Chapter 4
Hydrogenation and Related Reductions of Carbon Dioxide with Molecular Catalysts

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Abbreviations

Bcat	catecholborane
Bpin	pinacolborane
bpy	bipyridine
cat.	catalyst
Cp*	pentamethylcyclopentadienyl
Cy	cyclohexyl group
DBU	1,8-diazabicycloundec-7-ene
DFT	density functional theory
DHBP	4,4′-dihydroxy-2,2′-bipyridine
DHPT	4,7-dihydroxy-1,10-phenanthroline
DMFC	direct methanol fuel cells
dmpe	1,3-bis(dimethylphophino)ethane
dppm	1,2-bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane
EMIMCl	1-ethyl-3-methylimidazolium chloride
FLP	frustrated Lewis pairs
hex	hexyl group
IL	ionic liquid
iPr	isopropyl group
IR	infrared spectroscopy
KIE	kinetic isotope effect
MD	molecular dynamics
Me	methyl group
Mes	mesityl groups

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MTA	methanol-to-aromatics
MTD	metadynamics
MTG	methanol-to-gasoline
MTO	methanol-to-olefins
*m*tppms	sodium diphenylphosphinobenzene-3-sulfonate
NHC	N-heterocyclic carbene
NMR	nuclear magnetic resonance spectroscopy
OAc	acetoxy group
OTf	triflate group
Ph	phenyl group
PNP	pincer ligand (P donor atoms on the side arms N ~ in the middle); analogue PNN PCP
RT	room temperature
SDQ	single doubles quadruples
tBu	tert-butyl group
TOF	turnover frequency
TON	turnover number
TMP	tetramethylpiperidine
TS	transition state
Verkade's base	2,8,9-triisopropyl-2,5,8,9-tetraaza-1-phosphabicyclo-[3, 3, 3]undecane
X	halide anions such as Cl^- Br^-

4.1 Introduction

In today's chemical industry, most of the product chains are based on fossil resources like petroleum, coal, or natural gas. Although it is known that these resources are limited, the major part is "just" burned as fuels, and CO_2 is emitted into the atmosphere with incalculable risks for climate change [1].

Therefore, new concepts for the future have to be developed to meet the increasing demand of energy and materials by ensuring environmental safety. Using the abundant greenhouse gas CO_2 as C1 building block to produce chemicals and fuels would close the anthropogenic carbon cycle and save natural resources [2].

However, the thermodynamic stability and the low reactivity of CO_2 require highly active catalysts and high energy starting materials. Nature shows that such a transformation is practicable. By using photosynthesis, the biological reduction of CO_2 with sunlight and water to organic carbohydrates, $385 \cdot 10^9$ t of CO_2 is fixed annually net [3]. Therefore, enzymes and different kind of mechanism have been evolved and optimized in billions of years by nature. Biochemical studies on active sites of these enzymes can be of benefit for understanding and developing new synthetic catalysts capable of CO_2 activation [4].
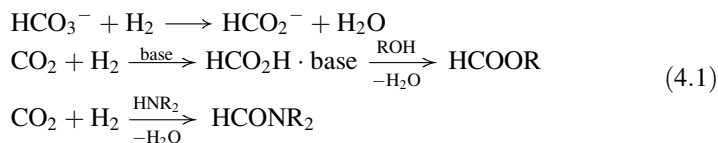
In the last decades, chemists have followed this dream and pioneering work toward catalytic transformation of CO_2 has been reported [5–7]. Especially, the reduction of CO_2 to products of higher hydrogen content is of great interest. For example, direct hydrogenation of CO_2 to MeOH with green, nonfossil-based hydrogen is discussed to be a key step for building up a methanol economy as MeOH can be converted into fuels as well as valuable chemicals such as olefins and aromatics [6, 8, 9].

Despite all improvements in the last years, the catalyst costs of homogeneous catalysts for hydrogenation of CO_2 are still too high for industrial applications and only few heterogeneous processes are established [10, 11]. However, in the last 10 years significant progress was observed that makes it more likely that industrial processes based on homogeneous catalysis will be set up, too.

This chapter summarizes recent developments in this field starting at 2005 including hydrogen and other hydride reagents. Earlier findings have been well presented by Jessop, Leitner, and others [12–15].

Before 2005, active catalyst systems have been developed to give HCOOH and formamides and their mechanism have been intensively studied. However, the separation of HCOOH from base and catalyst as well as the use of CO_2 as hydrogen storage material have been neglected—but are hot topics in this decade. Following the principles of Green Chemistry, new systems have been developed in the last years using green solvents, ambient conditions, bio-inspired catalysts, as well as non-precious metals [16]. As the combustion of fossil fuels is one of the major reasons for increasing CO_2 amount in the atmosphere, the synthesis of fuels out of CO_2 using clean, nonfossil-based H_2 is highly desirable [17]. Therefore, reducing CO_2 to MeOH or CH_4 is of great interest, and promising catalytic systems have been reported recently for gaining MeOH. Homogeneous catalysts capable of hydrogenating CO_2 to CH_4 with H_2 are still unreported, but interesting activities have been achieved using a combination of boranes and silanes.

4.2 Hydrogenation of CO_2/HCO_3^- to Formic Acid Derivatives

$$
\begin{aligned}
&HCO_3^- + H_2 \longrightarrow HCO_2^- + H_2O \\
&CO_2 + H_2 \xrightarrow{\text{base}} HCO_2H \cdot \text{base} \xrightarrow[-H_2O]{ROH} HCOOR \\
&CO_2 + H_2 \xrightarrow[-H_2O]{HNR_2} HCONR_2
\end{aligned}
\tag{4.1}
$$

The direct hydrogenation of CO_2 to HCOOH is an endergonic reaction. Therefore, base is often applied to drive the thermodynamics by proton transfer. Available products are formates, formic acid–base adducts, as well as alkyl formates in the presence of alcohols and formamides by using primary or secondary amines (Eq. 4.1).

Catalytic systems reported before 2005 are usually noble-metal systems with mono- or bisphosphine ligands as well as a few examples of bipyridine-based ligand structures. The best catalyst presented until 2005 is the $(PMe_3)_4RuCl(OAc)$ catalyst from Jessop which hydrogenates CO_2 at 50 °C and 200 bar of H_2/CO_2 with high TON of 32,000 and an astonishing TOF of 95,000 h^{-1} [18].

Since then, new ligand structures have been developed and applied successfully in the hydrogenation of CO_2 to formic acid derivatives. This section gives an overview of recent results subdivided by ligand classes.

4.2.1   Using Mono- and Bidentate Phosphine Ligands

As mentioned above, the Ru trimethylphosphine catalyst system [18] was one of the most active ones until 2005. Regarding the high interest in understanding the mechanism, several computational and analytical studies have been reported identifying possible reaction species (Scheme 4.1). All of them have in common that a Ru dihydride species **1** with four phosphine ligands exists. The dissociation of one phosphine ligand leads to cis-$Ru(H)_2(PMe_3)_3$. Here, Sakaki started his investigations with DFT and MP4(SDQ) methods to figure out differences between this real catalyst and the model catalyst cis-$Ru(H)_2(PH_3)_3$ [19]. As the PMe_3 group is more donating than its analog, the trialkyl phosphine ligand showed a stronger $trans$-influence than PH_3. Both, strong donating ligands and polar solvents, made the CO_2 insertion into the metal-H bond more favorable. This step is proposed to be the rate-determining step in the hydrogenation of CO_2 with **2** in absence of water. The catalytic cycle can be described in the following steps: CO_2 insertion into Ru(II)-H, isomerization of the ruthenium(II)-η^1-formate intermediate **3**, six-centered σ-bond-metathesis of the η^1-formate with a dihydrogen molecule **4**, and dissociation of formic acid to give again the dihydride species (Scheme 4.1, phosphine dissociation mechanism (a), phosphine groups are drawn as P for clarity).

Taking into account that water was observed to accelerate the catalytic system, the group of Sakaki presented a second computational study using cis-Ru $(H)_2(PMe_3)_3(H_2O)_2$ as catalytic intermediate [20]. They figured out that aqua ligands can accelerate the nucleophilic attack of the hydride ligand on the CO_2 molecule by forming hydrogen bonds (**6**). The resulting ruthenium(II)-η^1-formate **3** isomerizes fast in the presence of water which suppresses the deinsertion of CO_2. The rate-determining step now is believed to be the coordination of the H_2 molecule to the ruthenium(II)-η^2-formate complex. The last step, the heterolytic H_2 cleavage, is facilitated again by water molecules (**7**). However, Jessop's NMR results have been inconsistent with such a phosphine dissociation mechanism. For this reason, he proposed a different cycle based on the unsaturated, cationic ruthenium species $[(PMe_3)_4RuH]^+$ **8** [21]. This mechanism also explains the necessity of the added base. The base on the one hand traps the formic acid and on the other hand helps to form the active catalytic species by abstracting a hydride ligand leading from **1** to **8**.
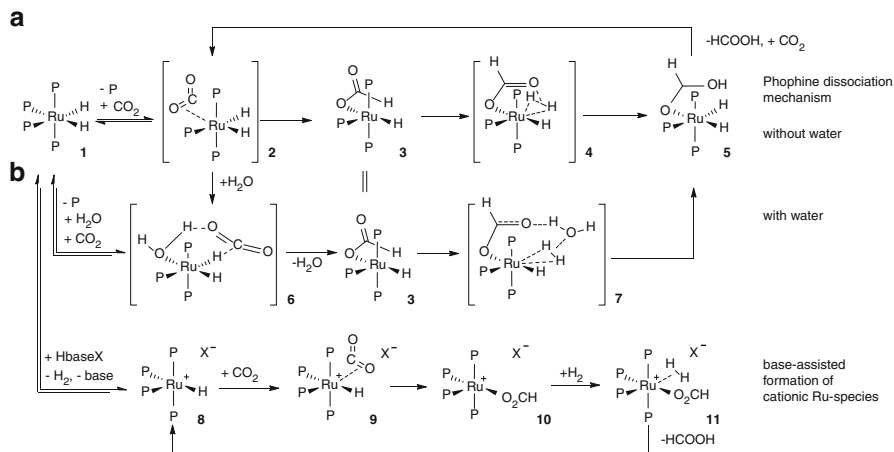
Scheme 4.1 Two different reaction pathways for the (PMe$_3$)$_4$RuCl(OAc) system proposed by Sakaki and Jessop

Most recently, our group synthesized benzoyl- and naphthoyl-substituted phosphines which are stable to air and moisture [22]. The related Ru complexes showed good activity in the bicarbonate reduction with H$_2$ at 80 °C (TON up to 1,600). CO$_2$ as well as carbonyl compounds could be hydrogenated, too.

Using simple phosphite ligands at the Ru center such as [*trans*-RuCl$_2${P(OMe)$_3$}$_4$], the group of Thiel achieved good TON up to 6,630 and TOF of 1,655 h^{-1} under supercritical conditions [23]. This was the first time phosphite ligands have been shown to form active complexes for the hydrogenation of CO$_2$. However, the application of the expensive base DBU in the presence of C$_6$F$_5$OH is a drawback and an exchange through cheaper bases is highly desirable.

Taking advantage of the water-accelerating effect, Zhao and Joó published a water-soluble [RhCl(*m*tppms)$_3$] catalyst capable of CO$_2$ hydrogenation to free formic acid in aqueous HCOONa solutions [24]. However, only low TON < 150 was observed after 20 h at 100 bar pressure (CO$_2$/H$_2$ – 1:1) and 50 °C. This might be due to the low basicity of the formate.

The hydrogenation of CO$_2$ to HCOOH is reversible. Hence, many catalyst systems have been developed which efficiently and selectively decompose HCOOH to hydrogen and CO$_2$ [25–27]. Hydrogen, ideally produced by renewable energy sources, for example, by electrolysis of water, is a potentially explosive, volatile gas which is usually stored in high pressure tanks [28–31]. By reacting it with CO$_2$ or bicarbonate, H$_2$ can be stored and transported easily as liquid or solid and H$_2$ can be released easily if needed. Therefore, researchers developed different systems capable of storing hydrogen based on CO$_2$/HCOOH or bicarbonate/formate. Both the groups of Papp and Joó [32] as well as our group [33] presented at the same time catalyst systems able of recharging H$_2$ based on a bicarbonate/formate cycle. In comparison to CO$_2$, bicarbonate is well soluble in water and its solutions are easy to handle and can be converted catalytically under mild conditions. As these systems work amine-free, no base evaporation is possible with the H$_2$ stream.
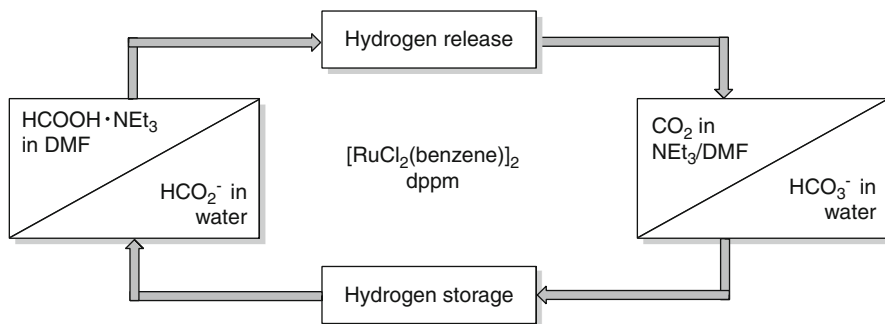
Scheme 4.2 One catalyst—two hydrogen storage systems based on CO_2 or bicarbonate by the group of Beller

Papp and Joó observed reversibility with the $[RuCl_2(mtppms)_2]_2$ complex in aqueous bicarbonate solution in a sapphire NMR tube [32]. They showed three cycles of both the hydrogenation of bicarbonate to formate and the dehydrogenation of formate to bicarbonate. However, the decomposition of the formate slows down significantly at around 50 % conversion. Therefore, only half of the formate amount can be used for hydrogen storage in this system. Higher yields for the dehydrogenation of formates at even lower temperature (70 % at 40 °C) were shown by our group with a $[RuCl_2(benzene)]_2$ precursor in the presence of 4 eq of dppm as ligand [33]. In comparison to earlier studies [34], the yields for the bicarbonate reduction could be improved to 96 % at 70 °C, using 80 bar of H_2 in a water-THF mixture without additional CO_2. A good TON of 1,108 was achieved after 2 h. Exchanging the sodium cation through NH_4^+ or Li^+, K^+, Mg^{2+}, and Ca^{2+} cations, the productivity decreases and often a significant amount of CO_2 is released with the H_2 during the formate decomposition. Our group also demonstrated that the catalyst is capable of hydrogen storage at RT based on CO_2/HCOOH·NEt$_3$ (Scheme 4.2). The catalyst system runs eight cycles without showing significant decrease in activity [35].

For the hydrogenation at RT, high formic acid amine ratios up to 2.31 were observed with TON up to 3,200. In addition, we could present an astonishing TON up to 800,000 for continuous H_2 liberation using $[RuCl_2(benzene)]_2$ and dppe. However, it should be noted that the gravimetric hydrogen content of formic acid is limited to 4.4 % which is further reduced by the addition of amine or solvent.

To clarify possible reaction mechanisms for complexes with bidentate phosphine ligands, ab initio MTD and MD studies were performed by the group of Baiker for the dihydride catalyst $[Ru(dmpe)_2(H)_2]$ **13** [36]. This study was supported by further DFT calculations as well as IR and NMR experiments [37]. The authors concluded the coordination of molecular H_2 to the complex is the rate-determining step. That requires dissociation of the formate from the Ru center **14** to leave a free coordination site for the H_2. The formate anion then interacts weakly with the $Ru(H_2)^+$ complex **15** (Scheme 4.3). The activation energy for the H_2 adduct was found to be lower for the complex where the two hydrides are in *trans* position to each other (**13**). However, in solution more than 95 % of the *cis*-complex **12** was observed. The CO_2 insertion is
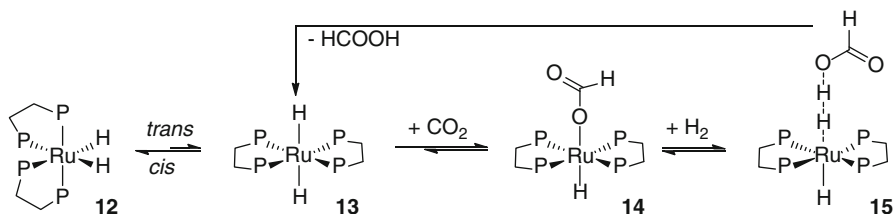
Scheme 4.3 Proposed mechanism for the $[Ru(dmpe)_2(H)_2]$ catalyzed CO_2 hydrogenation by Baiker
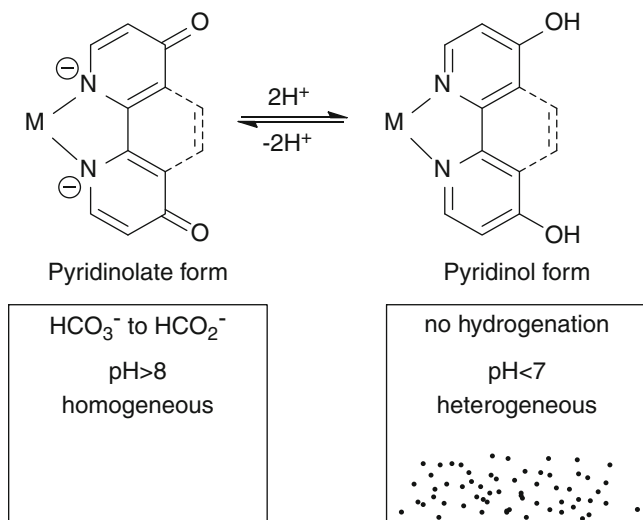
believed to happen via a concerted mechanism where the Ru-H bond breaks at the same time as the Ru-O-bond is formed. This can be imagined as a "formate ion" rotation.

Based on kinetic measurements by using stop-flow technique, Schindler's group calculated activation parameters for a Rh catalyst involving $[(dppp)_2RhH]$ as the active species [38]. For this complex, the following mechanism was proposed: the formation of an ionic Rh(I) formate complex through insertion of CO_2 into the Rh-H bond and subsequent dissociation of formate, followed by oxidative addition of H_2 to give an ionic Rh(III) dihydride formate complex which under reductive elimination of formic acid yields again the neutral Rh(I) complex.

In addition to catalyst variations and mechanistic studies, different kinds of concepts have been developed to solve the problem of the formic acid separation from base and catalyst. For example, the groups of Han and Leitner presented independently two systems based on ionic liquids. That the equilibrium of CO_2/H_2 to HCOOH is more favored in IL than in H_2O, due to the strong solvation of HCOOH in IL, was shown by Nakahara [39]. The idea of Han was to use an IL with an extra amine function **16** in combination with a ruthenium catalyst bound on silica [40]. By inserting a second amine function on the IL (**17**), the activity could be increased from 100 h^{-1} up to 920 h^{-1} TOF with a TON of 1,840 using 90 bar of H_2 and a total pressure of 180 bar [41]. Both systems were recycled four times using the procedure described in Fig. 4.1. Addition of water accelerates the reaction, maybe due to a decreased viscosity, interaction of water in the catalytic cycle, or bicarbonate formation as the true substrate.

Leitner and co-workers were using the IL as stationary phase containing the precursors $[Ru(cod)(methallyl)_2]$ and $PBu_4^+mtppms^-$ as well as additional base [42]. The formic acid extraction occurs with supercritical CO_2 in a continuous-flow single process unit where $scCO_2$ serves as mobile and extracting phase at the same time. With the base NEt_3 and EMIM Cl as IL, a TON of 516 was achieved after half an hour at 50 °C and 50 bar of both CO_2 and H_2. By exchanging the anion of the IL through HCO_2^- to give **18**, increased TON and TOF were observed.

Another interesting concept for the production and separation of pure formic acid was presented by Schaub and Paciello [43]. Key to success is the skillful choice of solvents by taking advantage of the diverse solubility and miscibility of all components (Fig. 4.2).

Fig. 4.1 Concepts for HCOOH separation using IL presented by Han and Leitner

Fig. 4.2 Liquid-liquid phase process for formic acid formation and separation by Schaub and Paciello [43]

Here, in the first step, CO_2 is hydrogenated with the $[Ru(H)_2(PnBu_3)_4]$ catalyst in the presence of $NHex_3$ and a diol. The formed formic acid salts $[NHex_3 \cdot HCOOH]$ are not miscible in free amine, but good soluble in the diol phase. At the same time, most of the lipophilic catalyst stays in the unpolar amine phase. To get rid of the remaining catalyst traces, the diol phase is extracted with the resulting amine of the formic acid salt cleavage. The amine is then recycled to the hydrogenation vessel, whereas the formic acid salt enriched diol phase is treated thermally under mild conditions to give pure formic acid and free $NHex_3$ which forms again a two-phase system with the diol. Both phases are back transferred to close the process cycle.

4.2.2 Using Bipyridine-Based and Carbene-Type Ligands

A second ligand class known for CO_2 hydrogenation is based on the bipyridine structure. In this context, the groups of Ogo and Fukuzumi started kinetic

Scheme 4.4 pH switchable catalysts for CO_2 hydrogenation reported by Himeda

investigations of Ir(III) and Ru(II) bpy complexes in citric buffer solutions (pH = 3) to obtain pure formic acid [44]. By comparing TON in dependence of H_2 or CO_2 pressure, they concluded that in the case of ruthenium, the H_2 coordination to the corresponding aqua complex is rate determining. This is in contrast to the iridium complexes. Here, the authors believe that the rate-determining step is the CO_2 insertion into the active hydride complex.

By inserting hydroxy groups in *para-* or *ortho*-position at the pyridine rings, interesting behavior of the catalysts in dependence of the pH was reported. This ligand class shows an acid–base equilibrium between the pyridinol and pyridinolate form (Scheme 4.4) which influences the catalytic activity and water solubility.

In 2007, Himeda presented different catalysts for the CO_2 hydrogenation in aqueous KOH solutions to potassium formate using Ru, Ir, and Rh half-sandwich complexes bearing DHPT or DHBP ligands [45]. Under basic conditions, the deprotonated, water-soluble form exists showing strong electronic donation properties. High TON up to 220,000 was observed for an Ir DHPT complex at 120 °C and 60 bar of each CO_2 and H_2 in 48 h. Lowering the pH to acidic conditions, the pyridinol form of the catalyst predominates. The catalyst becomes insoluble in water and precipitates. Now, the catalyst can be reused easily and showed maintaining activity even after four cycles. To confirm the importance of the formation of the pyridinolate species, the hydroxy groups have been methylated resulting in significantly less active complexes. Other groups in *para*-position like carboxy or methyl groups are inferior, too [46]. For further details see review [47].

To study the effects of the ligand structure in more detail, Himeda and Fujita synthesized new iridium half-sandwich complexes differing in position and quantity of the hydroxy groups (Scheme 4.5).
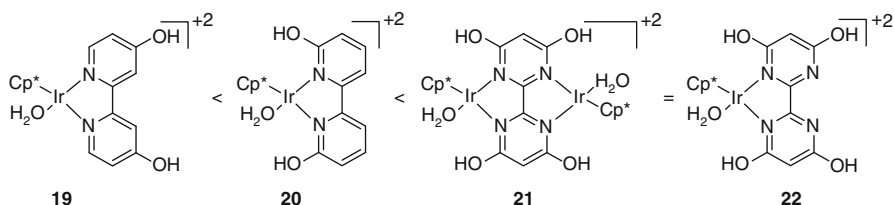
Scheme 4.5 Ligand structure study on the reactivity of Ir half-sandwich complexes by Himeda

Moving the hydroxy groups from *para* to *ortho* position (**19–20**) resulted in a rate enhancement by a factor of 2 comparing the initial TOF after 10 min [48]. Doubling both the quantity of the hydroxy groups as well as the amount of Ir centers **21**, another increase in the reactivity in order of 2.5 was observed for the hydrogenation of CO_2. Surprisingly, the dinuclear complex **22** showed similar activity as the mononuclear one with four hydroxy groups **21**. To explain these results, DFT studies and deuteration experiments have been performed [49]. The computational study identified the water-assisted heterolysis of H_2 to be the rate-determining step. This is in line with the NMR experiments as kinetic isotope effects of H_2O, H_2, and bicarbonate have only been observed for the ligands containing hydroxy groups in *ortho* position, not *para*. This is the first time a kinetic isotope effect was proved for the hydrogenation of CO_2, revealing that H_2O is involved in the rate-determining step. The significant increase in reactivity is believed to be caused by the high σ-donor strengths of the four O^- groups and the accelerated proton transfer by forming water bridges.

Using the binuclear Ir complex **21**, Himeda, Fujita, and Hull showed that their system is not only capable of CO_2 hydrogenation but also can decompose HCOOH to CO_2 and H_2 under acidic conditions [50]. High TON of 308,000 and very good TOF of 228,000 h^{-1} were achieved for the decomposition at 80–90 °C in the presence of HCOOH/HCOONa (1:1). Increasing the pH to basic conditions, the same catalyst hydrogenates CO_2 with TON of 153,000 and TOF of 53,800 h^{-1} in the presence of bicarbonate at 50 °C/80 °C. To rule out bicarbonate as only substrate, a test reaction without CO_2 was run yielding only a low formate production. However, long reaction times and the necessity of adding stoichiometric amounts of base or acid to switch the reaction make it so far unpractical for industrial application.

The same concept of hydrogen storage was reported by Fukuzumi using the water-soluble, proton-switchable phenylpyrazolyl organoiridium aqua complex **23** (Scheme 4.6) [51]. Both the hydrogenation of CO_2 under slightly basic conditions at RT under atmospheric pressure of H_2 and CO_2 and the formic acid decomposition under acidic conditions are possible. Due to KIE effects, the authors concluded that the rate-determining step is the formic acid decomposition via β-hydride elimination of the formate to release CO_2. In case of the hydrogenation of bicarbonate, both the catalyst and bicarbonate are believed to be involved in the rate-determining step as the TOF raises with increasing amount of bicarbonate. A more general view on these Ir-H complexes is presented in a review [52].
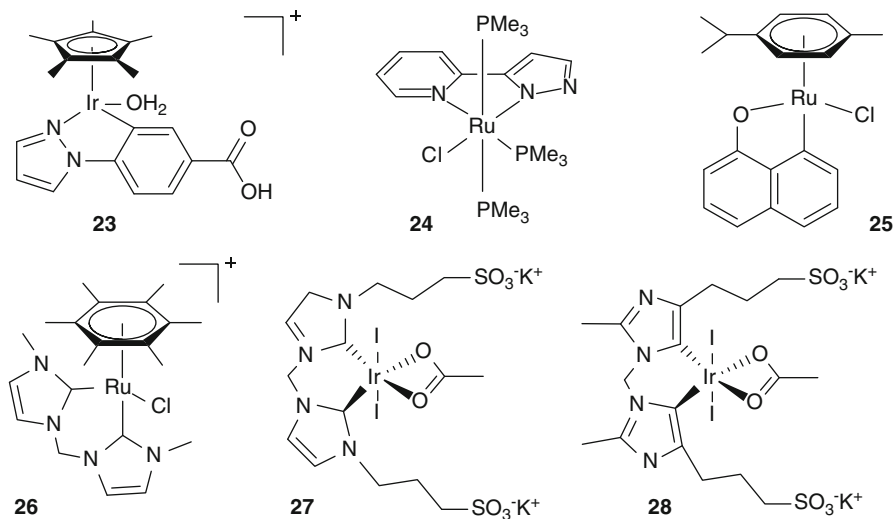
Scheme 4.6 Catalysts capable of HCOOH production by Fukuzumi, Thiel, Süss-Fink, and Peris

Further systems capable of CO_2 hydrogenation were presented by Niedner-Schatteburg, van Wüllen, and Thiel [53] using catalyst **24** and the group of Süss-Fink [54] including the arene ruthenium oxinato complex **25**. However, in all of these cases only moderate TONs were achieved.

Another interesting ligand class for the activation of CO_2 was discovered by Peris. A series of bis-*N*-heterocyclic carbene complexes with Ru **26** and Ir **27** were tested in both CO_2 hydrogenation and transfer hydrogenation [55]. As these chelating NHC ligands are known for their high thermal stability, reaction temperatures up to 200 °C are tolerated. Interestingly, if the carbene position is blocked by a methyl group, a bis-abnormal coordination of the NHC ligand to the iridium center is observed [56]. This complex **28** is even more active and the highest known TON of 1,320 was reported for transfer hydrogenation of CO_2 using *i*PrOH in aqueous KOH solutions.

4.2.3 Using Pincer Ligands

For more than 30 years, pincer-type ligands have been known [57]. The high stability of this complexes are due to the strong coordination between the tridentate ligand and the metal center. At the same time, they offer interesting redox chemistry as these noninnocent ligands are directly involved in the reaction mechanism. This enabled new and unknown reactivities. Catalytic applications of these ligand-metal cooperations are, for example, arylation and coupling reactions, alkane dehydrogenations, hydroaminations, and a bunch of hydrogenation reactions [58–61].
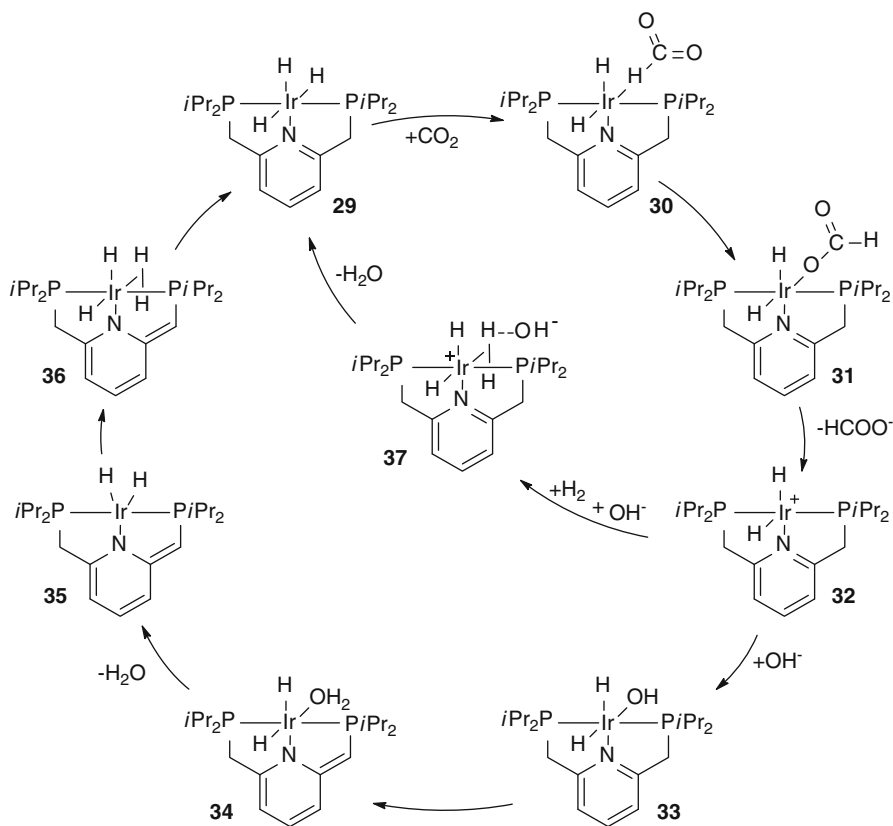
Scheme 4.7 Possible reaction mechanism for the Ir-trihydride-pincer complex of Nozaki

Recently, the first example of CO_2 hydrogenation to formate with this ligand class was presented by Nozaki. This system is highly efficient and was highlighted in 2010 [62]. In fact, Nozaki's $Ir(III)(H)_3$-pincer complex **29** achieved astonishing TON up to 3,500,000 in 48 h at 120 °C and TOF of 150,000 h^{-1} after 2 h at 200 °C using each 30 bar of CO_2 and H_2 in an aqueous KOH solution of 1 M [63]. The proposed mechanism is presented in Scheme 4.7. The first step is the CO_2 insertion into Ir-H bond of **29** forming complex **30** with the formato group in *cis* position to the N atom. After dissociation of the formate, the Ar-CH_2-$PiPr_2$ moiety of the ligand is deprotonated followed by dearomatization of the pyridine ring. To this amido iridium dihydride complex **35**, a hydrogen molecule coordinates which is then heterolytically cleaved to give the full-aromatized $Ir(H)_3$ **29** back. Yang reported a different pathway by studying computationally PNP-pincer complexes with $Ir(H)_3$ and Fe/Co $(H)_2(CO)$ [64]. He claimed that the OH^--triggered H_2 cleavage (**37**) is more favorable than Nozaki's aromatization/dearomatization mechanism as well as Ahlquist's suggestions based on DFT studies [65]. In response Nozaki and Morokuma presented their own computational study for the CO_2 hydrogenation with complex **29** [66].

As a result, both pathways, the aromatization/dearomatization reaction as well as the hydrogenolysis suggested by Yang, are possible as their transition state energies are very similar. Deeper insight in the mechanism was provided by Hazari who examined the *trans*-influence of various ligands for insertion of CO_2 into the Ir-H bond of **29** [67]. The strongest *trans*-effect was observed by the hydride ligand which is believed to weaken the Ir-H bond by increasing the nucleophilicity of this hydride making the CO_2 insertion more favorable.

Other non-considered mechanisms were pointed out by Milstein's group. They proposed a double deprotonation by methylating a Ni(II) PNP complex where the negative charge is delocalized in the amido-type backbone [68] as well as a methylated Co(I)-pincer complex which lost a H radical by homolytic C-H bond cleavage [69]. Here, the unpaired electron is delocalized in the ligand backbone and evidence for the remaining aromaticity of the pyridine ring was detected. The abstraction of the H radical is believed to be caused by the solvent as an increase of the reaction rate was observed in aliphatic solvents.

4.2.4   Using Non-precious Metals

Despite increasing scientific interest in the hydrogenation of CO_2, the use of bio-relevant metals such as iron, manganese, or cobalt as catalysts has scarcely been investigated compared to noble-metal-based systems. Before 2005, only a few examples were reported yielding higher TON than 10 [70]. However, long reaction times and harsh conditions are needed.

In 2011, Yang predicted computationally an iron-pincer complex to be capable of CO_2 hydrogenation [64]. In the same year, Milstein presented an analog Fe complex **38** (Scheme 4.8) not only active in CO_2 hydrogenation but also in the bicarbonate reduction to formate [71]. In aqueous solutions, bicarbonate can be converted to the corresponding formate at ambient pressure and 80 °C with a moderate yield 30 % and a TON of 320. Using CO_2, even higher TON up to 600 was achieved. Based on IR and NMR experiments, a similar mechanism as for the $Ir(H)_3$-pincer complex **29** is proposed.

Whereas mono-, bi-, and tridentate phosphine ligands are well investigated for noble metals in the catalytic hydrogenation of CO_2, tetradentate ligands have not been presented at all. The application of the tetradentate phosphine ligand $P(CH_2CH_2PPh_2)_3$ in combination with $Fe(BF_4)_2 \cdot 6H_2O$ in MeOH led to the highly active complex **39** [72]. With this complex, our group showed that bicarbonate can be reduced to formate in high yields (88 %) and TON (up to 610) at 80 °C and 60 bar of H_2. Testing a variety of bidentate and tridentate ligands which failed all in generating an active catalyst in situ, it seemed to be that iron needs a very well-defined environment. Even other iron sources instead of $Fe(BF_4)_2 \cdot 6H_2O$ gave significant lower yield. Replacing bicarbonate by CO_2, methyl formate was produced in the presence of NEt_3 and the corresponding formamides were observed by using dialkyl amines as base yielding TON up to 730.
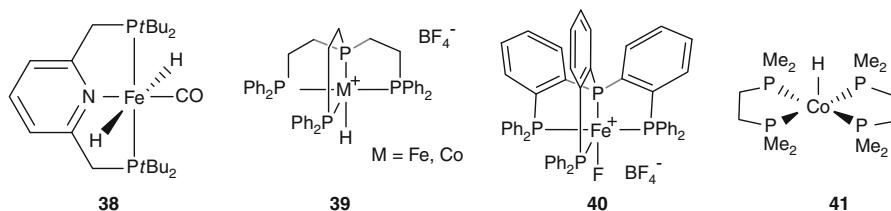
Scheme 4.8 Non-precious metals active in CO_2 hydrogenation published by Milstein, Beller, and Linehan

Changing the metal from Fe to Co, slightly higher yields were observed for the bicarbonate reduction and higher temperature was tolerated. In addition, lower H_2 pressure is applicable [73]. TON up to 3,900 for sodium formate and 1,300 for DMF could be detected. By synthesizing Co monohydride and Co dihydrogen complexes and testing them in the catalytic hydrogenation of bicarbonate, the monohydride complex was excluded as possible active species, whereas the Co dihydrogen complex was active. These results were in correlation with the performed NMR studies.

By synthesizing the phenyl-bridged analog of the tetradentate phosphine ligand mentioned above and combining it with $Fe(BF_4)_2 \cdot 6H_2O$, the most active and stable iron catalyst **40** known for the hydrogenation of bicarbonate and CO_2 was developed [74]. The crystal structure of **40** exhibited an unusual Fe-F bond, where the F^- originally came from the BF_4^- anion. Both the in situ system and the well-defined complex **40** showed the same activity, resulting in TON up to one order of magnitude higher than the previously reported Fe systems for the bicarbonate reduction (TON 7,550). With higher catalyst loading, the reaction reached its equilibrium already after 5 h with TOF up to 770 h^{-1}. Furthermore, the hydrogenation of CO_2 in the presence of base gave formic acid, methyl formate, and formamides, the latter in TON up to 5,100. NMR studies indicated that a Bianchini-type complex [75] has been formed being in equilibrium with a Fe-hydride complex where the dihydrogen ligand has been exchanged by a solvent or a CO_2 molecule. Through base-assisted heterolytic hydrogen cleavage, an active dihydride Fe complex was proposed to be formed into which CO_2 inserts to give the hydride formate complex. Dissociation of the formate followed by the coordination of a dihydrogen molecule led back to the Bianchini-type complex and HCOOH·base adduct.

Very recently, the group of Linehan published NMR experiments where Co(I)(dmpe)$_2$H shows very high TOF up to 74,000 h^{-1} for the hydrogenation of CO_2 to formate [76]. However, by using other bases than the expensive and very unusual Verkade's base, the activity dropped down dramatically. Even with much higher catalyst loading and the use of the expensive, in CO_2 hydrogenation successfully tested base DBU, almost no activity was observed. A scale-up of this process is therefore very unlikely.

Table 4.1 Reported catalysts for the hydrosilylation of CO_2 to silyl formate

Entry	Catalyst	T [°C]	CO_2 [atm]	TON	TOF [h^{-1}]	Ref.
1	$Ru_2Cl_5(MeCN)_7$	40	14	4,619	231	[77]
2	cis-[$RuCl_2(MeCN)_4$]	85	10 g	–	3,700	[78]
3	Iridium complex	RT	3	112	0.8	[80]
4	Zinc complex	100	6.8	1,006	2.9	[81]
5	Cu bisphosphine complex (Ph)	60	1	8,100	1,350	[82]
6	[(NHC)Cu(OtBu)]	60	1	7,489	1,248	[83]
7	Cu bisphosphine complex (iPr)	60	1	70,000	2,917	[79]
8	$Rh_2(OAc)_4$	50	1	180	90	[84]
9	[Et_3SiPh][$B(C_6F_5)_4$]	30	1	–	–	[85]

4.2.5 Using Other Hydride Reagents

Parallel to the hydrogenation of CO_2, catalysts for the reduction of CO_2 to silyl formate with Hsilanes have been reported. The most recent systems are listed in Table 4.1.

In case of the $Ru_2Cl_5(MeCN)_7$, the catalyst could be recycled 10 times, resulting in an overall TON up to 4,600 [77]. The same group achieved with the similar catalyst cis-[$RuCl_2(MeCN)_4$] and MePhSiH high TOF of 3,400 h^{-1} yielding 96 % of silyl formate at 85 °C [78]. The highest TONs were achieved by the copper (1,2-bis(diisopropylphosphino)benzene) complex [79] with a very good TON of 70,000 after 24 h at 1 atm of CO_2 pressure.

From a mechanistic point of view, two different pathways are proposed depending on how CO_2 inserts. For the systems [79] and [80], in the first step, the silane is activated on the metal center resulting in the formation of a metal-hydride complex and the transfer of the silyl cation to an anionic ligand (Cl^- or triflate). In the second step, the silyl cation activates CO_2 and subsequent silyl formate is reductively eliminated (outer-sphere mechanism).

The other systems [79, 81–83] are believed to follow a different mechanism. Here, the active catalytic species is formed by the reaction of the precursor and silane to yield the corresponding metal-hydride complex. Into this metal-H bond inserts a CO_2 molecule to build up the metal formate complex. In the last step, this formate complex reacts with silane to regenerate the metal-H species and release silyl formate.

By adding water to silyl formate, formic acid is formed. This transformation is not really competitive with the reduction of CO_2 to formic acid using molecular hydrogen as for the latter even more active catalysts systems are known. However, using other nucleophiles, such as amines or Grignard reagents, offers new synthetic ways to a number of synthesis products (Scheme 4.9). For example, benzhydrol was formed in 77 % yield by reacting silyl formate with two equivalents of PhMgBr [84].

A stoichiometric metal-free reduction of CO_2 with trialkyl silanes and stoichiometric amounts of trityl borate was shown by the group of Müller [85]. They observed different products depending on the solvent applied. In PhCl, disilylated formic acid or disilyl methyl oxonium is formed. By quenching these intermediates
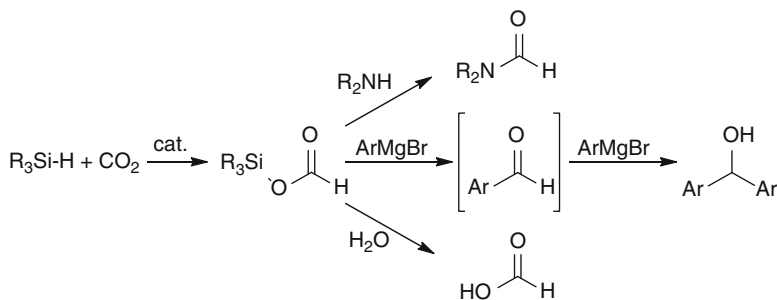
Scheme 4.9 Reduction of CO_2 to silyl formate and possible applications presented by Mizuno

with water, HCOOH and MeOH are obtained. In contrast, in PhH, the transformation of benzylic cations gives silyl ester or benzoic acid.

An example for a hydroboration of CO_2 to formate was presented by Labinger and Bercaw [86] using trialkyl boranes in the presence of Rh and Ni dmpe complexes to form formate-borane adducts. However, closing the catalytic cycle through breaking the formate-borane adducts failed.

In 2013, the group of Shintani and Nozaki presented a copper-NHC-catalyzed hydroboration of CO_2 to formic acid by quenching the reaction mixture with HCl [87]. This way, yields up to 87 % of formic acid have been observed. By adding primary or secondary amines to the reaction mixture instead of quenching with HCl, they isolated the corresponding formamides in good to very good yields (81–98 %). This *N*-formylation is also possible in one step by reacting CO_2 with pinacolborane in the presence of amine. However, the yields decreased slightly (e.g., from 84 to 71 % for *p*-anisidine).

4.3 Hydrogenation of CO_2 to MeOH

Searching for alternative sources of fuels and energy storage mediums, MeOH is considered for several good reasons. First, it can be dehydrogenated to give H_2 and, therefore, can serve as hydrogen storage carrier [88, 89]. Second, methanol has a high energy content of 22.7 MJ kg^{-1}, making it suitable for energy storage (CH_4: 24.3 MJ kg^{-1}) [6]. It can be used as liquid fuel (blended with gasoline or directly in direct methanol fuel cells, DMFC [90]) or can be converted to gasoline (MTG process). Last but not least, MeOH is a valuable feedstock as it can be transformed into ethylene or propylene in the MTO (methanol-to-olefins) process or to aromatics in the MTA (methanol-to-aromatics) process using zeolites. Therefore, MeOH covers all important basic chemicals for a wide range of product chains [6, 91]. The advantage of such a MeOH economy in comparison to the often discussed H_2-based technology is that MeOH as a liquid can be used analogous to petroleum and therefore can be transported and stored easily in the maintaining

infrastructure. In addition, MeOH is highly H_2 enriched (12.6 w%) in comparison to many other H_2 storage devices.

The most sustainable way for producing MeOH out of CO_2 and water combines the electrolysis of water to hydrogen and the subsequent hydrogenation of CO_2 to MeOH. The cost of this process will strongly depend on the electricity price for supplying the needed hydrogen amount. However, even today, this process can be competitive regarding the highly increased prices of gasoline in European countries [8]. The first commercial CO_2-to-renewable-methanol plant based on geothermal sources was established in 2012 in Iceland, producing annually 3,500 t of MeOH, and is planned to be expanded [9]. Industrial applications of homogeneous catalyst systems in this field are still far away from reality, but the first recent examples of the homogeneous catalyzed hydrogenation of carbon dioxide in the last 3 years are promising.

4.3.1 Catalytic Reduction with Hydrogen

$$CO_2 + 3\,H_2 \; \rightarrow CH_3OH + H_2O \qquad (4.2)$$
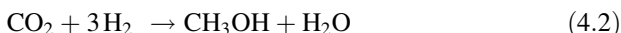
One of the first concepts for the hydrogenation of CO_2 to MeOH (Eq. 4.2) was presented by the group of Sanford [92]. They set up a cascade by using three different catalysts: $Ru(PMe_3)_4Cl(OAc)$ for the hydrogenation of CO_2 to formic acid, $Sc(OTf)_3$ as catalyst for the esterification of the formic acid to methyl formate, and finally the Ru PNN-pincer complex **42** which converted methyl formate to methanol. Key to success was the separation of the last catalyst from the second one to avoid deactivation. Therefore, methyl formate is transferred by a temperature ramp to an outer vessel containing the pincer complex **42**. The overall TON of 21 for the transformation of $^{13}CO_2$ to MeOH is low, but showed that this reaction is achievable by homogeneous catalysis. As one reason for this low activity, Sanford recognized an inhibition of the Ru PNN-pincer complex **42** by CO_2 [93]. Two products were observed under CO_2 atmosphere (Scheme 4.10). The kinetic product **43** is observed immediately under 1 atm of CO_2 by forming a C-C bond between the CO_2 and the phosphine arm. This process is reversible. By simply keeping the complex longer under CO_2 atmosphere or heating the solution, the irreversible product **44** is formed at the amine arm of the pincer complex and single crystals could be grown from the solution.

Milstein observed a similar phenomenon with a Ru PNP ligand with two phosphine arms [94]. Here, only a reversible addition of CO_2 to the phosphine arm was found confirming Sanford's results. Calculations reveal no solvent effect on the TS energies, indicating a concerted mechanism and the absence of a charge separation like Ru^+ COO^-. Another example of CO_2-ligand interactions was shown by Oro and Langer [95] using an Ir(I) dppm catalyst. Here, CO_2 inserts
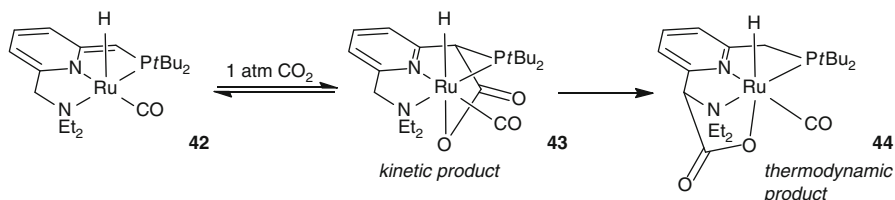
Scheme 4.10 CO_2 interactions with the Ru PNN-pincer complex observed by Sanford
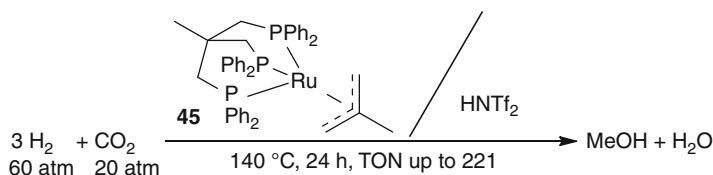
Scheme 4.11 The first homogeneous one-catalyst system for the reaction of CO_2 to MeOH reported by Leitner

into the C-H bond of the bisphosphine ligand to give the binuclear complex [IrCl(dppm)(H){(Ph$_2$P)$_2$C-COOH}]$_2$.

The first one-catalyst system for the production of methanol was reported by Klankermayer and Leitner [96]. Using the Ru catalyst **45** in the presence of 1 eq HNTf$_2$, MeOH is produced with a TON of 221 in a THF/EtOH mixture at 20 bar of CO_2 and 60 bar of H_2 (Scheme 4.11). They propose a cationic Ru hydrido dihydrogen complex to be the active species.

In addition to the systems mentioned above, a few concepts for the indirect conversion of CO_2 to MeOH were developed, reducing substrates which can be produced from CO_2 (Scheme 4.12). Pioneering work has been published by Milstein. Using the Ru-pincer complexes **42** or **46**, alkyl formates, organic carbonates, and carbamates [97] as well as challenging ureas [98] were converted under mild conditions in quantitative yield, often for the first time. Key to success is the unique behavior of the pincer complex being involved in the mechanism by metal-ligand cooperation. This work was also highlighted by Dixneuf [99] and Choudhury [100]. Notably, the activities need to be improved for industrial application and the economy of the process will also depend on H_2 cost.

One year later, Yang presented a DFT study on the dimethyl carbonate reduction to MeOH with the Ru NNP-pincer complex **42**. In addition, an analog Fe-pincer complex was proposed [101]. The suggested mechanism runs via three catalytic cycles, each with a direct hydride and ligand proton transfers. The cascade intermediates are methyl formate, followed by formaldehyde and subsequently MeOH as the product. The overall rate-determining step was found to be the formation of the second MeOH molecule from methyl formate in the second cycle.

However, it should be kept in mind that the reduction of dimethyl carbonate to methanol is uneconomic as the starting material with 1,000 US/t is much more
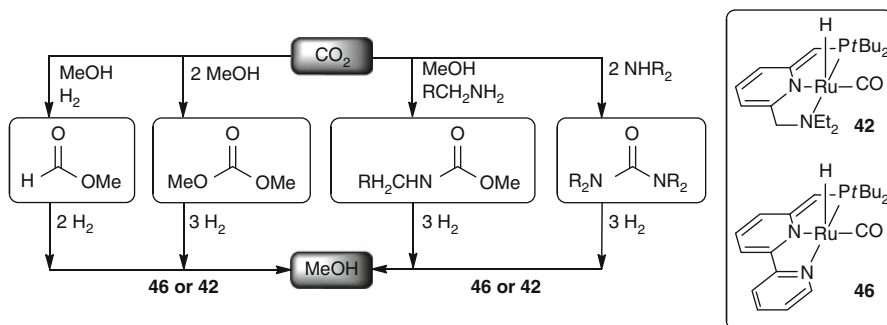
Scheme 4.12 Various ways for the indirect conversion of CO_2 to MeOH published by Milstein
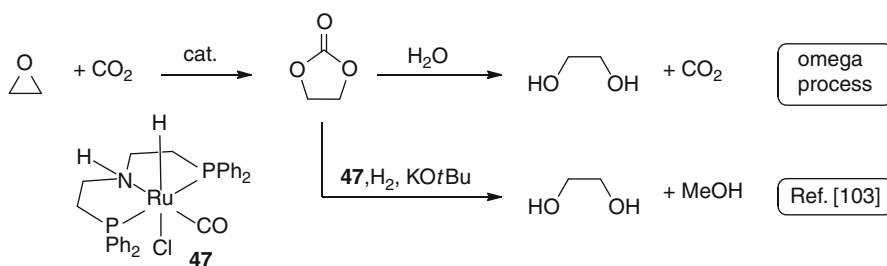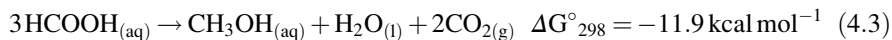

Scheme 4.13 Another concept for the indirect production of MeOH from CO_2 demonstrated by Ding

expensive than MeOH (400 US/t) [102]. Therefore, Ding et al. developed another indirect route for the MeOH production [102]. The idea is based on the omega process where ethylene carbonate, synthesized from CO_2 and ethylene oxide, is hydrolyzed to ethylene glycol and CO_2 (Scheme 4.13).

Instead of hydrolyzing the organic carbonate, this intermediate can be hydrogenated with the Ru PNP-pincer complex **47** in the presence of KOtBu to give ethylene glycol and MeOH. This opens a nice way to get two bulk chemicals at the same time from reacting CO_2 with ethylene oxide. With TON up to 87,000 and TOF of 1,200 h^{-1}, high activity could be observed at almost quantitative yields. In addition, deuterated methanol could be obtained in 99 % yield by deuteration of the sterically hindered tetramethyl ethylene carbonate with D_2. Furthermore, the catalyst is able to depolymerize the widely used material poly(propylene carbonate) by hydrogenating it to MeOH and the corresponding diol. Therefore, a recycling of this material to valuable products is possible [103].

An unusual way to gain methanol is the formic acid disproportionation (Eq. 4.3). Here, formic acid is both substrate and hydrogen source. In a HCOOH/water mixture at 60 °C, the molecular iridium catalyst [Cp*Ir(bpy)(H_2O)](OTf)$_2$ converts formic acid to methanol with a selectivity up to 12 % [104]. The selectivity increases with higher HCOOH concentration and lower temperature. Additional

H_2 suppresses the competing formate decomposition to CO_2 and H_2. As a side product methyl formate was observed through HCOOH esterification. Deuteration experiments indicate that formaldehyde is an intermediate of the catalytic cycle which is then hydrogenated to MeOH by HCOOH releasing CO_2.

$$3\,HCOOH_{(aq)} \rightarrow CH_3OH_{(aq)} + H_2O_{(l)} + 2\,CO_{2(g)} \quad \Delta G^{\circ}_{298} = -11.9\,\text{kcal mol}^{-1} \quad (4.3)$$

An interesting approach is the use of frustrated Lewis pairs which are capable of heterolytic H_2 activation [105]. Ashley and O'Hare applied TMP + $B(C_6F_5)_3$, forming a unique formato borate complex [TMPH]-[$HCO_2B(C_6F_5)_3$] with CO_2 under H_2 atmosphere (1–2 atm). After 6 days at 160 °C, $H_3COB(C_6F_5)_2$ was formed and 24 % yield of methanol was observed after distillation. However, the rendering of the catalytic cycle is still unachieved [106].

4.3.2 Catalytic Reduction with Other Hydride Reagents

There is a bunch of catalysts capable of reducing CO_2 using other hydride reagents such as aminoboranes, Hboranes and Hsilanes. For example, the group of Stephan presented a 1:2 mixture of $PMes_3$ and AlX_3 reacting with CO_2 to the corresponding phosphonium-carboxylate adduct. This intermediate then dehydrogenates amino-boranes at RT to give phosphonium methoxy aluminate in less than 15 min. Quenching with H_2O leads to 37–51 % yield of methanol [107].

The first catalytic metal-free hydrosilylation of CO_2 to MeOH was reported in 2009 by Zhang and Ying [108]. Using the NHC catalyst **49** under CO_2 atmosphere, first imidazolium carboxylate is formed which reacted then with diphenylsilane at RT to give CH_3OSiMe_3. Final quenching with water gives MeOH in 90 % yield based on the used Hsilane amount with TON of 1,840 and TOF of 25 h^{-1}. Therefore, it is competitive with known Ru catalysts lacking their typical draw-backs of moisture and air sensitivity. This system is even active under dried air. The first catalytic hydroboration of CO_2 to the methoxide level was reported by Guan, applying the nickel catalyst **48** [109] in the presence of HBcat. Hydrolysis gives MeOH with TON and TOF of 495 h^{-1} (based on B-H).

Comparing both systems by studying the mechanism quantum mechanically, Wang proposed that the most favorable pathway for both contains analog, exper-imentally detected intermediates like formoxy, acetal, and methoxide species [110, 111]. In addition, he predicted formaldehyde to be another intermediate in the catalytic cycle (Scheme 4.14). Both catalysts accelerate the hydride transfer in comparison to uncatalyzed reactions, but the mechanism of the hydride transfer is different. In the Ni/borane system, the Ni catalyst **48** acts as a shuttle, transferring the hydride from the HBcat to the C-O bonds. In the first step, CO_2 inserts into the [Ni]-H bond (**50**) forming Ni-formate. This complex reacts with catecholborane HBcat (**51**) to give formyl borate and [Ni]-H catalyst **48**. The catalyst then activates

Scheme 4.14 Comparing two catalytic systems based on the DFT studies by Wang for CO_2 to MeOH using hydroboration and hydrosilylation reagents

this product by forming the acetal species. The hydride transfer to [Ni] by a second HBcat results in formaldehyde and di(boryl)ether production. Formaldehyde then inserts into the [Ni]-H, yielding the corresponding methoxide complex. A third HBcat closes the catalytic cycle by reforming the [Ni]-H catalyst and gaining the final product CH_3OBcat.

In contrast, the NHC catalyst **49** "only" activates the Si-H bond by pushing electron density to the H atoms and simplifies this way the direct hydride transfer from Hsilane to the C-O bond (**52** top). However, the NHC catalyst **49** can react with CO_2 to the corresponding imidazolium carboxylate, too. This activated CO_2 adduct can be attacked more easily by Hsilanes than unbounded CO_2 (**52** bottom).

It is noteworthy that the CO_2 reduction catalyst and the hydride source must match for achieving high activity. Exchanging the hydride source for both systems, the reduction of CO_2 to MeOH failed. The reasons are a high kinetic barrier for the reaction of the Ni-formate with silanes and the formation of a thermodynamic stable intermediate between NHC and Hboranes.

Further examples of a catalytic hydroboration with Ru catalysts were presented by Sabo-Etienne using $[RuH_2(H_2)_2(PCy_3)_2]$ in combination with pinacolborane [112, 113] and by the group of Stephan applying the precursor $[Ru(PPh_3)Cl_2]$ and the ligand $N((CH_2)_2NHPiPr_2)_3$ in the presence of HBpin [114].

The first metal-free organocatalyst for hydroboration of CO_2 to MeOH was published by Maron and Fontaine [115]. The organocatalyst 1-Bcat-2-PPh$_2$-C$_6$H$_4$ reduces CO_2 with 3 eq of $BH_3 \cdot SMe_2$ to give subsequent MeOH with TON >3,000 and TOF >970 h^{-1}.

4.4   Other Homogeneous Catalytic Reductions of CO_2 Using Hydride Reagents

Beside methanol, the full reduction of CO_2 to methane is an attractive and actual goal for homogeneous catalysis. However, so far homogeneous catalysts capable of hydrogenating CO_2 to methane with molecular H_2 are still unknown (Eq. 4.4). In the meantime, some efforts have been undertaken using less benign reductants such as silanes.

$$CO_2 + 4\,H_2 \quad \rightarrow \quad CH_4 + 2\,H_2O \tag{4.4}$$
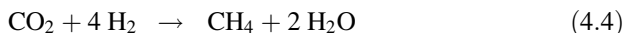
Interestingly, Musgrave's ab initio studies claim that even in the absence of a metal, the reduction of CO_2 with ammonia boranes via simultaneous hydride and proton transfer should be possible involving the intermediates HCOOH and hydrated formaldehyde to give finally methanol [116]. Unfortunately, ammonia boranes decompose easily in the presence of acid to H_2 and NH_2BH_2. Unless this problem will be solved, the reduction will stop at the HCOOH step. The group of Wehmschulte showed that strong Lewis acids such as $[Et_2Al]^+$ can catalyze the hydrosilylation of CO_2 to methane. However, after three cycles the activity decreased, likely caused by side reactions with the solvent C_6D_6 [117].

Combining borane complexes or additional borane with hydrosilylation reagents was the key to success for improved catalytic turnover numbers. All active systems have in common that different kind of metal complexes or frustrated Lewis pairs (FLP) are needed to activate the CO_2 to form the corresponding formate complexes. The following reduction steps are believed to be catalyzed by species $[R_3Si\text{-}H \cdots BR_3]$ involving the intermediates bis(silyl)acetal, methyl silyl ether, and finally methane. Active co-catalysts are presented in Scheme 4.15.

Activities and selectivities were low for the systems using **53** [118], **54** [119], and **55** [120], whereas a good TON of 2,156 was achieved in16 h by Turculet using the Pt-pincer borane complex **56** with Et$_3$SiH at 65 °C and 1 atm of CO_2 [121]. A high TON of 8,300 after 72 h at RT was published by Brookhart applying the Ir$^+$ PCP-pincer complex **57** [122] in the presence of Me$_2$PhSiH.

Finally, it is worth mentioning that carbon dioxide can be used as methylation reagent for amines in the presence of silanes. Our group [123] as well as the group of Cantat [124] realized the reduction of CO_2 with a simultaneous C-N bond formation. With this method it is possible to methylate primary amines with CO_2 as C1 feedstock.
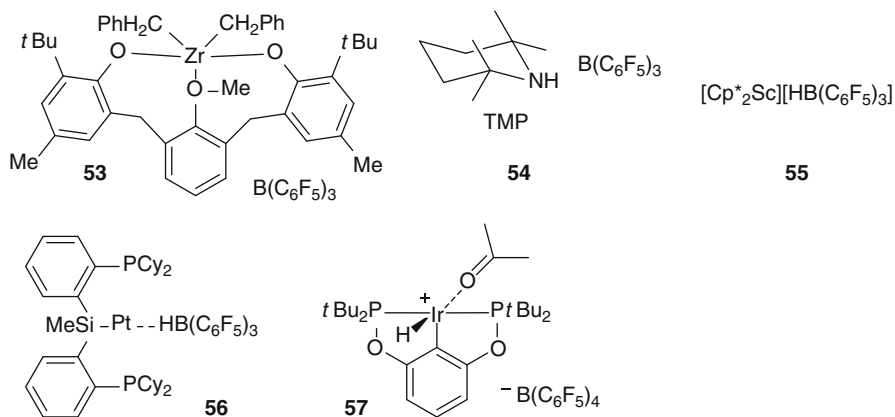
Scheme 4.15 Various co-catalysts for the $[R_3Si-H\cdots BR_3]$ catalyzed reduction of CO_2 to CH_4

4.5 Concluding Remarks

In the last decade, several improved organometallic catalysts for the hydrogenation of CO_2 to formic acid derivatives have been reported. Many of them show good activity even under ambient conditions. In addition, interesting concepts have been developed, combining both formic acid product separation and catalyst recycling. However, for industrial applications the activities and long-term stabilities of the catalysts still have to be improved. Meanwhile, also catalyst systems have been presented for hydrogen storage using carbon dioxide.

While non-precious metals such as Fe and Co were rarely known for the homogeneous CO_2 hydrogenation before 2009, much progress was achieved in this field in the last 3 years.

Very recently, also first promising systems capable of converting CO_2 to methanol became available opening new ways to a future methanol economy. On the other hand, the homogeneously catalyzed reduction of carbon dioxide to CH_4 using molecular hydrogen is still not known and more efforts are needed in this area. At this point it should be mentioned that related reductions of carbon dioxide using boranes or hydrosilylation reagents are interesting in order to understand the mechanism of such processes. Nevertheless, it should be clear that they will not be of preparative use due to price, sensitivity of the reagents, and waste generated.

What will be the future challenges in homogeneous CO_2 reductions? Obviously, for industrial implementations even better catalysts are needed. With regard to basic science, the hydrogenation of carbon dioxide with simultaneous C-C bond formation represents a grand challenge. As an example, the low temperature and selective Fischer-Tropsch reaction can be considered. Furthermore, reducing carbon dioxide directly to Co is of both industrial and academic interest. Such transformations would allow using carbon dioxide instead of toxic carbon monoxide. The key tools to achieve these goals will be catalysis and organometallic chemistry.

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