubstituted pyridylimidazoline analogue [Cp*Ir(N12)(OH₂)]²⁺. The high activity was not attributable to the deprotonation of NH in the imidazoline cycle under the reaction conditions.

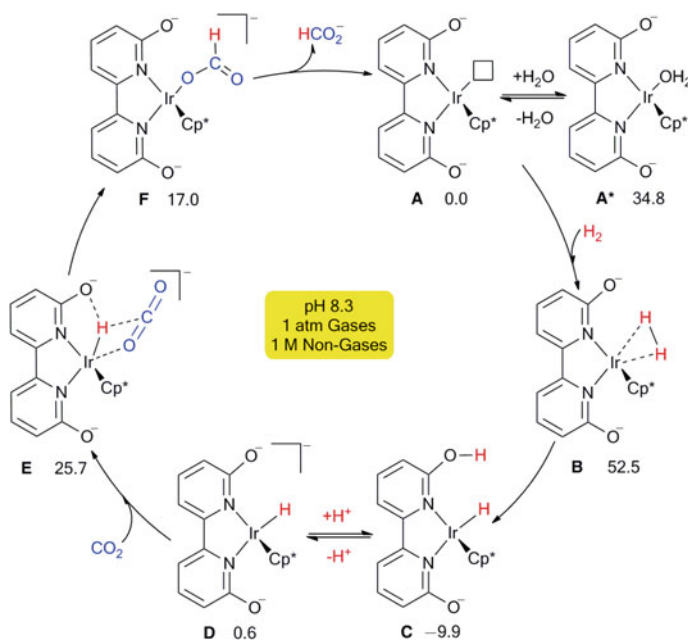
Pendant base effects. A hydroxy group near the metal center may act as an important functional group, which can facilitate hydrogen dissociation and production as found in Fe-guanylpuridinol cofactor in [Fe]-hydrogenase [80–82]. A computational study revealed that the pendant hydroxy group played an important role in the activation of H₂ by forming a hydrogen bond [83]. Inspired by these works, Himeda and Wang et al. developed a series of iridium complexes, [Cp*Ir(nDHBP)(OH₂)]²⁺ (nDHBP: *n,n'*-dihydroxy-2,2'-bipyridine, *n* = 3, 4, 5, 6), [(Cp*IrCl)₂(THBPM)]²⁺, and [Cp*Ir(Nn)(OH₂)]²⁺ (*n* = 2–6, Fig. 2.4), as catalysts for CO₂ hydrogenation and the reverse reaction formic acid dehydrogenation under mild conditions in water solvent [16, 18, 19, 84–86].

As shown in the Hammett plots (Fig. 2.3), the TOF (8050 h⁻¹) of [Cp*Ir(6DHBP)(OH₂)]²⁺ was considerably higher than that (5100 h⁻¹) of [Cp*Ir(4DHBP)(OH₂)]²⁺ under the same conditions. As the hydroxy groups at the *para* and *ortho*

positions have almost the same electron-donating ability, additional rate enhancement is attributed to the proximity of the hydroxy groups in 6DHBP to the metal center. The possible cooperative effect of the adjacent OH, namely, pendant base effect, was studied in detail by experimental and computational methods [16, 19, 86].

The mechanism study suggested that CO₂ hydrogenation generally involves three steps: H₂ heterolysis to generate metal hydride, CO₂ insertion into the hydride to give formate intermediate, and dissociation of formate. NMR experiments indicated that [Cp^{*}Ir(6DHBP)(OH₂)]²⁺ forms the Ir–H species considerably more easily than [Cp^{*}Ir(4DHBP)(OH₂)]²⁺ in the presence of H₂. For instance, 95% of [Cp^{*}Ir(6DHBP)(OH₂)]²⁺ converted to the Ir–H complex over 0.5 h under 0.2 MPa H₂, whereas only 90% of [Cp^{*}Ir(4DHBP)(OH₂)]²⁺ transformed to the corresponding Ir–H complex over 40 h under 0.5 MPa H₂. DFT calculations using complex [Cp^{*}Ir(6DHBP)(OH₂)]²⁺ suggested that the heterolysis of dihydrogen is the RDS under basic conditions (pH 8.3) [16]. Furthermore, the calculations showed that the adjacent oxyanions, which deprotonated from hydroxy groups under basic conditions, became pendant bases and assisted the heterolysis of H₂ (Scheme 2.9A–D).

A study on the deuterium kinetic isotope effect (KIE) further found clear evidence for the involvement of a water molecule in the heterolysis of H₂ using [Cp^{*}Ir(6DHBP)(OH₂)]²⁺ and [Cp^{*}Ir(N₂)(OH₂)]²⁺ bearing a pendant base [19]. Water participation enhanced proton transfer through the formation of a water bridge in

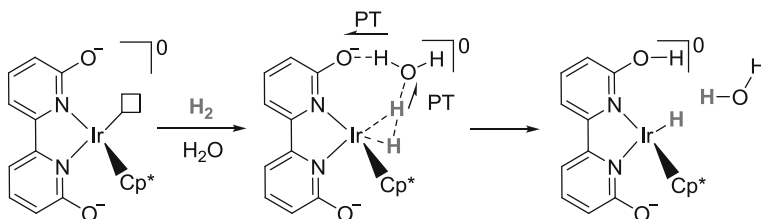


Scheme 2.9 Proposed mechanism for CO₂ hydrogenation by [Cp^{*}Ir(6DHBP)(OH₂)]²⁺. Reproduced from Ref. [16] with permission from the Royal Society of Chemistry

rate-limiting H₂ heterolysis. The KIE study was implemented with D₂/KDCO₃/D₂O instead of H₂/KHCO₃/H₂O. When D₂ was used instead of H₂, an apparent decrease in reaction rate was found both in KHCO₃/H₂O (KIE: 1.19) and KDCO₃/D₂O (KIE: 1.20) solution using [Cp^{*}Ir(4DHBP)(OH₂)]²⁺, which bears no pendant OH. Replacing H₂O with D₂O did not lead to a substantial rate decrease in H₂/KDCO₃ (KIE: 0.98). This result indicated that D₂ participated in the RDS for [Cp^{*}Ir(4DHBP)(OH₂)]²⁺. By contrast, for [Cp^{*}Ir(6DHBP)(OH₂)]²⁺ and [Cp^{*}Ir(N₂)(OH₂)]²⁺ bearing pendant OH groups, D₂O led to a larger rate decrease than that with D₂. This result suggested that D₂O participated in the RDS for [Cp^{*}Ir(6DHBP)(OH₂)]²⁺ and [Cp^{*}Ir(N₂)(OH₂)]²⁺. Therefore, it can be concluded that water participated in the rate-limiting heterolysis of H₂ for [Cp^{*}Ir(6DHBP)(OH₂)]²⁺ and [Cp^{*}Ir(N₂)(OH₂)]²⁺ and not for [Cp^{*}Ir(4DHBP)(OH₂)]²⁺. This study suggests that a water molecule interacts with the pendant base and H₂ at the metal center, and assists the heterolysis of H₂ via a proton relay (Scheme 2.10). DFT calculations supported the participation of H₂O in the transition state. The calculated transition state with a water molecule is 14.2 kJ mol⁻¹ lower than that without H₂O. This finding first proved the involvement of a water molecule in the H₂ heterolysis using complexes bearing pendant OH groups.

Recently, Wang et al. developed a series of new proton-responsive imidazoline-based complexes [Cp^{*}Ir(Nn)(OH₂)]²⁺ (*n* = 6–9) for highly efficient CO₂ hydrogenation in aqueous systems [87]. [Cp^{*}Ir(N9)(OH₂)]²⁺, which contains two OH groups at the *ortho* and *para* positions on a coordinating pyridine ring, achieved an unprecedented TOF of 106 h⁻¹ and TON of 7280 for 336 h at 25 °C under 0.1 MPa CO₂ and H₂. The high efficiency of this system was attributed to the combined effects of the strong electron-rich imidazoline moiety and pendant base (OH groups).

The combined electronic and pendant base effects significantly improved the activity of the bioinspired complexes [Cp^{*}Ir(6DHBP)(OH₂)]²⁺, [Cp^{*}Ir(N₂)(OH₂)]²⁺ (N₂ = 2,2',6,6'-tetrahydroxy-4,4'-bipyrimidine), and [(Cp^{*}IrCl)₂(THBPM)]²⁺. [(Cp^{*}IrCl)₂(THBPM)]²⁺ provided an extraordinary TOF of 65 h⁻¹ and TON of 7200 (336 h) under ambient conditions (25 °C, 1 atm H₂/CO₂) in CO₂ hydrogenation. [Cp^{*}Ir(N₂)(OH₂)]²⁺ showed comparable activity with [(Cp^{*}IrCl)₂(THBPM)]²⁺.



Scheme 2.10 Proposed mechanism for H₂ heterolysis assisted by the pendant base and a water molecule through proton relay. PT indicates proton transfer. Reprinted with permission from Ref. [19]. Copyright (2013) American Chemical Society

2.1.3.3 Ir Complexes with C,C- and C,N-Chelated Ligands

Peris et al. developed a series of water-soluble complexes **44–46** using *bis*-NHC (*N*-heterocyclic carbenes) as electron-donating ligands (Fig. 2.6) [21, 88]. By introducing hydroxy or sulfonate groups to the side carbon chains, the water solubility was improved. Thus, the activity was remarkably enhanced for the CO₂ hydrogenation to HCO₂K. Another merit of *bis*-NHC ligands is that they endowed high thermal stability to the corresponding complexes. Finally, a high TON of 190,000 was achieved with complex IrI₂(AcO)(*bis*-NHC) **46**, under 6 MPa H₂/CO₂ (1/1) at 200 °C for 75 h.

Fukuzumi et al. developed C,N-chelated water-soluble Ir complex **47** bearing a carboxyl group [22]. Aqua complex **47** can be deprotonated to give benzoate complex **48** and hydroxo complex **49**. The p*K*_a values of complexes **47** and **48** are determined to be 4.0 and 9.5, respectively (Fig. 2.7). Complex **48** was utilized for CO₂ hydrogenation in 0.1 M K₂CO₃ solution (pH 8.8) by bubbling H₂/CO₂ (1/1, 50 mL/min) under atmospheric pressure at 30 °C. A TOF of 6.8 h⁻¹ and a TON of more than 100 were obtained over 20 h. In the same manner, the TOF increased to 22.1 h⁻¹ at 60 °C.

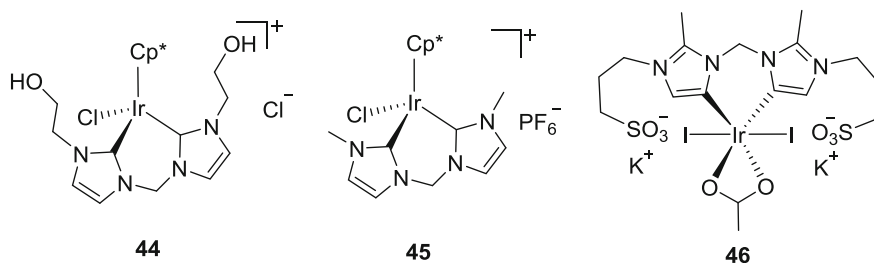


Fig. 2.6 Peris et al.'s NHC Ir complexes for CO₂ hydrogenation in water

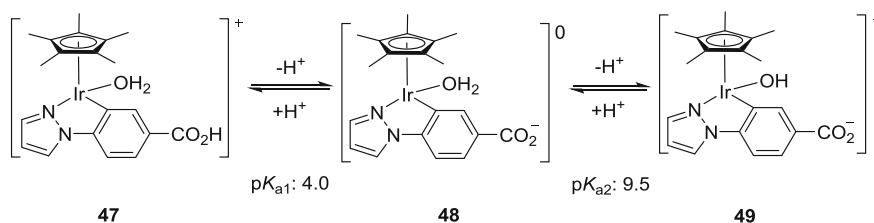


Fig. 2.7 Fukuzumi et al.'s catalyst for CO₂ hydrogenation in water. Reprinted with permission from Ref. [22]. Copyright (2012) Royal Society of Chemistry

2.2 CO₂ Hydrogenation Using Non-precious Metals

Although noble metals, such as Ir, Rh, and Ru, are widely used for CO₂ hydrogenation and great success has been achieved, their high cost is one drawback for their practical application. Therefore, various non-precious metals, such as Ni, Fe, Co, and Mo, were investigated. Efficient ligands for noble metals-based complexes are usually also capable to construct effective complexes of non-precious metals. However, some exceptions exist; for example, the Co analogues of the highly efficient Ir complexes [Cp^{*}Ir(nDHBP)(OH₂)]²⁺ ($n = 4$ or 6) showed low activity because of their low stability [89]. Nevertheless, versatile phosphine and pincer ligands are applied to develop efficient non-precious metal complexes.

2.2.1 Using Phosphine Ligands

In the pioneer work of Inoue, they used a complex Ni(dppe)₂ (dppe: 1,2-bis(diphenylphosphino)ethane) as catalyst and obtained a TON of 7 for 20 h at room temperature under 5 MPa H₂/CO₂ (1/1) [1]. In 2010, Beller and Laurenczy et al. reported the first hydrogenation of bicarbonate to formate with Fe(BF₄)₂ · 6H₂O and P(CH₂CH₂PPh₂)₃ (PP₃), which forms iron hydride complexes [FeH(PP₃)]BF₄ and [FeH(H₂)(PP₃)]BF₄ under the reaction conditions [40]. The catalytic reaction under 60 bar H₂ at 80 °C provided sodium formate with an excellent yield of 88% and a high TON of 610 for 20 h. The activity of the iron catalyst is comparable to that of a noble metal analogue [{RuCl₂(benzene)}₂]/PP₃ (TON = 624). Two years later, Beller et al. reported the cobalt analogue Co(BF₄)₂ · 6H₂O and PP₃ for hydrogenation of sodium bicarbonate [41]. A high TON of 3880 was obtained under 60 bar H₂ at 120 °C with a yield of 71%. They further prepared a phosphine ligand tris(2-(diphenylphosphino)phenyl)phosphine in a one-pot reaction [90]. The multidentate ligand combined with Fe(BF₄)₂ · 6H₂O served as an efficient catalyst for CO₂ or bicarbonate hydrogenation. The in situ catalyst provided a high TON of 1600 under 60 bar H₂ at 80 °C for bicarbonate substrate in MeOH over 20 h.

Linehan et al. utilized Co(dmpe)₂H (dmpe: 1,2-bis(dimethylphosphino)ethane) for CO₂ hydrogenation and achieved a remarkable TON of 9400 after 1 h in THF under 20 atm H₂/CO₂ (1/1) at 21 °C in the presence of Verkade's base [43]. The cobalt-based system is similar to the fastest catalysts based on iridium at room temperature [12]. The mechanism study indicated a significant effect of the strong base [91].

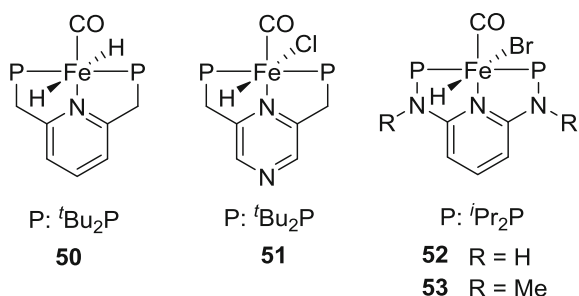
Copper catalysts are less investigated [92]. Copper complexes with tridentate 1,1,1-tris-(diphenylphosphinomethyl)ethane were studied by Appel et al. and provided a TON up to 500 under 4 MPa H₂/CO₂ (1/1) at 140 °C for 20 h [93, 94].

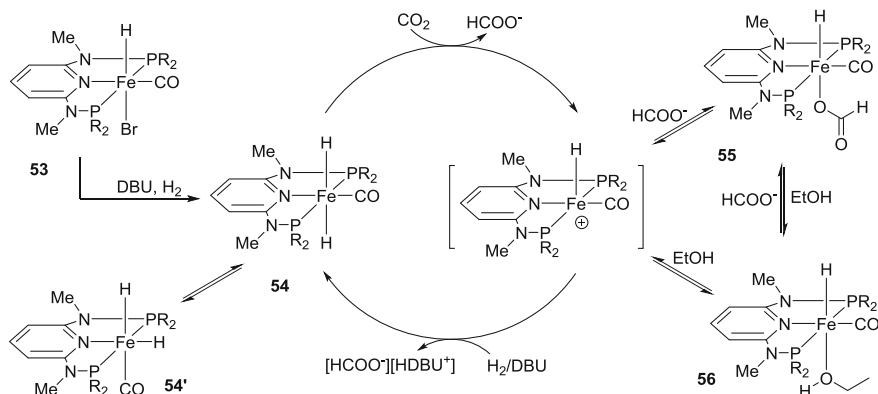
2.2.2 Using Pincer Ligands

In 2011, Milstein and co-workers reported an active pincer iron complex, *trans*-[FeH₂(CO)(PNP)] (**50**), which provided a high TON of 788 and TOF of 156 h⁻¹ under low pressure (0.6–1 MPa) in H₂O/THF (10/1) at 80 °C [42]. The observed activity was comparable to known noble metal catalysts and highlighted the enormous potential of iron-based catalysts for possible applications. The mechanism study suggested that the reaction proceeds through direct attack of the iron hydride to CO₂, followed by replacement of the resulting formate ligand by water. Dihydrogen coordination, prior to heterolytic cleavage of H₂ by hydroxide or de-aromatization, and subsequent proton migration were plausible pathways for the regeneration of the *trans*-dihydride complex **50** (Fig. 2.8). Milstein and co-workers also developed pyrazine-based pincer Fe complex **51** (Fig. 2.8), which provided a moderate TON of 388 for CO₂ hydrogenation in H₂O/THF (10/1) under 10 bar H₂/CO₂ (6.3/3.3) for 16 h [95].

In 2016, Kirchner and Gonsalvi prepared several iron pincer complexes, among which complexes [Fe(PNP^{H-*i*Pr})(H)(CO)(Br)] (**52**) and [Fe(PNP^{Me-*i*Pr})(H)(CO)(Br)] (**53**) were found to be active catalysts for hydrogenation of CO₂ and NaHCO₃ to formate under mild conditions (Fig. 2.8) [45]. Notably, the hydrogenation of NaHCO₃ to HCO₂Na with complex **52** proceeded even at room temperature in H₂O/THF (4/1), giving a TON of 188 after 72 h. In the presence of DBU, complex **53** afforded sodium formate with a TON of 856 after 21 h and 1032 after 72 h under an initial pressure of 80 bar in EtOH at 25 °C. A catalytic cycle with **53** was proposed based on the NMR study (Scheme 2.11). Dihydrido intermediate **54** was first formed from **53** in the presence of H₂ and DBU. CO₂ insertion into **54** gave hydrido formate complex **55**. Further formate elimination and hydrogenolysis regenerated **54** with the assistance of DBU. Solvent-assisted formate decoordination may occur to afford a pentacoordinate cationic Fe(II) hydrido carbonyl species. However, it was not observed. Under NMR, EtOH stabilized intermediate **56** was detected. DFT studies indicated an outer sphere mechanism with hydrido formate

Fig. 2.8 Pincer Fe complexes for CO₂ hydrogenation





Scheme 2.11 Proposed catalytic cycle for CO₂ hydrogenation with complex **53**. Redrawn based on Ref. [45]

complex **55** as the catalyst resting state. Water molecule is involved in the catalytic process and stabilizes the reaction intermediates by forming hydrogen bond with the free formate ion. It facilitates formate elimination from the coordination sphere of the metal, thereby promoting catalysis. The excess DBU enhances the overall reaction by acid base reaction with the formic acid product.

In 2015, Bernskoetter and Hazari et al. developed a family of pincer iron complexes supported by PNP ligands containing a secondary or tertiary amine (Fig. 2.9) [96]. Among them, complexes **57** and **58** exhibited high activity. Using Lewis acid, such as LiOTf, as a cocatalyst can significantly enhance the reactivity. Complex **57** with secondary amine gave a TON of 8910 in THF under 6.9 MPa H₂/CO₂ (1/1) for 24 h in the presence of DBU at 80 °C. By contrast, under the same conditions, complex **58** bearing a tertiary amine achieved an unprecedented TON of 58,990 and initial TOF up to 18,050 h⁻¹. The formate complex, which was stabilized by an intramolecular hydrogen bond between the N–H moiety of PNP ligand and the carbonyl oxygen of a formate ligand, was identified as the catalytic resting state. The primary roles of LA are to disrupt the intramolecular hydrogen bond and assist formate extrusion. In 2016, Bernskoetter et al. reported a cobalt analogue for hydrogenation of CO₂ [44]. When paired with the Lewis acid lithium triflate, pincer cobalt complex **59** afforded a TON near 30,000 (at 1000 psi, 45 °C). This finding represents a notable improvement in for the activity for cobalt catalysts. The authors successfully synthesized a series of low-valent pincer–molybdenum catalysts for CO₂ hydrogenation [46]. Complexes **60** with PN^{Me}P (MeN(CH₂CH₂PPh₂)₂) ligand provided a modest TON of 35 under 6.9 MPa H₂/CO₂ (1/1) for 24 h with the addition of Lewis acid LiOTf (Fig. 2.9).

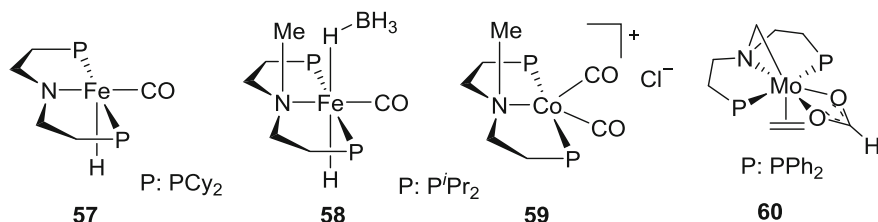


Fig. 2.9 Bernskoetter's catalysts for CO₂ hydrogenation

2.3 CO₂ Hydroboration and Hydrosilylation to Formate

Formic acid production from CO₂ hydrogenation with H₂ is thermodynamically unfavorable. The addition of a base is one strategy to promote the reaction because stable formate salt is generated. Hydrosilane and boranes are used as hydrogen sources for CO₂ reduction to overcome the unfavorable thermodynamics. The reduction of CO₂ to formate, acetal, methoxide (see Chap. 4), and methane is feasible by using appropriate catalysts [97–103]. The products, silyl formate or boron formate, can readily release formic acid by the addition of water. This reaction pathway is a simple method to produce formic acid from CO₂. A number of catalytic systems have been reported.

2.3.1 CO₂ Hydrosilylation

The hydrosilylation of CO₂ to formate dates back to 1981. Koinuma et al. first reported the reaction with complex RuCl₂(PPh₃)₃ using hydrosilanes HSiMeEt₂ or HSiMe(OMe)₂ to produce HCO₂SiR₃ albeit in low yields (up to 14%) [104].

Pitter et al. found that commercially available RuCl₃ · nH₂O is a good catalyst for hydrosilylation of CO₂ in MeCN with *n*-Hex₃SiH into *n*-Hex₃SiOOCH and with Me₂PhSiH into Me₂PhSiOOCH [105]. The initially formed [Ru^{II}Cl(MeCN)₅] [Ru^{III}Cl₄(MeCN)₂] (**61**) was found to be the most active catalyst, which provided a TON of 465 and a TOF of 233 h⁻¹ within 2 h at 60 °C. In addition, the reactions using Et₂SiH₂, Ph₂SiH₂, and *p*-C₆H₄-(Me₂SiH)₂ yielded Et₂Si(OOCH)₂, Ph₂Si(OOCH)₂, and *p*-C₆H₄-(Me₂SiOOCH)₂, respectively. When silyl formate was exposed to moisture, formic acid was readily released and simultaneously gave silanediols. Using complex Ru₂Cl₅(MeCN)₇ (**61**), the authors performed a recycling test. They found that Me₂PhSi(OOCH) could be isolated by distillation. Therefore, the residue was reused for the next run. After 10 successive experiments, they achieved a high TON of 4619 [106].

In 2012, Baba et al. utilized cheap Cu(OAc)₂ · H₂O and 1,2-bis(diphenylphosphino)benzene ligand as a catalyst and achieved a high TON of 8100 under 1 atm CO₂ at 60 °C after 6 h using an inexpensive hydrosilane polymethylhydrosiloxane

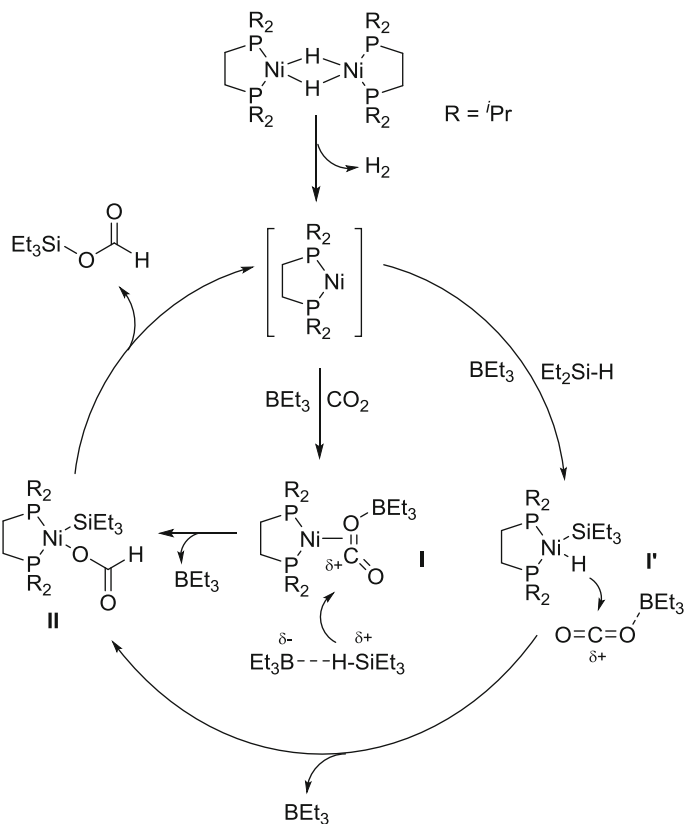
(PMHS) [107]. Afterward, they investigated the ligand effect by using other diphosphines [108]. 1,2-Bis(diisopropylphosphino)benzene was demonstrated to be the most effective ligand, which achieved a high TON of approximately 70,000 and TOF of 2900 h⁻¹ after 24 h under 1 atm of CO₂ at 60 °C.

In 2013, Hou et al. reported *N*-heterocyclic carbene–copper complex [Cu(O^{*i*}Bu)(IPr)] (IPr: 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) as a highly efficient catalyst, which showed a high TON of 7489 and a TOF of 1248 h⁻¹ under the same conditions [109]. The reaction of [Cu(O^{*i*}Bu)(IPr)] with triethoxysilane at room temperature instantly afforded [CuH(IPr)]. Subsequent reaction with CO₂ gave a Cu formate complex [Cu(OCHO)(IPr)], which was isolated and characterized with single-crystal X-ray diffraction. This study provided an important insight into the catalytic mechanism.

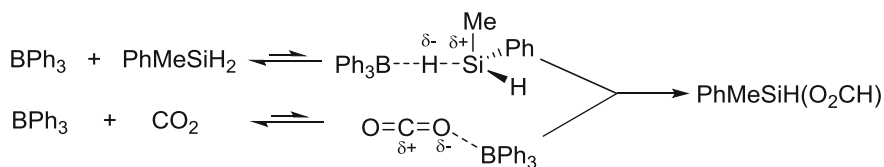
In 2013, García et al. reported the first hydrosilylation of CO₂ using the nickel complex [(dippe)Ni(μ-H)]₂ (**62**) (dippe: 1,2-bis(diisopropylphosphino)ethane) as a catalytic precursor in combination with Et₃B to give silyl formate (Et₃SiOC(O)H) in high yields (85–89%) at 80 °C for 1 h [110]. Ninety-five percent of Et₃SiH was converted to yield 88% of silyl formate corresponding to a TOF of 87.7 h⁻¹. The proposed two pathways for CO₂ hydrosilylation are depicted in Scheme 2.12. In one pathway, CO₂ coordination to the nickel center gives intermediate **I**. Next, the coordination of Et₃B to CO₂ and silane assists a nucleophilic attack of the hydride over CO₂ yielding species **II**. Reductive elimination releases the product Et₃SiOOH and regenerates the nickel catalyst. In another pathway, an oxidative addition of Et₃SiH over nickel(0) afforded hydride intermediate **I'**. The insertion of the CO₂ · BEt₃ adduct into the Ni–H bond generates nickel formate **II**, which releases Et₃SiOOH.

Okuda et al. reported triphenylborane (BPh₃) as an efficient catalyst in highly polar, aprotic solvents (CH₃CN or CH₃NO₂) for CO₂ hydrosilylation. Under mild conditions (1 bar CO₂, 40 °C), it provided silyl formates with high chemoselectivity (>95%) within 7 h [111]. Okuda et al. proposed a similar mechanism as García's (Scheme 2.13). Weak or dynamic coordination of BPh₃ to CO₂ and to the Si–H moiety generates two partially polarized species, respectively. Hydridic H attacks C of CO₂, ultimately resulting in the formate product. Highly polar solvents are supposed to enhance the reaction by stabilizing partially charged species.

Rodríguez and Conejero et al. have prepared platinum complex [Pt(I^{*i*}Bu')(I^{*i*}Bu)][BAR^F] (**63**) (BAR^F: tetrakis(3,5-trifluoromethyl)phenyl]borate) [112]. Although complex **63** is inert in the presence of CO₂, it can be transferred into Pt silyl derivative [Pt(SiHET₂)(I^{*i*}Bu)₂][BAR^F] (**64**) and platinum hydride [Pt(H)(I^{*i*}Bu)₂][BAR^F] (**65**) with Et₂SiH₂ (Scheme 2.14). Among these complexes, **63** is proven to be the most efficient for CO₂ hydrosilylation. When catalyst **63** (0.5%) was used with *n*BuSiH₃ under 5 atm of CO₂, silylformate *n*BuSiH₂(OCOH) was almost quantitatively obtained at approximately 15 min at room temperature corresponding to TON and TOF values of 200 and 714 h⁻¹, respectively. The high reactivity and selectivity toward mono-silylformates were attributed to the enhanced electrophilicity of the silicon atom in the silane through its coordination to platinum.



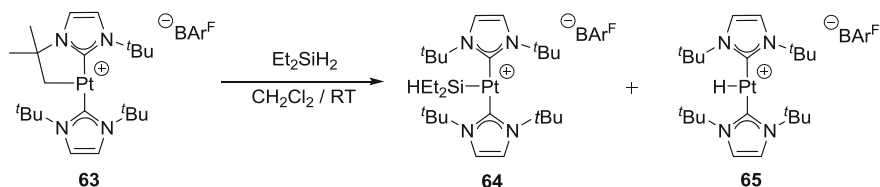
Scheme 2.12 Mechanistic proposal for CO₂ hydrosilylation. Reprinted with permission from Ref. [110]. Copyright (2013) American Chemical Society



Scheme 2.13 Proposed dual activation mechanism for BPh₃-catalyzed CO₂ hydrosilylation in highly polar solvents

2.3.2 CO₂ Hydroboration

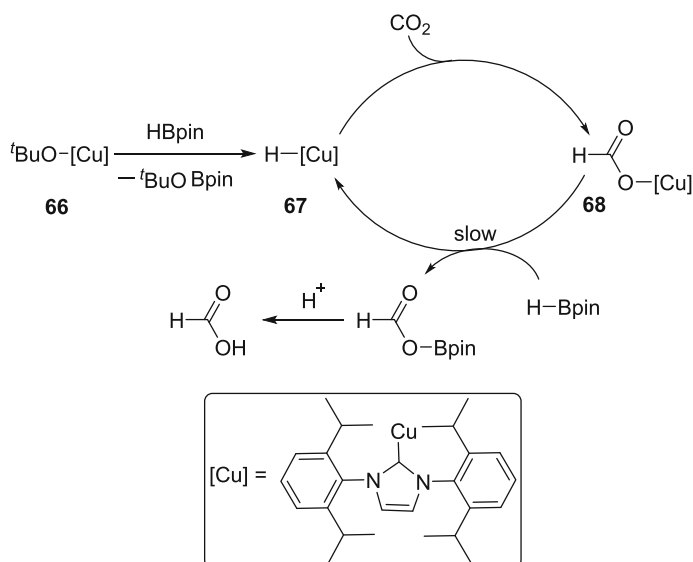
Compared with CO₂ hydrosilylation to formate, CO₂ hydroboration to formate is less reported because of its low selectivity to formate. Most of the CO₂ reductions



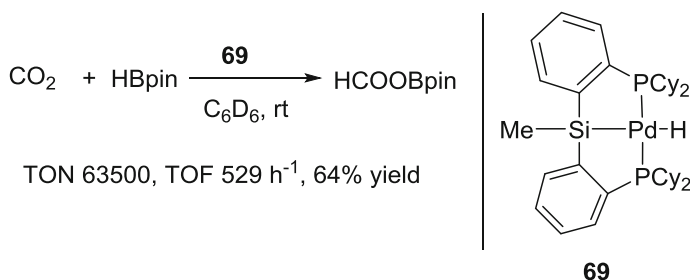
Scheme 2.14 Transformation of **63** to **64** and **65** in the presence of Et₂SiH₂. Redrawn based on Ref. [112]. Copyright (2016) Wiley-VCH GmbH & Co. KGaA, Weinheim

with hydroboranes generated mixtures or methoxyboranes as the end product (see Chap. 4) [113–115].

In 2013, Shintani and Nozaki first developed a copper/*N*-heterocyclic carbene-catalyzed hydroboration of CO₂ under mild conditions to give formic acid selectively [116]. When pinacolborane (HBpin) and catalyst [Cu(O^{*t*}Bu)(IPr)] (**66**, 10 mol%) were treated with 1 atm CO₂ under 35 °C, single product formic acid was obtained with 85% yield. Based on a series of experiments, the authors proposed a mechanism (Scheme 2.15). The hydroboration of CO₂ initially underwent the reaction of [Cu(O^{*t*}Bu)(IPr)] with HBpin generating [CuH(IPr)] (**67**). CO₂ insertion to **67** gave [Cu(OCHO)(IPr)] (**68**). Subsequent reaction of [Cu(OCHO)(IPr)] (IPr) with HBpin was turnover limiting and provided boron formate along with the regeneration of copper hydride. Finally, boron formate afforded formic acid by treatment with aqueous HCl.



Scheme 2.15 Proposed catalytic cycle for the copper-catalyzed hydroboration of CO₂. Reprinted with permission from Ref. [116]. Copyright (2013) American Chemical Society



Scheme 2.16 Selective reduction of CO₂ with HBpin into formic acid catalyzed by Pd(II) pincer complex **69**

In 2014, Hazari et al. described selective reduction of CO₂ with HBpin into formic acid catalyzed by Pd(II) pincer complex **69** (Scheme 2.16) [117]. An excellent TON of 63,500 was obtained in the hydroboration of CO₂ under room temperature. The selectivity was ascribed to the bulky steric hindrance of HBpin. The decline in selectivity was observed when HBpin was replaced with less steric hindrance HBcat (catecholborane).

References

1. Inoue Y, Izumida H, Sasaki Y, Hashimoto H (1976) Catalytic fixation of carbon dioxide to formic acid by transition-metal complexes under mild conditions. *Chem Lett* 5(8):863–864
2. Ezhova NN, Kolesnichenko NV, Bulygin AV, Slivinskii EV, Han S (2002) Hydrogenation of CO₂ to formic acid in the presence of the Wilkinson complex. *Russ Chem Bull* 51 (12):2165–2169. doi:[10.1023/A:1022162713837](https://doi.org/10.1023/A:1022162713837)
3. Jessop PG, Ikariya T, Noyori R (1994) Homogeneous catalytic hydrogenation of supercritical carbon dioxide. *Nature* 368(6468):231–233. doi:[10.1038/368231a0](https://doi.org/10.1038/368231a0)
4. Munshi P, Main AD, Linehan JC, Tai CC, Jessop PG (2002) Hydrogenation of carbon dioxide catalyzed by ruthenium trimethylphosphine complexes: The accelerating effect of certain alcohols and amines. *J Am Chem Soc* 124(27):7963–7971. doi:[10.1021/ja0167856](https://doi.org/10.1021/ja0167856)
5. Wang W-H, Himeda Y (2012) Recent Advances in transition metal-catalysed homogeneous hydrogenation of carbon dioxide in aqueous media. In: *Hydrogenation*. InTech, pp 249–268. doi:[10.5772/48658](https://doi.org/10.5772/48658)
6. Wang W, Wang S, Ma X, Gong J (2011) Recent advances in catalytic hydrogenation of carbon dioxide. *Chem Soc Rev* 40(7):3703–3727. doi:[10.1039/c1cs15008a](https://doi.org/10.1039/c1cs15008a)
7. Leitner W (1995) Carbon dioxide as a raw material: synthesis of formic acid and its derivatives from CO₂. *Angew Chem Int Ed* 34(20):2207–2221. doi:[10.1002/anie.199522071](https://doi.org/10.1002/anie.199522071)
8. Jessop PG, Ikariya T, Noyori R (1995) Homogeneous hydrogenation of carbon-dioxide. *Chem Rev* 95(2):259–272. doi:[10.1021/cr00034a001](https://doi.org/10.1021/cr00034a001)
9. Leitner W, Dinjus E, Gassner F (1998) CO₂ Chemistry. In: Cornils B, Herrmann WA (eds) *Aqueous-phase organometallic catalysis, concepts and applications*. Wiley-VCH, Weinheim, pp 486–498
10. Jessop PG, Joó F, Tai CC (2004) Recent advances in the homogeneous hydrogenation of carbon dioxide. *Coord Chem Rev* 248(21–24):2425–2442. doi:[10.1016/j.ccr.2004.05.019](https://doi.org/10.1016/j.ccr.2004.05.019)

11. Jessop PG (2007) Homogeneous hydrogenation of carbon dioxide. In: De Vries JG, Elsevier CJ (eds) Handbook of homogeneous hydrogenation, vol 1. Wiley-VCH, Weinheim, pp 489–511
12. Tanaka R, Yamashita M, Nozaki K (2009) Catalytic hydrogenation of carbon dioxide using Ir(III)-Pincer complexes. *J Am Chem Soc* 131(40):14168–14169. doi:[10.1021/ja903574e](https://doi.org/10.1021/ja903574e)
13. Tanaka R, Yamashita M, Chung LW, Morokuma K, Nozaki K (2011) Mechanistic studies on the reversible hydrogenation of carbon dioxide catalyzed by an Ir-PNP complex. *Organometallics* 30(24):6742–6750. doi:[10.1021/om2010172](https://doi.org/10.1021/om2010172)
14. Schmeier TJ, Dobereiner GE, Crabtree RH, Hazari N (2011) Secondary coordination sphere interactions facilitate the insertion step in an Iridium(III) CO₂ reduction catalyst. *J Am Chem Soc* 133(24):9274–9277. doi:[10.1021/ja2035514](https://doi.org/10.1021/ja2035514)
15. Himeda Y (2007) Conversion of CO₂ into formate by homogeneously catalyzed hydrogenation in water: tuning catalytic activity and water solubility through the acid-base equilibrium of the ligand. *Eur J Inorg Chem* 25:3927–3941. doi:[10.1002/ejic.200700494](https://doi.org/10.1002/ejic.200700494)
16. Wang W-H, Hull JF, Muckerman JT, Fujita E, Himeda Y (2012) Second-coordination-sphere and electronic effects enhance iridium(III)-catalyzed homogeneous hydrogenation of carbon dioxide in water near ambient temperature and pressure. *Energy Environ Sci* 5(7):7923–7926. doi:[10.1039/c2ee21888g](https://doi.org/10.1039/c2ee21888g)
17. Himeda Y, Onozawa-Komatsuzaki N, Sugihara H, Kasuga K (2007) Simultaneous tuning of activity and water solubility of complex catalysts by acid-base equilibrium of ligands for conversion of carbon dioxide. *Organometallics* 26(3):702–712. doi:[10.1021/om060899e](https://doi.org/10.1021/om060899e)
18. Hull JF, Himeda Y, Wang W-H, Hashiguchi B, Periana R, Szalda DJ, Muckerman JT, Fujita E (2012) Reversible hydrogen storage using CO₂ and a proton-switchable iridium catalyst in aqueous media under mild temperatures and pressures. *Nat Chem* 4(5):383–388. doi:[10.1038/nchem.1295](https://doi.org/10.1038/nchem.1295)
19. Wang W-H, Muckerman JT, Fujita E, Himeda Y (2013) Mechanistic insight through factors controlling effective hydrogenation of CO₂ catalyzed by bioinspired proton-responsive Iridium(III) complexes. *ACS Catal* 3(5):856–860. doi:[10.1021/cs400172j](https://doi.org/10.1021/cs400172j)
20. Onishi N, Xu S, Manaka Y, Suna Y, Wang W-H, Muckerman JT, Fujita E, Himeda Y (2015) CO₂ hydrogenation catalyzed by iridium complexes with a proton-responsive ligand. *Inorg Chem* 54(11):5114–5123. doi:[10.1021/ic502904q](https://doi.org/10.1021/ic502904q)
21. Azua A, Sanz S, Peris E (2011) Water-soluble Ir(III) N-Heterocyclic Carbene based catalysts for the reduction of CO₂ to formate by transfer hydrogenation and the deuteration of Aryl Amines in water. *Chem-Eur J* 17(14):3963–3967. doi:[10.1002/chem.201002907](https://doi.org/10.1002/chem.201002907)
22. Maenaka Y, Suenobu T, Fukuzumi S (2012) Catalytic interconversion between hydrogen and formic acid at ambient temperature and pressure. *Energy Environ Sci* 5(6):7360–7367. doi:[10.1039/c2ee03315a](https://doi.org/10.1039/c2ee03315a)
23. Muller K, Sun Y, Thiel WR (2013) Ruthenium(II) phosphite complexes as catalysts for the hydrogenation of carbon dioxide. *ChemCatChem* 5(6):1340–1343. doi:[10.1002/cctc.201200818](https://doi.org/10.1002/cctc.201200818)
24. Moret S, Dyson PJ, Laurenczy G (2014) Direct synthesis of formic acid from carbon dioxide by hydrogenation in acidic media. *Nature Commun* 5:4017–4023. doi:[10.1038/ncomms5017](https://doi.org/10.1038/ncomms5017)
25. Lau CP, Chen YZ (1995) Hydrogenation of carbon dioxide to formic acid using a 6,6'-cichloro-2,2'-bipyridine complex of ruthenium, *cis*-[Ru(6,6'-Cl₂bpy)₂(H₂O)₂](CF₃SO₃)₂. *J Mol Catal A* 101(1):33–36. doi:[10.1016/1381-1169\(95\)00068-2](https://doi.org/10.1016/1381-1169(95)00068-2)
26. Khan MMT, Halligudi SB, Shukla S (1989) Reduction of CO₂ by molecular-hydrogen to formic acid and formaldehyde and their decomposition to CO and H₂O. *J Mol Catal* 57(1):47–60. doi:[10.1016/0304-5102\(89\)80126-9](https://doi.org/10.1016/0304-5102(89)80126-9)
27. Laurenczy G, Joó F, Nadasdi L (2000) Formation and characterization of water-soluble hydrido-ruthenium(II) complexes of 1,3,5-triaza-7-phosphaadamantane and their catalytic activity in hydrogenation of CO₂ and HCO₃⁻ in aqueous solution. *Inorg Chem* 39(22):5083–5088. doi:[10.1021/ic000200b](https://doi.org/10.1021/ic000200b)

28. Elek J, Nadasdi L, Papp G, Laurenczy G, Joó F (2003) Homogeneous hydrogenation of carbon dioxide and bicarbonate in aqueous solution catalyzed by water-soluble ruthenium(II) phosphine complexes. *Appl Catal A-Gen* 255(1):59–67. doi:[10.1016/S0926-860X\(03\)00644-6](https://doi.org/10.1016/S0926-860X(03)00644-6)
29. Federsel C, Jackstell R, Boddien A, Laurenczy G, Beller M (2010) Ruthenium-catalyzed hydrogenation of bicarbonate in water. *Chemsuschem* 3(9):1048–1050. doi:[10.1002/cssc.201000151](https://doi.org/10.1002/cssc.201000151)
30. Hsu S-F, Rommel S, Eversfield P, Muller K, Klemm E, Thiel WR, Plietker B (2014) A rechargeable hydrogen battery based on Ru catalysis. *Angew Chem Int Ed* 53(27):7074–7078. doi:[10.1002/anie.201310972](https://doi.org/10.1002/anie.201310972)
31. Filonenko GA, van Putten R, Schulpén EN, Hensen EJM, Pidko EA (2014) Highly efficient reversible hydrogenation of carbon dioxide to formates using a Ruthenium PNP-Pincer catalyst. *ChemCatChem* 6(6):1526–1530. doi:[10.1002/cctc.201402119](https://doi.org/10.1002/cctc.201402119)
32. Huff CA, Sanford MS (2013) Catalytic CO₂ hydrogenation to formate by a Ruthenium Pincer complex. *ACS Catal* 3(10):2412–2416. doi:[10.1021/cs400609u](https://doi.org/10.1021/cs400609u)
33. Filonenko GA, Conley MP, Coperet C, Lutz M, Hensen EJM, Pidko EA (2013) The impact of metal-ligand cooperation in hydrogenation of carbon dioxide catalyzed by Ruthenium PNP Pincer. *ACS Catal* 3(11):2522–2526. doi:[10.1021/cs4006869](https://doi.org/10.1021/cs4006869)
34. Graf E, Leitner W (1992) Direct formation of formic-acid from carbon-dioxide and dihydrogen using the [(Rh(Cod)Cl)₂]Ph₂P(CH₂)₄PPh₂ catalyst system. *Chem Commun* (8):623–624. doi:[10.1039/C39920000623](https://doi.org/10.1039/C39920000623)
35. Gassner F, Leitner W (1993) Hydrogenation of carbon dioxide to formic acid using water-soluble rhodium catalysts. *Chem Commun* (19):1465–1466. doi:[10.1039/C39930001465](https://doi.org/10.1039/C39930001465)
36. Zhao G, Joó F (2011) Free formic acid by hydrogenation of carbon dioxide in sodium formate solutions. *Catal Commun* 14(1):74–76. doi:[10.1016/j.catcom.2011.07.017](https://doi.org/10.1016/j.catcom.2011.07.017)
37. Bays JT, Priyadarshani N, Jeletic MS, Hulley EB, Miller DL, Linehan JC, Shaw WJ (2014) The influence of the second and outer coordination spheres on Rh(diphosphine)₂ CO₂ hydrogenation catalysts. *ACS Catal* 4(10):3663–3670. doi:[10.1021/cs5009199](https://doi.org/10.1021/cs5009199)
38. Wesselbaum S, Hintermair U, Leitner W (2012) Continuous-flow hydrogenation of carbon dioxide to pure formic acid using an integrated scCO₂ process with immobilized catalyst and base. *Angew Chem Int Ed* 51(34):8585–8588. doi:[10.1002/anie.201203185](https://doi.org/10.1002/anie.201203185)
39. Jantke D, Pardatscher L, Drees M, Cokoja M, Herrmann WA, Kuhn FE (2016) Hydrogen production and storage on a formic acid/bicarbonate platform using water-soluble N-Heterocyclic Carbene complexes of late transition metals. *Chemsuschem* 9(19):2849–2854. doi:[10.1002/cssc.201600861](https://doi.org/10.1002/cssc.201600861)
40. Federsel C, Boddien A, Jackstell R, Jennerjahn R, Dyson PJ, Scopelliti R, Laurenczy G, Beller M (2010) A well-defined iron catalyst for the reduction of bicarbonates and carbon dioxide to formates, alkyl formates, and formamides. *Angew Chem Int Ed* 49(50):9777–9780. doi:[10.1002/anie.201004263](https://doi.org/10.1002/anie.201004263)
41. Federsel C, Ziebart C, Jackstell R, Baumann W, Beller M (2012) Catalytic hydrogenation of carbon dioxide and bicarbonates with a well-defined cobalt dihydrogen complex. *Chem-Eur J* 18(1):72–75. doi:[10.1002/chem.201101343](https://doi.org/10.1002/chem.201101343)
42. Langer R, Diskin-Posner Y, Leitner G, Shimon LJW, Ben-David Y, Milstein D (2011) Low-pressure hydrogenation of carbon dioxide catalyzed by an iron pincer complex exhibiting noble metal activity. *Angew Chem Int Ed* 50(42):9948–9952. doi:[10.1002/anie.201104542](https://doi.org/10.1002/anie.201104542)
43. Jeletic MS, Mock MT, Appel AM, Linehan JC (2013) A cobalt-based catalyst for the hydrogenation of CO₂ under ambient conditions. *J Am Chem Soc* 135(31):11533–11536. doi:[10.1021/ja406601v](https://doi.org/10.1021/ja406601v)

44. Spentzos AZ, Barnes CL, Bernskoetter WH (2016) Effective Pincer Cobalt precatalysts for Lewis acid assisted CO₂ hydrogenation. *Inorg Chem* 55(16):8225–8233. doi:[10.1021/acs.inorgchem.6b01454](https://doi.org/10.1021/acs.inorgchem.6b01454)
45. Bertini F, Gorgas N, Stöger B, Peruzzini M, Veiros LF, Kirchner K, Gonsalvi L (2016) Efficient and mild carbon dioxide hydrogenation to formate catalyzed by Fe(II) Hydrido Carbonyl complexes bearing 2,6-(Diaminopyridyl)diphosphine Pincer ligands. *ACS Catal* 6(5):2889–2893. doi:[10.1021/acscatal.6b00416](https://doi.org/10.1021/acscatal.6b00416)
46. Zhang Y, Williard PG, Bernskoetter WH (2016) Synthesis and characterization of Pincer-Molybdenum precatalysts for CO₂ hydrogenation. *Organometallics* 35(6):860–865. doi:[10.1021/acs.organomet.5b00955](https://doi.org/10.1021/acs.organomet.5b00955)
47. Jessop PG, Hsiao Y, Ikariya T, Noyori R (1996) Homogeneous catalysis in supercritical fluids: hydrogenation of supercritical carbon dioxide to formic acid, alkyl formates, and formamides. *J Am Chem Soc* 118(2):344–355. doi:[10.1021/ja953097b](https://doi.org/10.1021/ja953097b)
48. Joó F, Laurenczy G, Nadasdi L, Elek J (1999) Homogeneous hydrogenation of aqueous hydrogen carbonate to formate under exceedingly mild conditions—a novel possibility of carbon dioxide activation. *Chem Commun* (11):971–972. doi:[10.1039/A902368B](https://doi.org/10.1039/A902368B)
49. Katho A, Opre Z, Laurenczy G, Joó F (2003) Water-soluble analogs of [RuCl₃(NO)(PPh₃)₂] and their catalytic activity in the hydrogenation of carbon dioxide and bicarbonate in aqueous solution. *J Mol Catal A-Chem* 204:143–148. doi:[10.1016/S1381-1169\(03\)00293-0](https://doi.org/10.1016/S1381-1169(03)00293-0)
50. Kovacs G, Schubert G, Joó F, Papai I (2006) Theoretical investigation of catalytic HCO₃⁻ hydrogenation in aqueous solutions. *Catal Today* 115(1):53–60. doi:[10.1016/j.cattod.2006.02.018](https://doi.org/10.1016/j.cattod.2006.02.018)
51. Horvath H, Laurenczy G, Katho A (2004) Water-soluble (η⁶-arene)ruthenium(II)-phosphine complexes and their catalytic activity in the hydrogenation of bicarbonate in aqueous solution. *J Organometal Chem* 689(6):1036–1045. doi:[10.1016/j.jorganchem.2003.11.036](https://doi.org/10.1016/j.jorganchem.2003.11.036)
52. Erlandsson M, Landaeta VR, Gonsalvi L, Peruzzini M, Phillips AD, Dyson PJ, Laurenczy G (2008) (Pentamethylcyclopentadienyl)iridium-PTA (PTA = 1,3,5-triaza-7-phosphaadamantane) complexes and their application in catalytic water phase carbon dioxide hydrogenation. *Eur J Inorg Chem* 4:620–627. doi:[10.1002/ejic.200700792](https://doi.org/10.1002/ejic.200700792)
53. Laurenczy G, Jedner S, Alessio E, Dyson PJ (2007) In situ NMR characterisation of an intermediate in the catalytic hydrogenation of CO₂ and HCO₃⁻ in aqueous solution. *Inorg Chem Commun* 10(5):558–562. doi:[10.1016/j.inoche.2007.01.020](https://doi.org/10.1016/j.inoche.2007.01.020)
54. Muller K, Sun Y, Heimermann A, Menges F, Niedner-Schatteburg G, van Wullen C, Thiel WR (2013) Structure-reactivity relationships in the hydrogenation of carbon dioxide with ruthenium complexes bearing pyridinylazolato ligands. *Chem-Eur J* 19(24):7825–7834. doi:[10.1002/chem.201204199](https://doi.org/10.1002/chem.201204199)
55. Drake JL, Manna CM, Byers JA (2013) Enhanced carbon dioxide hydrogenation facilitated by catalytic quantities of bicarbonate and other inorganic salts. *Organometallics* 32(23):6891–6894. doi:[10.1021/om401057p](https://doi.org/10.1021/om401057p)
56. Zhang P, Ni SF, Dang L (2016) Steric and electronic effects of bidentate phosphine ligands on ruthenium(II)-catalyzed hydrogenation of carbon dioxide. *Chem Asian J* 11(18):2528–2536. doi:[10.1002/asia.201600611](https://doi.org/10.1002/asia.201600611)
57. Gunanathan C, Milstein D (2011) Metal-ligand cooperation by aromatization-dearomatization: a new paradigm in bond activation and “Green” catalysis. *Acc Chem Res* 44(8):588–602. doi:[10.1021/ar2000265](https://doi.org/10.1021/ar2000265)
58. Zhang J, Leitus G, Ben-David Y, Milstein D (2006) Efficient homogeneous catalytic hydrogenation of esters to alcohols. *Angew Chem Int Ed* 45(7):1113–1115. doi:[10.1002/anie.200503771](https://doi.org/10.1002/anie.200503771)
59. Praneeth VKK, Ringenberg MR, Ward TR (2012) Redox-active ligands in catalysis. *Angew Chem Int Ed* 51(41):10228–10234. doi:[10.1002/anie.201204100](https://doi.org/10.1002/anie.201204100)
60. Vogt M, Gargir M, Iron MA, Diskin-Posner Y, Ben-David Y, Milstein D (2012) A new mode of activation of CO₂ by metal-ligand cooperation with reversible C–C and M–O bond formation at ambient temperature. *Chem-Eur J* 18(30):9194–9197. doi:[10.1002/chem.201201730](https://doi.org/10.1002/chem.201201730)

61. Huff CA, Kampf JW, Sanford MS (2012) Role of a noninnocent pincer ligand in the activation of CO₂ at (PNN)Ru(H)(CO). *Organometallics* 31(13):4643–4645. doi:[10.1021/om300403b](https://doi.org/10.1021/om300403b)
62. Filonenko GA, Hensen EJM, Pidko EA (2014) Mechanism of CO₂ hydrogenation to formates by homogeneous Ru-PNP pincer catalyst: from a theoretical description to performance optimization. *Catal Sci Technol* 4(10):3474–3485. doi:[10.1039/c4cy00568f](https://doi.org/10.1039/c4cy00568f)
63. Kothandaraman J, Goepfert A, Czaun M, Olah GA, Surya Prakash GK (2016) CO₂ capture by amines in aqueous media and its subsequent conversion to formate with reusable ruthenium and iron catalysts. *Green Chem* 18(21):5831–5838. doi:[10.1039/c6gc01165a](https://doi.org/10.1039/c6gc01165a)
64. Tsai JC, Nicholas KM (1992) Rhodium-catalyzed hydrogenation of carbon-dioxide to formic acid. *J Am Chem Soc* 114(13):5117–5124. doi:[10.1021/ja00039a024](https://doi.org/10.1021/ja00039a024)
65. Lilio AM, Reineke MH, Moore CE, Rheingold AL, Takase MK, Kubiak CP (2015) Incorporation of pendant bases into Rh(diphosphine)₂ complexes: synthesis, thermodynamic studies, and catalytic CO₂ hydrogenation activity of [Rh(P₂N₂)₂]⁺ complexes. *J Am Chem Soc* 137(25):8251–8260. doi:[10.1021/jacs.5b04291](https://doi.org/10.1021/jacs.5b04291)
66. Yang XZ (2011) Hydrogenation of carbon dioxide catalyzed by pnp pincer iridium, iron, and cobalt complexes: a computational design of base metal catalysts. *ACS Catal* 1(8):849–854. doi:[10.1021/cs2000329](https://doi.org/10.1021/cs2000329)
67. Li J, Yoshizawa K (2011) Catalytic hydrogenation of carbon dioxide with a highly active hydride on Ir(III)-Pincer complex: mechanism for CO₂ insertion and nature of metal-hydride bond. *Bull Chem Soc Jpn* 84(10):1039–1048. doi:[10.1246/bcsj.20110128](https://doi.org/10.1246/bcsj.20110128)
68. Feller M, Gellrich U, Anaby A, Diskin-Posner Y, Milstein D (2016) Reductive cleavage of CO₂ by metal-ligand-cooperation mediated by an iridium pincer complex. *J Am Chem Soc* 138(20):6445–6454. doi:[10.1021/jacs.6b00202](https://doi.org/10.1021/jacs.6b00202)
69. Kang P, Cheng C, Chen Z, Schauer CK, Meyer TJ, Brookhart M (2012) Selective electrocatalytic reduction of CO₂ to formate by water-stable iridium dihydride pincer complexes. *J Am Chem Soc* 134(12):5500–5503. doi:[10.1021/ja300543s](https://doi.org/10.1021/ja300543s)
70. Bolinger CM, Sullivan BP, Conrad D, Gilbert JA, Story N, Meyer TJ (1985) Electrocatalytic reduction of CO₂ based on polypyridyl complexes of rhodium and ruthenium. *Chem Commun* (12):796–797. doi:[10.1039/C39850000796](https://doi.org/10.1039/C39850000796)
71. Caix C, ChardonNoblat S, Deronzier A (1997) Electrocatalytic reduction of CO₂ into formate with [(η⁵-Me₅C₅)M(L)Cl]⁺ complexes (L = 2,2'-bipyridine ligands; M = Rh(III) and Ir(III)). *J Electroanal Chem* 434(1):163–170. doi:[10.1016/S0022-0728\(97\)00058-2](https://doi.org/10.1016/S0022-0728(97)00058-2)
72. Hayashi H, Ogo S, Abura T, Fukuzumi S (2003) Accelerating effect of a proton on the reduction of CO₂ dissolved in water under acidic conditions. Isolation, crystal structure, and reducing ability of a water-soluble ruthenium hydride complex. *J Am Chem Soc* 125(47):14266–14267. doi:[10.1021/ja036117f](https://doi.org/10.1021/ja036117f)
73. Wang WH, Himeda Y, Muckerman JT, Manbeck GF, Fujita E (2015) CO₂ Hydrogenation to formate and methanol as an alternative to photo- and electrochemical CO₂ reduction. *Chem Rev* 115(23):12936–12973. doi:[10.1021/acs.chemrev.5b00197](https://doi.org/10.1021/acs.chemrev.5b00197)
74. Ohnishi YY, Matsunaga T, Nakao Y, Sato H, Sakaki S (2005) Ruthenium(II)-catalyzed hydrogenation of carbon dioxide to formic acid. theoretical study of real catalyst, ligand effects, and solvation effects. *J Am Chem Soc* 127(11):4021–4032. doi:[10.1021/ja043697n](https://doi.org/10.1021/ja043697n)
75. Himeda Y, Onozawa-Komatsuzaki N, Sugihara H, Arakawa H, Kasuga K (2004) Half-sandwich complexes with 4,7-dihydroxy-1,10-phenanthroline: water-soluble, highly efficient catalysts for hydrogenation of bicarbonate attributable to the generation of an oxyanion on the catalyst ligand. *Organometallics* 23(7):1480–1483. doi:[10.1021/om030382s](https://doi.org/10.1021/om030382s)
76. Himeda Y, Onozawa-Komatsuzaki N, Sugihara H, Kasuga K (2006) Highly efficient conversion of carbon dioxide catalyzed by half-sandwich complexes with pyridinol ligand: the electronic effect of oxyanion. *J Photochem Photobio A* 182(3):306–309. doi:[10.1016/j.jphotochem.2006.04.025](https://doi.org/10.1016/j.jphotochem.2006.04.025)
77. Himeda Y, Miyazawa S, Hirose T (2011) Interconversion between formic acid and H₂/CO₂ using rhodium and ruthenium catalysts for CO₂ fixation and H₂ storage. *Chemsuschem* 4(4):487–493. doi:[10.1002/cssc.201000327](https://doi.org/10.1002/cssc.201000327)

78. Crabtree RH (2011) Multifunctional ligands in transition metal catalysis. *New J Chem* 35 (1):18–23. doi:[10.1039/c0nj00776e](https://doi.org/10.1039/c0nj00776e)
79. Xu S, Onishi N, Tsurusaki A, Manaka Y, Wang W-H, Muckerman JT, Fujita E (2015) Himeda Y (2015) efficient Cp*Ir catalysts with imidazoline ligands for CO₂ hydrogenation. *Eur J Inorg Chem* 34:5591–5594. doi:[10.1002/ejic.201501030](https://doi.org/10.1002/ejic.201501030)
80. Shima S, Lyon EJ, Sordel-Klippert MS, Kauss M, Kahnt J, Thauer RK, Steinbach K, Xie XL, Verdier L, Griesinger C (2004) The cofactor of the iron-sulfur cluster free hydrogenase Hmd: structure of the light-inactivation product. *Angew Chem Int Ed* 43 (19):2547–2551. doi:[10.1002/anie.200353763](https://doi.org/10.1002/anie.200353763)
81. Shima S, Pilak O, Vogt S, Schick M, Stagni MS, Meyer-Klaucke W, Warkentin E, Thauer RK, Ermler U (2008) The crystal structure of Fe-hydrogenase reveals the geometry of the active site. *Science* 321(5888):572–575. doi:[10.1126/science.1158978](https://doi.org/10.1126/science.1158978)
82. Shima S, Ermler U (2011) Structure and function of Fe-Hydrogenase and its Iron-Guanylylpyridinol (FeGP) cofactor. *Eur J Inorg Chem* 7:963–972. doi:[10.1002/ejic.201000955](https://doi.org/10.1002/ejic.201000955)
83. Yang X, Hall MB (2009) Monoiron hydrogenase catalysis: hydrogen activation with the formation of a dihydrogen, Fe–H–H–O, bond and methenyl-H4MPT⁺ triggered hydride transfer. *J Am Chem Soc* 131(31):10901–10908. doi:[10.1021/ja902689n](https://doi.org/10.1021/ja902689n)
84. Manaka Y, Wang W-H, Suna Y, Kambayashi H, Muckerman JT, Fujita E, Himeda Y (2014) Efficient H₂ generation from formic acid using azole complexes in water. *Catal Sci Technol* 4(1):34–37. doi:[10.1039/c3cy00830d](https://doi.org/10.1039/c3cy00830d)
85. Wang W-H, Xu S, Manaka Y, Suna Y, Kambayashi H, Muckerman JT, Fujita E, Himeda Y (2014) Formic acid dehydrogenation with bioinspired Iridium complexes: a kinetic isotope effect study and mechanistic insight. *ChemSuschem* 7(7):1976–1983. doi:[10.1002/cssc.201301414](https://doi.org/10.1002/cssc.201301414)
86. Suna Y, Ertem MZ, Wang W-H, Kambayashi H, Manaka Y, Muckerman JT, Fujita E, Himeda Y (2014) Positional effects of hydroxy groups on catalytic activity of proton-responsive half-sandwich Cp*Iridium(III) complexes. *Organometallics* 33(22):6519–6530. doi:[10.1021/om500832d](https://doi.org/10.1021/om500832d)
87. Wang L, Onishi N, Murata K, Hirose T, Muckerman JT, Fujita E, Himeda Y (2017) Efficient hydrogen storage and production using a catalyst with an Imidazoline-based, proton-responsive ligand. *ChemSusChem* 10(6):1071–1075. doi:[10.1002/cssc.201601437](https://doi.org/10.1002/cssc.201601437)
88. Sanz S, Benitez M, Peris E (2010) A new approach to the reduction of carbon dioxide: CO₂ reduction to formate by transfer hydrogenation in iPrOH. *Organometallics* 29(1):275–277. doi:[10.1021/om900820x](https://doi.org/10.1021/om900820x)
89. Badii YM, Wang W-H, Hull JF, Szalda DJ, Muckerman JT, Himeda Y, Fujita E (2013) Cp*Co(III) catalysts with proton-responsive ligands for carbon dioxide hydrogenation in aqueous media. *Inorg Chem* 52(21):12576–12586. doi:[10.1021/ic401707u](https://doi.org/10.1021/ic401707u)
90. Ziebart C, Federsel C, Anbarasan P, Jackstell R, Baumann W, Spannenberg A, Beller M (2012) Well-defined iron catalyst for improved hydrogenation of carbon dioxide and bicarbonate. *J Am Chem Soc* 134(51):20701–20704. doi:[10.1021/ja307924a](https://doi.org/10.1021/ja307924a)
91. Jeletic MS, Helm ML, Hulley EB, Mock MT, Appel AM, Linehan JC (2014) A cobalt hydride catalyst for the hydrogenation of CO₂: pathways for catalysis and deactivation. *ACS Catal* 4(10):3755–3762. doi:[10.1021/cs5009927](https://doi.org/10.1021/cs5009927)
92. Watari R, Kayaki Y, Hirano S-I, Matsumoto N, Ikariya T (2015) Hydrogenation of carbon dioxide to formate catalyzed by a Copper/1,8-Diazabicyclo[5.4.0]undec-7-ene System. *Adv Syn Catal* 357(7):1369–1373. doi:[10.1002/adsc.201500043](https://doi.org/10.1002/adsc.201500043)
93. Zall CM, Linehan JC, Appel AM (2015) A molecular copper catalyst for hydrogenation of CO₂ to formate. *ACS Catal* 5(9):5301–5305. doi:[10.1021/acscatal.5b01646](https://doi.org/10.1021/acscatal.5b01646)
94. Zall CM, Linehan JC, Appel AM (2016) Triphosphine-Ligated copper hydrides for CO₂ hydrogenation: structure, reactivity, and thermodynamic studies. *J Am Chem Soc* 138 (31):9968–9977. doi:[10.1021/jacs.6b05349](https://doi.org/10.1021/jacs.6b05349)
95. Rivada-Wheeler O, Dauth A, Leitus G, Diskin-Posner Y, Milstein D (2015) Synthesis and reactivity of iron complexes with a new pyrazine-based pincer ligand, and application in

- catalytic low-pressure hydrogenation of carbon dioxide. *Inorg Chem* 54(9):4526–4538. doi:[10.1021/acs.inorgchem.5b00366](https://doi.org/10.1021/acs.inorgchem.5b00366)
96. Zhang Y, MacIntosh AD, Wong JL, Bielinski EA, Williard PG, Mercado BQ, Hazari N, Bernskoetter WH (2015) Iron catalyzed CO₂ hydrogenation to formate enhanced by Lewis acid co-catalysts. *Chem Sci* 6(7):4291–4299. doi:[10.1039/c5sc01467k](https://doi.org/10.1039/c5sc01467k)
97. LeBlanc FA, Piers WE, Parvez M (2014) Selective hydrosilylation of CO₂ to a bis(silylacetal) using an anilido bipyridyl-ligated organoscandium catalyst. *Angew Chem Int Ed* 53(3):789–792. doi:[10.1002/anie.201309094](https://doi.org/10.1002/anie.201309094)
98. Deglmann P, Ember E, Hofmann P, Pitter S, Walter O (2007) Experimental and theoretical investigations on the catalytic hydrosilylation of carbon dioxide with ruthenium nitrile complexes. *Chem-Eur J* 13(10):2864–2879. doi:[10.1002/chem.200600396](https://doi.org/10.1002/chem.200600396)
99. Lalrempuia R, Iglesias M, Polo V, Sanz Miguel PJ, Fernández-Alvarez FJ, Pérez-Torrente JJ, Oro LA (2012) Effective fixation of CO₂ by Iridium-catalyzed hydrosilylation. *Angew Chem Int Ed* 51(51):12824–12827. doi:[10.1002/anie.201206165](https://doi.org/10.1002/anie.201206165)
100. Jiang Y, Blacque O, Fox T, Berke H (2013) Catalytic CO₂ activation assisted by rhenium hydride/B(C₆F₅)₃ frustrated Lewis pairs–metal hydrides functioning as FLP bases. *J Am Chem Soc* 135(20):7751–7760. doi:[10.1021/ja402381d](https://doi.org/10.1021/ja402381d)
101. Scheuermann ML, Semproni SP, Pappas I, Chirik PJ (2014) Carbon dioxide hydrosilylation promoted by cobalt pincer complexes. *Inorg Chem* 53(18):9463–9465. doi:[10.1021/ic501901n](https://doi.org/10.1021/ic501901n)
102. Itagaki S, Yamaguchi K, Mizuno N (2013) Catalytic synthesis of silyl formates with 1 atm of CO₂ and their utilization for synthesis of formyl compounds and formic acid. *J Mol Catal A-Chem* 366:347–352. doi:[10.1016/j.molcata.2012.10.014](https://doi.org/10.1016/j.molcata.2012.10.014)
103. Rios P, Curado N, Lopez-Serrano J, Rodriguez A (2016) Selective reduction of carbon dioxide to bis(silyl)acetal catalyzed by a PBP-supported nickel complex. *Chem Commun* 52(10):2114–2117. doi:[10.1039/C5CC09650B](https://doi.org/10.1039/C5CC09650B)
104. Koinuma H, Kawakami F, Kato H, Hirai H (1981) Hydrosilylation of carbon dioxide catalyzed by ruthenium complexes. *Chem Commun* (5):213–214. doi:[10.1039/C39810000213](https://doi.org/10.1039/C39810000213)
105. Jansen A, Gorls H, Pitter S (2000) *trans*-[(Ru^{II}Cl)(MeCN)₅][(Ru^{III}Cl₄)(MeCN)₂]: a reactive intermediate in the homogeneous catalyzed hydrosilylation of carbon dioxide. *Organometallics* 19(2):135–138. doi:[10.1021/om990654k](https://doi.org/10.1021/om990654k)
106. Jansen A, Pitter S (2004) Homogeneously catalysed reduction of carbon dioxide with silanes: a study on solvent and ligand effects and catalyst recycling. *J Mol Catal A-Chem* 217(1–2):41–45. doi:[10.1016/j.molcata.2004.03.041](https://doi.org/10.1016/j.molcata.2004.03.041)
107. Motokura K, Kashiwame D, Miyaji A, Baba T (2012) Copper-catalyzed formic acid synthesis from CO₂ with Hydrosilanes and H₂O. *Org Lett* 14(10):2642–2645. doi:[10.1021/ol301034j](https://doi.org/10.1021/ol301034j)
108. Motokura K, Kashiwame D, Takahashi N, Miyaji A, Baba T (2013) Highly active and selective catalysis of Copper Diphosphine complexes for the transformation of carbon dioxide into Silyl formate. *Chem-Eur J* 19(30):10030–10037. doi:[10.1002/chem.201300935](https://doi.org/10.1002/chem.201300935)
109. Zhang L, Cheng J, Hou Z (2013) Highly efficient catalytic hydrosilylation of carbon dioxide by an N-heterocyclic carbene copper catalyst. *Chem Commun* 49(42):4782–4784. doi:[10.1039/c3cc41838c](https://doi.org/10.1039/c3cc41838c)
110. González-Sebastián L, Flores-Alamo M, García JJ (2013) Nickel-catalyzed hydrosilylation of CO₂ in the presence of Et₃B for the synthesis of formic acid and related formates. *Organometallics* 32(23):7186–7194. doi:[10.1021/om400876j](https://doi.org/10.1021/om400876j)
111. Mukherjee D, Sauer DF, Zanardi A, Okuda J (2016) Selective metal-free hydrosilylation of CO₂ catalyzed by Triphenylborane in highly polar, Aprotic solvents. *Chem-Eur J* 22(23):7730–7733. doi:[10.1002/chem.201601006](https://doi.org/10.1002/chem.201601006)
112. Rios P, Diez J, Lopez-Serrano J, Rodriguez A, Conejero S (2016) Cationic Platinum(II) sigma-SiH complexes in carbon dioxide hydrosilation. *Chem-Eur J* 22(47):16791–16795. doi:[10.1002/chem.201603524](https://doi.org/10.1002/chem.201603524)

113. Zeng G, Maeda S, Taketsugu T, Sakaki S (2016) Catalytic hydrogenation of carbon dioxide with Ammonia-Borane by Pincer-type phosphorus compound: a theoretical prediction. *J Am Chem Soc* 138(41):13481–13484. doi:[10.1021/jacs.6b07274](https://doi.org/10.1021/jacs.6b07274)
114. Bontemps S, Vendier L, Sabo-Etienne S (2014) Ruthenium-catalyzed reduction of carbon dioxide to formaldehyde. *J Am Chem Soc* 136(11):4419–4425. doi:[10.1021/ja500708w](https://doi.org/10.1021/ja500708w)
115. Bontemps S, Vendier L, Sabo-Etienne S (2012) Borane-mediated carbon dioxide reduction at Ruthenium: formation of C₁ and C₂ compounds. *Angew Chem Int Ed* 51(7):1671–1674. doi:[10.1002/anie.201107352](https://doi.org/10.1002/anie.201107352)
116. Shintani R, Nozaki K (2013) Copper-catalyzed hydroboration of carbon dioxide. *Organometallics* 32(8):2459–2462. doi:[10.1021/om400175h](https://doi.org/10.1021/om400175h)
117. Suh H-W, Guard LM, Hazari N (2014) A mechanistic study of allene carboxylation with CO₂ resulting in the development of a Pd(ii) pincer complex for the catalytic hydroboration of CO₂. *Chem Sci* 5(10):3859–3872. doi:[10.1039/c4sc01110d](https://doi.org/10.1039/c4sc01110d)

Transformation of Carbon Dioxide to Formic Acid and
Methanol

Wang, W.-H.; Feng, X.; Bao, M.

2018, VI, 123 p. 76 illus., 16 illus. in color., Softcover

ISBN: 978-981-10-3249-3