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Ruthenium-promoted reductive transformation of CO_2

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The reductive transformation of CO_2 to energy related products including formic acid, CO, formamide, methanol and methylamine could be a promising option to supply renewable energy. In this aspect, ruthenium has found wide application in hydrogenation of various carbonyl groups, and has successfully been applied to reductive transformation of CO_2 with high catalytic efficiency and excellent selectivity. In addition, ruthenium complexes have also served as effective photosensitizers for CO_2 photoreduction. Classified by reductive products, this review summarizes and updates advances in the Ru-catalyzed reduction of CO_2 along with catalyst development on the basis of mechanistic understanding at a molecular level.

carbon dioxide chemistry, homogeneous catalysis, reductive transformation, ruthenium, sustainable chemistry

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1 Introduction

The concentration of carbon dioxide has been increasing continuously in the atmosphere in recent decades [1]. With the rapid consumption of fossil fuels, it is urgent to develop alternative energy sources in a sustainable way. Therefore, the utilization of CO_2 as a raw material to afford valuable compounds has drawn considerable attention [1g]. During the last decades, CO_2 has been intensively investigated as a promoter [2], reaction media [3] and sustainable chemical feedstock [4] for organic synthesis. Among versatile applications of CO_2, the reduction of CO_2 to formic acid, CO, formamide, methanol, methylamine and CH_4, has aroused increasing interest recently due to potential utilization of CO_2 as a nontoxic, nonflammable, cheap and renewable raw material for chemical production or as an energy vector to store or harvest renewable energy [5]. In this aspect, because of its thermodynamic stability and kinetic inertness [6], activation of both CO_2 and H_2 could be crucial to performing CO_2 reduction successfully.

Among versatile metal catalysts, Ru complexes have been found to be robust with high efficiency to afford various reductive compounds such as formic acid, CO, formamide, methanol, methylamine. From the mechanistic point of view, Ru works in a similar catalytic pathway for the reduction of both CO_2 and other carbonyl compounds [7]. As such, the hydride of the Ru–H species readily moves to the carbon atom of the carbonyl group. As a result, the catalytic species still remains active even in a strong basic environment [8]. On the other hand, heterogeneous ruthenium catalysis has also been established in the early stage to facilely recover the noble metal catalysts [9], although homogeneous catalysis provides great efficiency. In addition, Ru complexes have also been utilized for CO_2 electroreduction and photoreduction. In the case of CO_2 photoreduction, the Ru-bpy complex is used as a kind of active heterogeneous photosensitizer [10]. In this minireview, we would like to summarize recent progress in the reductive transformation of CO_2 catalyzed by

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Ru complexes, in particular, the activation methodologies for both CO_2 and hydrogen molecules, which leads to the improvement in the reduction efficiency and product selectivity.

2 Reduction of CO_2 to formic acid

Formic acid has been widely employed for the production of leather, textile and latex rubber in industry [11]. On the other hand, formic acid is also considered to be a hydrogen-store material with capacity of resolving or releasing H_2 [12]. Although the hydrogenation of CO_2 with hydrogen produces formic acid with 100% atom efficiency [5e,13], this is thermodynamically unfavorable when CO_2 and H_2 are the gas phase (Scheme 1(a)) [14]. In order to render the reaction smoothly (ΔG<0), an additional base is required (Scheme 1(b)). If water or other solvent that can form hydrogen bonding to stabilize formic acid is employed as reaction media, the reaction can readily perform in a thermodynamically favorable manner (Scheme 1(c)) [5e,13].

The aluminum oxide-supported ruthenium is the first heterogeneous catalyst for hydrogenation of CO_2 to formic acid [9], unfortunately the turnover number (TON) is only 120. On the other hand, the first homogeneous Ru catalyst, $K[Ru^{III}(EDTA\text{-}H)Cl]\cdot 2H_2O$, was reported in 1989 [15]. In contrast to the Rh-based catalysts [16], Ru shows higher activity. Herein we would like to give an overview on the catalyst development in terms of ligand designing as well as mechanistic analysis.

2.1 Phosphine ligand

In 1994, Jessop *et al.* [17] introduced $RuH_2(PMe_3)_4$ and $RuCl_2(PMe_3)_4$ as the $scCO_2$-soluble (supercritical CO_2) catalyst for the hydrogenation of CO_2 to formic acid in NEt_3 and MeOH with turnover frequency (TOF) up to 1400 h^{-1} and TON up to 7200 at 50 °C under 20.5 MPa ($scCO_2$). The addition of basic additive further improves the reaction efficiency, thus the TOF of 95000 h^{-1} with $RuCl(O_2CCH_3)(PMe_3)_4$ is obtained in the presence of NEt_3 and pentafluorophenol [18]. The *in situ* nuclear magnetic resonance (NMR) study under pressure shows that the alcoholic additive induces the catalyst precursor to generate the cationic species and the alcohol works as a hydrogen bonding donor. Besides organic bases, inorganic bases are also effective. Laurenczy *et al.* reported the hydrogenation of CO_2 in $NaHCO_3$ aqueous solution by employing the water-soluble $[RuCl_2(TPPMS)_2]_2$ (TPPMS=monosulfonated triphenylphosphane) [19] and $RuCl_2(PTA)_4$ (PTA=1,3,5-triaza-7-phosphaadamantane) [20]. In these reactions, HCO_3^- is actually hydrogenated with the maximum TOFs of 807 and 9600 h^{-1} respectively. The PTA as a ligand plays an important role in CO_2 hydrogenation [20,21]. The nitrogen atom of PTA, which has a strong basicity, can serve as a hydrogen bonding or proton acceptor to activate HCO_3^-. In this context, the formation of $[\eta^6\text{-}(C_6H_6)RuH(PTA)_2]^+$ is regarded as the major hydride species, and a possible mechanism involving hydride transfer to bicarbonate is proposed as depicted in Scheme 2 [21b,21c].

(a) $CO_2\,(g) + H_2\,(g) \rightleftharpoons HCOOH\,(l)$

$\Delta G^0 = +32.8$ kJ/mol, $\Delta H^0 = -31.5$ kJ/mol, $\Delta S^0 = -215$ J/(K mol)

(b) $CO_2\,(g) + H_2\,(g) + NH_3\,(aq) \rightleftharpoons HCOO^-\,(aq) + NH_4^+\,(aq)$

$\Delta G^0 = -9.5$ kJ/mol, $\Delta H^0 = -84.3$ kJ/mol, $\Delta S^0 = -250$ J/(K mol)

(c) $CO_2\,(g) + H_2\,(g) \rightleftharpoons HCOOH\,(aq)$

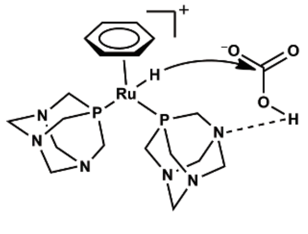
$\Delta G^0 = -9.5$ kJ/mol

Scheme 1 The thermodynamic parameters of CO_2 hydrogenation to formic acid.

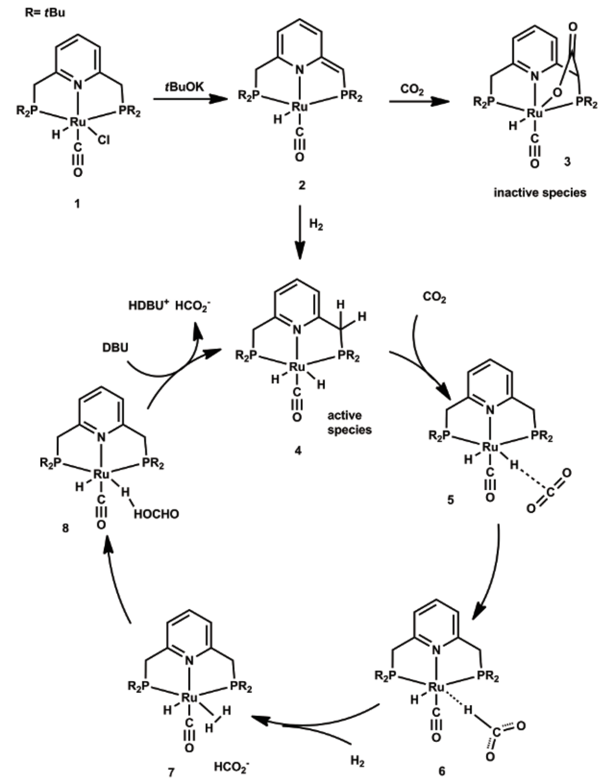
Furthermore, biphosphine ligands are also proven to be efficacious. The $[RuCl_2(C_6H_6)]_2$ has been reported as a catalyst precursor cooperating with dppm [bis(diphenylphosphino)methane] for efficient hydrogenation of CO_2 in aqueous $NaHCO_3$ [22].

2.2 Pincer ligand

Pincer ligands have been widely applied in CO_2 hydrogenation to formic acid with excellent TONs and TOFs, being attributed to the strong chelating abilities. This geometrically restricted structure can affect the coordination of the substrate to metal, thus resulting in enhanced the product selectivity [23]. Recently, the highest TOF (1100000 h^{-1}) has been achieved by using Ru-complex as reported by Pidko and co-workers [24]. The Ru-PNP complex i.e. RuCl(H)(CO)(PNP) **1** [PNP=2,6-$(CH_2P\mathit{t}Bu_2)_2C_5H_3N$] shares a similar structure to that of Ir-PNP complex (Scheme 3) [25]. DFT calculation and *in situ* NMR technique have been intensively applied to mechanistic investigation (Scheme 3) [24b]. As speculated, the bis-hydride Ru complex **4** is regarded as the active species, while the ligand-assisted CO_2 adduct **3** is inactive. The two routes that do not involve the metal-ligand cooperation are predicted to be predominant, which can be controlled by changing H_2 pressure. Recently, Ru(Acriphos)$(PPh_3)(Cl)(PhCO_2)$ [Acriphos=4,5-bis(diphenylphosphino)acridine] has been developed for the hydrogenation of CO_2 to formic acid in dimethyl sulfoxide (DMSO) or DMSO/



Scheme 2 The proposed active intermediate/transition state.



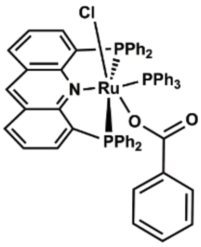
Scheme 3 Possible catalytic cycle for CO_2 hydrogenation to formate promoted by [RuCl(H)(CO)(PNP)] **1**.

H_2O without the use of amine with TON up to 4200 and TOF up to 260 h^{-1} under 8 MPa H_2 and 4 MPa CO_2 as shown in Scheme 4 [26]. Notably, the thermodynamic equilibrium can be improved via addition of small amounts of acetate buffer, thus resulting in the enhanced TON of 16310 and TOF of 1019 h^{-1}.

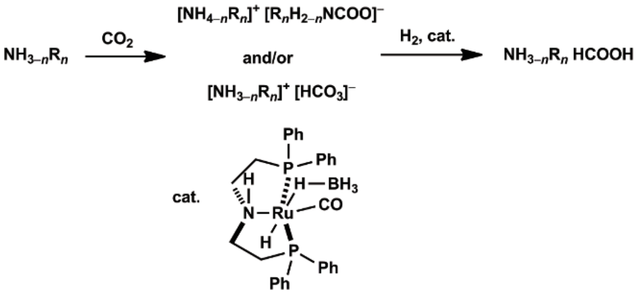
Recently, Olah *et al.* [27] have combined both CO_2 capture and *in situ* hydrogenation of the captured CO_2 by employing Ru-PNP complex as an efficient catalyst (Scheme 5). A TON of 7375 is obtained by using 1,1,3,3-tetramethylguanidine (TMG) as the base in aqueous media at 55 °C for 20 h. Notably, the concept of "CO_2 capture and utilization" (CCU) strategy proposed for the first time by He *et al.* [28] would be promising to utilize CO_2 from air with energy and economy benefits.

3 Reduction of CO_2 to CO

Although known as a poisonous and pollution gas, CO is one of most important basic chemicals widely applied in chemical, energy and medical industry [29]. As an abundant C_1 source, the conversion of CO_2 to CO is a promising method to produce CO along with reducing carbon emission. Considering the excellent catalytic efficiency of Ru complexes, we in this section mainly summarize Ru complexes for electrochemical and photochemical reduction of CO_2 to CO.



Scheme 4 [Ru(Acriphos)(PPh_3)(Cl)($PhCO_2$)].

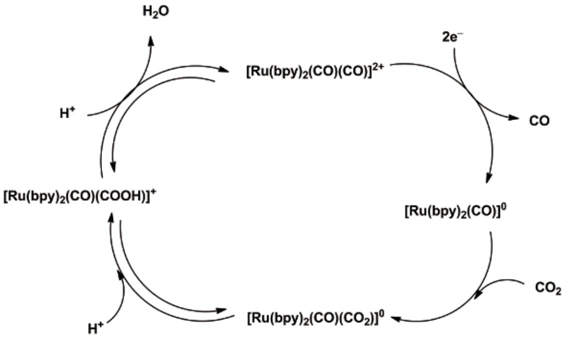


Scheme 5 CO_2 captured by amines and subsequent conversion to formic acid.

In 1983, Tanaka and co-workers [30] found that there is an equilibrium between $[Ru(bpy)_2(CO)_2]^{2+}$, $[Ru(bpy)_2(CO)(C(O)OH)]^{+}$, and $[Ru(bpy)_2(CO)(CO_2)]^{0}$ (bpy=2,2′-bipyridine) influenced by pH. A generally accepted mechanism for $[Ru(bpy)_2(CO)_2]^{2+}$ in the conversion of CO_2 to CO is described in Scheme 6. The bond between Ru atom and carbonyl group becomes unstable when the $[Ru(bpy)_2(CO)_2]^{2+}$ obtains two electrons to produce CO and $[Ru(bpy)_2CO]^{0}$. Then the electrophilic attack of CO_2 at $[Ru(bpy)_2CO]^{0}$ reproduces $[Ru(bpy)_2(CO)_2]^{2+}$ through dehydration with the assistance of proton [31].

Although further studies reveal that the acidic media can enhance CO productivity, the yield remains still far from satisfactory [32]. Accordingly, a kind of polymeric $[Ru(bpy)(CO)_2]_n^{0}$ film is applied to modify the carbon electrode for CO_2 electrocatalytic reduction with 94% current efficiencies of CO in aqueous media [33]. The CO selectivity relies on the functional groups at the 4,4′-positions of the bpy, whose electron donating groups are in favor of the CO formation. Recently, Ott's group [34] has prepared a series of highly active electrocatalysts $[Ru(tBu_3tpy)(bpy)(NCCH_3)]^{2+}$ (tpy=2,2′:6′,2″-terpyridine) for further exploring the steric and electronic effects. The introduction of methyl at the *ortho* position of the bpy ligand results in the bpy plane tilting away from the tpy plane, forming a hydrogen bonding with CO_2 and reducing high overpotential once operated for electrochemical CO_2 reduction.

Lehn's group [35] conducted the first photochemical reduction of CO_2 to CO catalyzed by $Ru(bpy)_3^{2+}/Co^{II}$ system under visible light irradiation with low TON in 1983. Soon after-

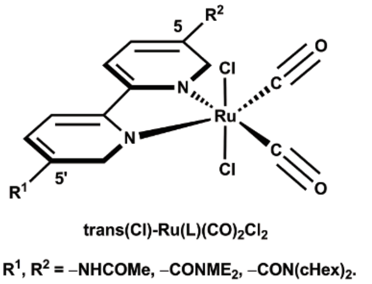


Scheme 6 The mechanism for CO_2 reduction to CO catalyzed by $[Ru(bpy)_2(CO)_2]^{2+}$.

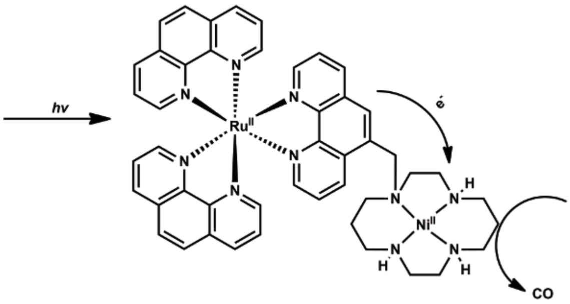
wards, 1-benzyl-1,4-dihydronicotinamide (BNAH) was used as an excellent electron donor for photochemical reduction of CO_2 to CO. $[Ru(bpy)_3]^{2+}$ was used as photosensitizer and $[Ru(bpy)_2(CO)_2]^{2+}$ served as catalyst [36]. In addition, H_2O plays a vital role in photochemical reduction of CO_2 to produce CO since no CO is found in the CO_2-saturated dry *N*,*N*-dimethylformamide (DMF). A series of *trans*-(Cl)-$[Ru(L)(CO)_2Cl_2]$-type complexes (Scheme 7), with bpy bearing amide groups at the 5,5′-positions, are also employed for photocatalytic reduction of CO_2 [37]. $[Ru(bpy)_3]^{2+}$ is in this reaction used as photosensitizerand, BNAH as the electron donor, a mixture of CO_2-saturated *N*,*N*-dimethylacetamide/water as solvent. DFT calculations also verify the amide groups and the structural twist of the amide group with respect to the bpy plane make a contribution to improve the level of the LUMO of the ruthenium complex, resulting in enhancing the catalytic activities.

A series of trials have been performed to promote the activity of photocatalysts and to broaden the visible light absorption. The $[Ru(phen)_2(phen\text{-}cyclam\text{-}Ni)]^{4+}$ (phen=1,10-phenanthroline, cyclam=1,4,8,11-tetraazacyclotetradecane) (Scheme 8) combining photosensitizer $Ru^{II}(phen)_3$ and reductant Ni^{II}(cyclam) into one molecule, was used for CO_2 photoreduction to CO [38]. This catalyst is found to be more stable than $Ru(phen)_3^{2+}$ and shows higher activity than the mixture of $Ru(phen)_3^{2+}$ and $Ni(cyclam)^{2+}$ due to excellent reduction activity of Ni^{II}(cyclam) and facile photoexcitation properties of $Ru^{II}(phen)_3$. Furthermore, a [Ni(cyclam)]-$[Ru(bpy)_3]$-ascorbic acid system for the photoreduction of $scCO_2$ is conducted on the interface between an aqueous solution and $scCO_2$ [39]. This interfacial photoreduction system is 7-fold increase in formation of CO than reaction conducted in aqueous solution probably because complexation of CO_2 with the Ni^{II}(cyclam) can take place at the water-$scCO_2$ interface easily.

Recently, similar to $[Ru(phen)_2(phen\text{-}cyclam\text{-}Ni)]^{4+}$, several bimetallic catalysts with phenanthroline-extended tetramesityl porphyrin as ligand have been employed for the light-induced CO_2 reduction [40]. The unique structure of porphyrin allows a metal reside in the cavity, and phen ligand also has ability to coordinate the second metal center selectively. The catalysts are designed by attaching porphyrin unit containing a redox-active metal center (Fe and Co) to a photosensitizer phenanthroline coordinating $[Ru(tbbpy)_2]^{2+}$ (tbbpy=4,4′-di-tert-butyl-2,2′-bipyridine), and the addition of $Ru(tbbpy)_2^{2+}$ broads the visible light absorption, thus leading to promoting the reduction.



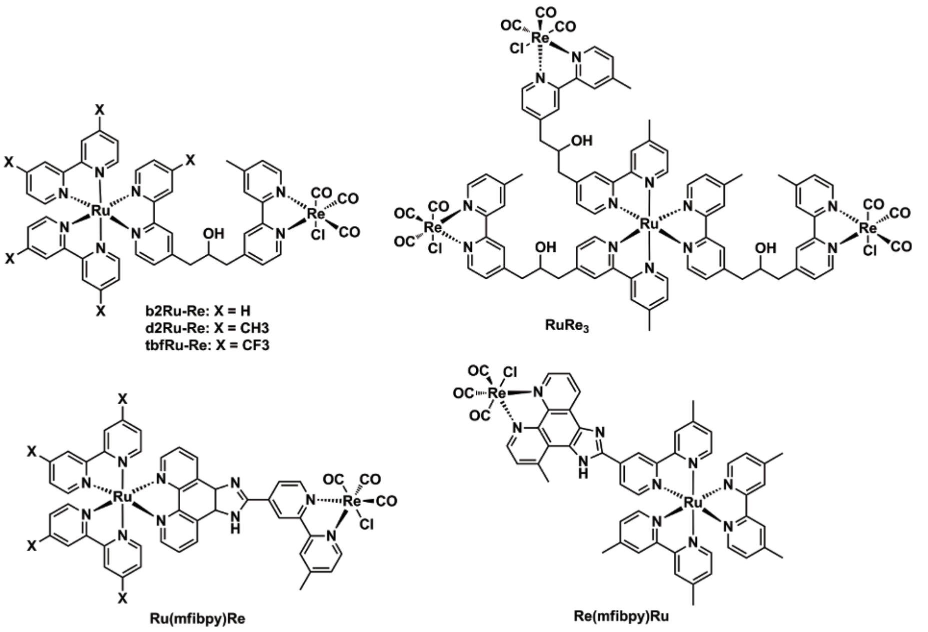
Scheme 7 *trans*-(Cl)-$[Ru(L)(CO)_2Cl_2]$ with bpy bearing amide groups at the 5,5’-positions.



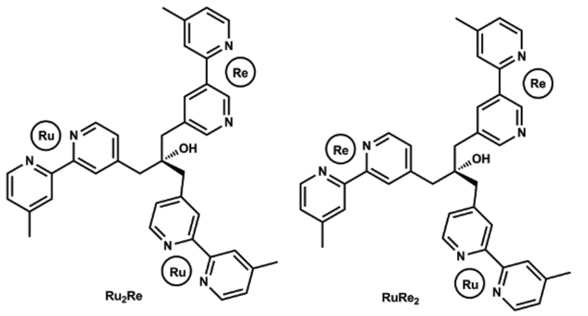
Scheme 8 Reduction of CO_2 to CO catalyzed by $Ru(phen)_2(phen\text{-}cyclam\text{-}Ni)^{4+}$.

Both of Ru and Re polypyridine complexes have drown more and more attention in the photocatalytic reduction of CO_2 due to their photochemical and redox properties as well as good stability. For the first time, Ishitani *et al.* [41] have reported a series of Ru^{II}-Re^{I} multinuclear complexes (Scheme 9) linked by bridging ligands for the CO_2 photoreduction under the visible light. These Ru^{II}-Re^{I} catalysts provide CO as the dominant product in triethanolamine (TEOA)/DMF solutions using BNAH as electron donor under irradiation. Accodingly, this kind of Ru^{II}-Re^{I} multinuclear complexes offers an inspiration to effectively form photocatalysts for CO_2 reduction.

Different types of linking bridge between Ru unit and Re unit are further studied. The Ru^{II}-Re^{I} mixed-metal complexes with tripodal ligand (Scheme 10) are demonstrated 2-fold-improved photocatalytic activity than monometallic model complexes under otherwise identical reaction conditions [42]. The intramolecular electron transfers through the bridging tripodal ligand and the increased molar ratio of Re^{I} to Ru^{II} are beneficial to the CO formation from CO_2.



Scheme 9 Ru^{II}-Re^{I} multinuclear complexes linked by bridging ligands.



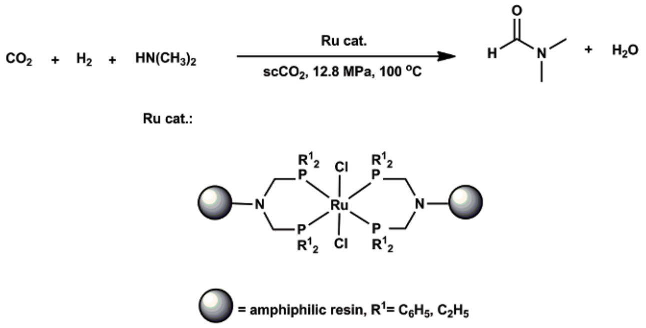
Scheme 10 Ru^{II}-Re^{I} mixed-metal complexes with tripodal ligand.

Ru^{II}-Re^{I} binuclear photocatalysts linked by $-CH_2XCH_2-$ (X=O, S, CH_2) or ethylene chain are also studied in the reduction of CO_2 to CO [43]. The photocatalyst connected by $-CH_2OCH_2-$ exhibits excellent performance because the introduction of O atom can promote the excited state of the Ru photosensitizer and the intramolecular electron transfer. The activity of the Ru^{II}-Re^{I} binuclear photocatalyst connected by one ethylene chain with $BI(CO_2H)H$ (2-(1,3-dimethyl-2,3-dihydro-1*H*-benzo[d]imidazol-2-yl)be-nzoic acid) as the reductant can reach approximately 5.6-fold higher than that of the best catalyst in the lierature [43c]. Besides, Ru^{III}-substituted polyoxometalate [44] and Ru-enzyme-modified nanoparticle [45] are also employed for CO_2 photoreduction.

4 Reductive functionalization of CO_2 to formamide

Formamides are a family of important chemicals serving as intermediates and reagents in industry. Among various synthetic methods to obtain formamides, the general process is based on the formylation of amines with formylating agents such as formic acid, formate, chloral and CO [46]. For example, DMF is produced by the formylation of dimethylamine (DMA) with toxic CO catalyzed by $NaOCH_3$. As a C_1 feedstock, CO_2 with advantages of abundance and non-toxicity is an attractive carbonylating reagent. In 1970, Hayne *et al.* [47] reported the first example of homogeneous catalysis for formylation of DMA with CO_2 and H_2 at 100– 125 °C in toluene, $RuCl_2(PPh_3)_3$ was used as an alternative catalyst. From then on, a variety of studies have been published about the homogeneous formylation using CO_2. Considering that CO_2 can play a dual role as both reactant and solvent, the formylation of DMA catalyzed by $RuCl_2(PMe_3)_4$ at 100 °C in $scCO_2$ is carried out with TON up to 370000, 100-fold higher than the previous result (TON of 3400) due to high diffusion rate [48]. Comparable results are also obtained in the formylation of DMA catalyzed by $RuCl_2(dppe)_2$ [dppe=(1,2-bis(diphenylphosphino)ethane)] in $scCO_2$ [49] or $scCO_2$/IL biphasic system [50].

On the other hand, heterogeneous catalysts have drawn attention gradually for the convenience of separating product from reaction system along with the catalyst recycling. The silica gel-like ruthenium complexes were applied for the formylation of DMA in $scCO_2$ with TON up to 110800 with perfect selectivity [51]. Amphiphilic resin-supported ruthenium complexes were also used as recyclable catalysts for the synthesis of DMF from $scCO_2$, DMA and H_2 at 100 °C (Scheme 11) [52]. The amphiphilic resin plays a role in recycling catalyst and facilitating mass transfer in the reaction mixture.



Scheme 11 The formylation of DMA catalyzed by amphiphilic resin-supported Ru^{II} catalyst.

Aside from DMF, various kinds of formamides are also obtained smoothly by the use of the ruthenium catalyst. The formylation of cyclic amines and primary amines is implemented using CO_2 and H_2 in the presence of $RuCl_2(dppe)_2$ at 100–120 °C as shown in Scheme 12 [53]. The formation of formanilide from aniline is successfully carried out in the presence of DBU at 100 °C, using $RuCl_2(PMe_3)_4$ as the catalyst [54]. *N*-(3-methoxypropyl)formamide is also gained in $scCO_2$ by using highly active ruthenium catalysts generated *in situ* [55].

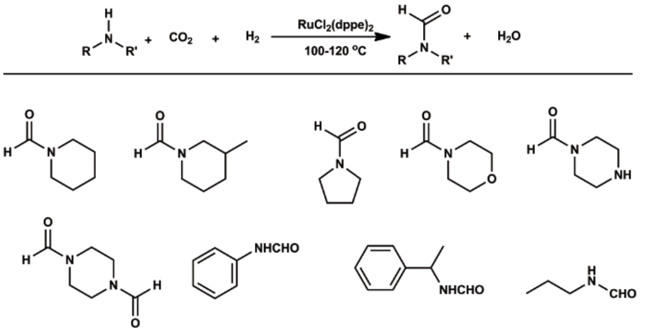
Recently, Ding and co-workers [56] have discovered the Ru^{II} or Ir^{III} complexes equipped with a tridentate ligand are efficient catalysts for *N*-formylation of various primary and secondary amines under mild reaction conditions (Scheme 13). The catalyst **9** can accelerate the *N*-formylation of morpholine with catalyst loading of 0.00005 mol%, the yield up to 97%, and the TON up to 1940000. Moreover, the catalyst **10** can be recycled for more than 12 runs at a loading of 0.002 mol%, providing a promising and potential technology for industrial scale production of DMF.

Apart from the methods mentioned above, electrochemical and photochemical reduction of CO_2 is explored for the formylation of amines. However, the electrochemical formation of DMF from DMA and CO_2 catalyzed by $[Ru(bpy)_2(CO)_2]^{2+}$ only accounts for 21.4% of total products [57]. A selective formation of formamides via photocatalytic CO_2 reduction is conducted smoothly with small amount of CO and HCOOH, $[Ru(bpy)_2(CO)_2]^{2+}/[Ru(bpy)_3]^{2+}/Me_2NH/Me_2NH^{2+}$ system is used in CH_3CN under visible light [58]. This selective formation of formamides depends on the formation rate of $[Ru(bpy)_2(CO)(CONR_2)]^+$, resulting from the nucleophilic attack of Me_2NH at $[Ru(bpy)_2(CO)_2]^{2+}$.

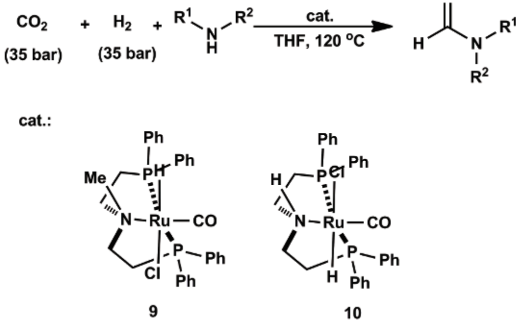
5 Reduction of CO_2 to MeOH

5.1 Direct hydrogenation of CO_2 to methanol

Methanol is a sustainable source of liquid fuels and one of the most useful organic chemicals. The production of methanol from CO_2 is attracting much interest in both academia and industry [6]. In 1993, Sasaki *et al.* [59] reported the hydrogenation of CO_2 using homogeneous $Ru_3(CO)_{12}$-KI catalytic system to afford methanol along with CO, CH_4 as depicted in Scheme 14. In this process, CO_2 is initially hydrogenated to CO, which goes through further reduction to afford methanol. Notably, iodide could contribute to the formation of the ionic Ru species thus stabilizing the Ru complex. It took another 20 years after these first observations before an organometallic catalyst was found for the selective homogeneous hydrogenation of CO_2 to methanol. In 2012, a catalyst comprising of Ru(triphos)(tmm) [triphos=1,1,1-tris(diphenylphosphinomethyl)ethane, tmm= trimethylene methane] and one equivalent of $HNTf_2$ [$HNTf_2$=bis(trifluoromethane)sulfonamide] has been developed for the hydrogenation of CO_2 to methanol with TON up to 221 (2 MPa CO_2, 6 MPa H_2, 140 °C) in THF/EtOH [60]. The experimental and theoretical results prove that this transformation occurs at a cationic Ru-triphos species as a molecularly-defined active site (Scheme 15) [61].



Scheme 12 Formylation of cyclic amines and primary amines with CO_2 catalyzed by $RuCl_2(dppe)_2$.



Scheme 13 *N*-formylation of morpholine catalyzed by pincer-type Ru^{II} complexes.

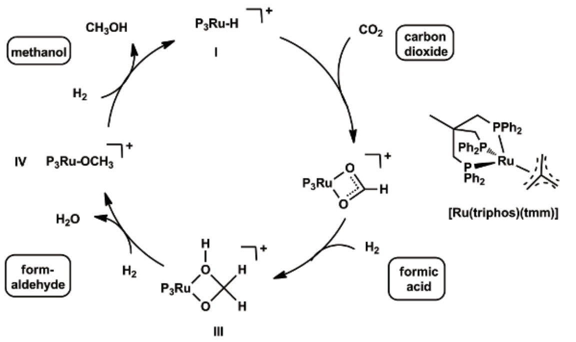
5.2 Indirect hydrogenation of CO_2 to methanol

Direct hydrogenation of CO_2 to methanol with homogeneous

$$CO_2 + H_2 \xrightarrow[\substack{CO_2/H_2 = 1:3,\ P_{total} = 8\ MPa \\ NMP,\ 240\ ^\circ C,\ 3\ h}]{Ru_3(CO)_{12}\text{-}KI} MeOH + CO + CH_4 + C_2H_6$$

NMP = *N*-methyl-2-pyrrolidone

Scheme 14 CO_2 hydrogenation with the $Ru_3(CO)_{12}$-KI system.

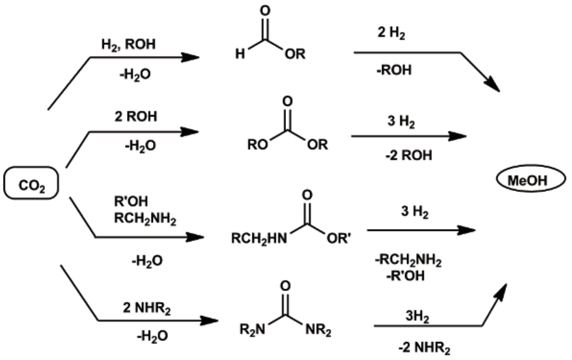


Scheme 15 Catalytic cycle for the hydrogenation of CO_2 to methanol by the Ru-triphos catalyst.

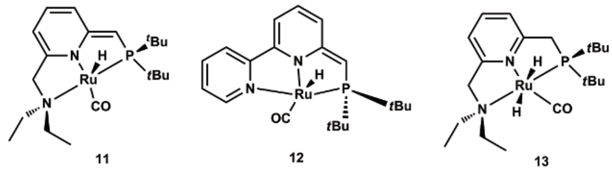
Ru catalysts generally requires high operating temperature (200–250 °C) and pressure (5–10 MPa). Recently, indirect hydrogenation of CO_2 to methanol has been intensively investigated, where CO_2 derivatives, such as organic carbonates and carbamates are efficiently converted into methanol at relatively mild reaction conditions with suitable catalysts [62].

In 2011, Milstein *et al.* [63] developed an indirect approach through hydrogenation of the CO_2-derived organic carbonates, carbamates, and formates to methanol (Scheme 16) by employing Ru^{II} pincer complexes (Scheme 17) under mild hydrogen pressure with high TONs, without the generation of any waste or by-products. For instance, the hydrogenation of diethyl carbonate catalyzed by **11** performs smoothly at 1 MPa and 145 °C. And the bpy-based Ru^{II}(PNN) pincer complex **12** gives a better result with higher TON of 4400 under 5 MPa of H_2. A postulated mechanism involving metal-ligand cooperation is supported by stoichiometric reactions of dimethyl carbonate and methyl formate with the dihydride complex **13**. Furthermore, **12** was successfully applied for the hydrogenation of the more challenging urea derivatives [64]. This offers an environmentally benign, atom economic approach for indirect transformation of CO_2 to methanol.

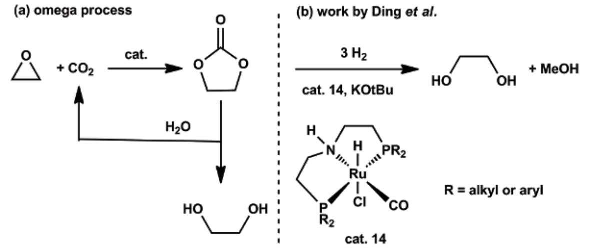
The insertion of CO_2 into ethylene oxide to produce ethylene carbonate (EC) is thermodynamically favorable and has been well developed as the key step in the "omega process". In this context, Ding *et al.* [65] developed a readily available Ru^{II}(PNP) catalyst **14** for homogeneous hydrogenation of cyclic carbonates to methanol and the corresponding 1,2-diols with excellent catalytic efficiency (Scheme 18). Employing **14** as catalyst, the reaction proceeds smoothly at 6 MPa of H_2 to afford methanol and ethylene glycol with a TON of 87000 and a TOF of 1200 h^{-1}. Notably, poly(propylene carbonate) also works well to produce methanol and 1,2-propyleneglycol in excellent yields. The combination of this reduction and the production of EC in the omega process would establish a new bridge from CO_2 and ethylene oxide to methanol and ethylene glycol. Furthermore, a possible catalytic mechanism is proposed, in which the NH moiety of the ligand proves to be crucial in facilitating the reduction of the C=O bond of carbonate via secondary coordination sphere interactions with substrates.



Scheme 16 Indirect hydrogenation of CO_2 to methanol.



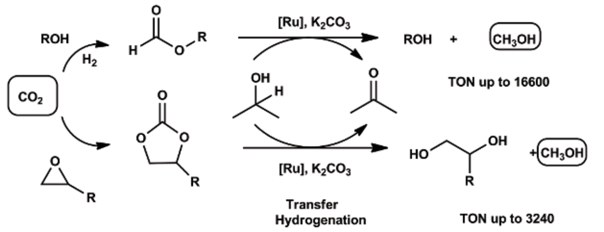
Scheme 17 Ru^{II}(PNN) pincer complexes.



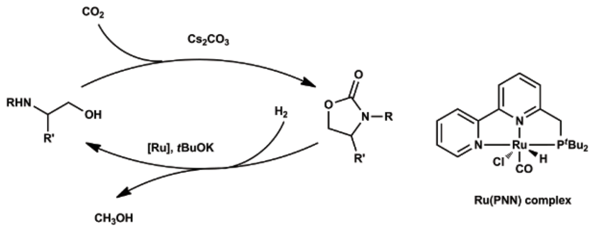
Scheme 18 (a) Shell omega process for the production of ethylene glycol; (b) Ding's approach to produce ethylene glycol and methanol.

High pressure is still required. Fortunately, the transfer hydrogenation employing a hydrogen donor is an attractive alternative. In this context, a readily available Ru-based catalyst is used for the transfer hydrogenation of organic formate and cyclic carbonate to methanol (Scheme 19) [66]. An approach is developed for CO_2 hydrogenation, in which CO_2 capture with aminoethanols at low pressure is coupled with hydrogenation of the captured CO_2, oxazolidinone, directly to MeOH, using a Ru(PNN) pincer complex (Scheme 20) [67].

Sanford and co-workers [68] believe that the hydrogenation



Scheme 19 Transfer hydrogenation of organic formates and cyclic carbonates to methanol.



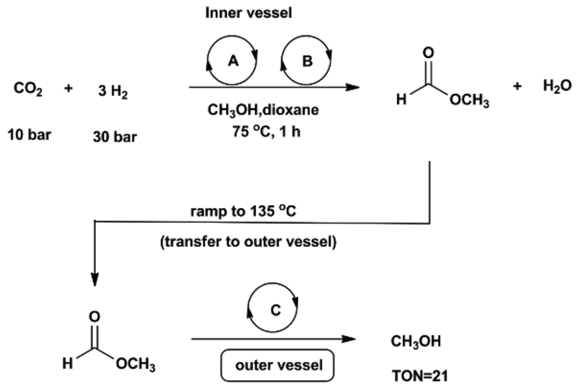
Scheme 20 CO_2 capture and hydrogenation to MeOH.

of CO_2 to MeOH is a multiple-step transformation. The multiple-step transformation involving several catalysts requires a three-step cascade catalysis sequence of: (1) generation of formic acid from CO_2 and H_2; (2) transformation of formic acid to formate ester; (3) MeOH production through hydrogenation of the ester (Scheme 21). Each step needs an independent catalyst. Although the rate and selectivity are tunable simply by changing the catalyst, the three kinds of catalysts are incompatible, especially catalysts **B** and **C** (Scheme 22). To solve the problem, a vapor transfer method has been proposed, that is, catalysts **A** and **B** are in an inner vessel to be separated from catalyst **C**, which is in an outer vessel, thus avoiding the deactivation of catalyst **C** by **B.** A TON of 21 can be obtained.

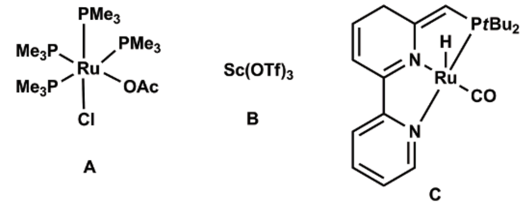
6 Reductive functionalization of CO_2 to methylamines

Methylamines are important intermediates which find wide applications in the synthesis of dyes, natural products and fine chemicals [69]. Generally, methylamines are often obtained from amines by employing formaldehyde, methyl iodide or dimethyl sulfate as methylating agent [70]. Using CO_2 as a C_1 building block provides an alternative and promising route to methylamines from amines. And various metal- [71] and organo- [72] catalyst systems have been developed for this purpose, in which the Ru-based catalysts show excellent performance.

The Ru-based catalyst comprising of $RuCl_2(dmso)_4$ and the bulky ligand $BuPAd_2$ (Ad=adamantyl)is developed for reductive methylation of amines with hydrosilane as reductant and CO_2 as C_1 source [73]. Various kinds of amines including aromatic and aliphatic, secondary and primary ones are successfully transformed into the desired *N*-methylated products in good to excellent yields under 3 MPa CO_2 and 100 °C. Based on series of control experiments, two possible reaction pathways for direct methylation with CO_2 are proposed: (1) direct reduction of CO_2 in the presence of amine generates formamide, which goes through further reduction to produce the corresponding methylamine product; (2) dehydration of ammonium carbamate affords urea, subsequent reduction delivers the desired product (Scheme 23).



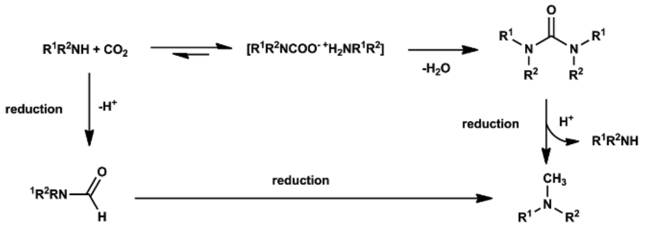
Scheme 21 The multiple-step method for the hydrogenation of CO_2 to MeOH.



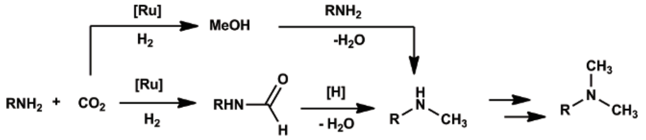
Scheme 22 Catalyst **A**, **B**, and **C**.

Reductive methylation with CO_2 and reducing agents such as hydrosilanes is an attractive synthetic approach. However, the availability for the reducing reagents remains an issue. Furthermore, the coupled by-products require downstream separation and potential recycling. The use of H_2 as reductant clearly overcomes such a limitation.

In 2013, the direct *N*-methylation of amines with CO_2 and molecular hydrogen as the building blocks was demonstrated for the first time [74]. An *in situ* combination of a Ru^{III} precursor, triphos, and either acid additives or LiCl proves to be the key to successful catalysis. The desired methylated products are obtained from primary and secondary amines with good to excellent yields in the presence of 2 MPa CO_2 and 6 MPa H_2 under 140 °C. Notably, selective monomethylation of diamines and convenient synthesis of the ^{13}C labelled drugs show the promising application of this novel method. Furthermore, control experiments are studied to identify the key intermediates. Therefore, the consecutive methylation reaction proceeds with formamide and methanol as major and minor intermediates, respectively (Scheme 24).



Scheme 23 Proposed pathways for the methylation of amines with CO_2.



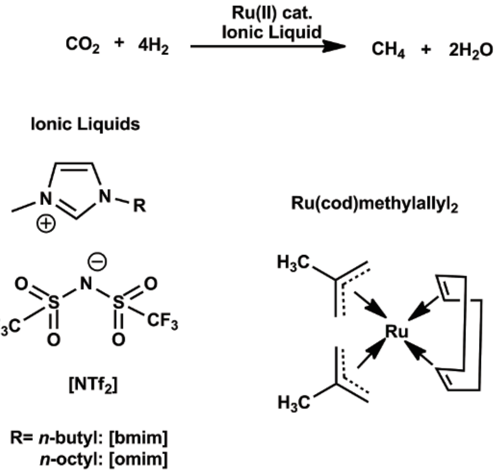
Scheme 24 Proposed reaction pathway for methylation of amines with CO_2.

Almost simultaneously, the molecularly defined and stable precursor complex Ru(triphos)(tmm) together with organic acids e.g. $HNTf_2$ was developed for the methylation of amines using CO_2 as C_1 source and H_2 as reducing agent [75]. Furthermore, the synthesis of trimethylamine was realized through a multicomponent combination of ammonia with CO_2 and molecular hydrogen. Subsequently, employing the identical catalyst system Ru(triphos)(tmm)/$HNTf_2$ enables the reductive methylation of isolated imines, as well as the direct coupling of amine with aldehyde and the subsequent reductive methylation of the *in situ* formed imine in the presence of 2 MPa CO_2 and 6 MPa H_2 [76]. Notably, this methodology is applied for the synthesis of butenafine as a model pharmaceutical product.

7 Other reductive products from CO_2

Except for HCOOH, CO, MeOH, methylamine and formamide, plenty of other useful chemicals can be obtained via the reduction of CO_2, for instance, CH_4, formaldehyde and alcohols.

As a clean energy, CH_4 has been playing a more and more important role in our society. For example, it can be employed to generate electrical power, to serve as a substitute for petroleum [77]. It is a promising strategy to obtain CH_4 from the CO_2 reduction. In 1973, Lunde *et al.* [78] reported the formation of CH_4 via the Sabatier reaction catalyzed by the alumina-supported ruthenium in a H_2/CO_2 flow at 205–360 °C. Rutile TiO_2-supported ruthenium nanoparticle is also employed for the conversion of CO_2 to CH_4, and exhibits higher activity than SiO_2 or Al_2O_3-supported ruthenium catalysts due to the effect of particle size and the number of the hydroxyl group [79]. Recently, ruthenium nanoparticle *in situ* generated in [omim][NTf_2] has been used for CO_2 hydrogenation to obtain CH_4 (Scheme 25). Ru(cod)methylallyl$_2$ is utilized as the Ru^{II} precursor because it can be decomposed to the ruthenium NPs in ILs. The imidazolium ionic liquid has dual catalytic roles in stabilizing the ruthenium catalyst and also serves as solvent in the reaction [80].

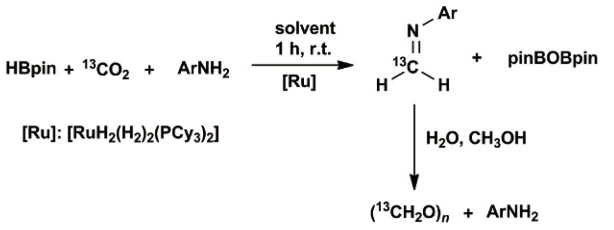


Scheme 25 Hydrogenation of CO_2 to CH_4 in ionic liquid catalyzed by ruthenium nanoparticles.

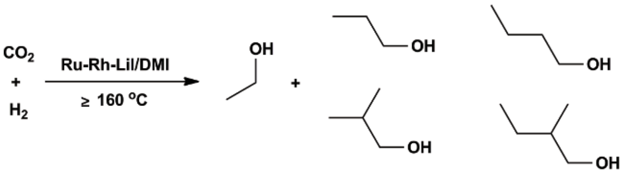
Actually, the formaldehyde can be obtained by a $4e^-$ reduction from CO_2. However, formaldehyde is too active to be isolated or even identified in the reaction. In 2014, Sabo-Etienne's group [81] provided the direct evidence for formaldehyde formation in CO_2 reduction by employing ^{13}C-labeled NMR technique with HBpin (pinacolborane) as reducing agent and $RuH_2(H_2)_2(PCy_3)_2$ (Cy=cyclohexyl) as catalyst. The generated formaldehyde is captured by condensation with a primary amine into imine, and then the imine is hydrolyzed to the primary amine and formalin solution (Scheme 26). And it is the first unquestionable evidence that CO_2 can be used as a C_1 feedstock to produce formaldehyde.

Treated as value-added chemicals, ethanol and larger alcohols also can be gained through CO_2 reduction. A $Ru_3(CO)_{12}$/$Rh_2(CO)_4Cl_2$-LiI system was employed to catalyze the hydrogenation of CO_2 to obtain two or more carbons alcohols in 1,3-dimethyl-2-imidazolidinone (DMI) (Scheme 27). LiI plays a crucial role in the reaction, the Lewis acidity of the Li^+ can provide suitable coordination site in the catalytic cycle and the nucleophilicity of I^- can promote the chain growth to gain long chain alcohols. LiI also has a function of stabilizing the catalyst [82]. And experiments reveal that methanol is initially formed and then is further transformed into larger alcohols.

Acetic acid also can be acquired via hydrocarboxylation of methanol with CO_2 and H_2 in DMI, $Ru_3(CO)_{12}$/$Rh_2(OAc)_4$ as catalyst and imidazole as ligand (Scheme 28) [83]. The $Rh_2(OAc)_4$ is used as major catalyst and the $Ru_3(CO)_{12}$ is a promoter. The synergistic effect between $Ru_3(CO)_{12}$ and $Rh_2(OAc)_4$ is one of key factors for reaching excellent activity. Imidazole is crucial to the reaction, probably stabilizing



Scheme 26 The synthesis of formalin through CO_2 using as a C_1 feedstock.



Scheme 27 Synthesis of ethanol and larger alcohols from CO_2 hydrogenation catalyzed by $Ru_3(CO)_{12}/Rh_2(CO)_4Cl_2$-LiI.

$$CH_3OH + CO_2 + H_2 \xrightarrow[\geq 180\ ^{\circ}C,\ DMI]{\text{Imidazole, LiI}\ Ru_3(CO)_{12}/Rh_2(OAc)_4} CH_3COOH + H_2O$$

Scheme 28 Synthesis of acetic acid by reaction of methanol with CO_2 and H_2 catalyzed by $Ru_3(CO)_{12}/Rh_2(OAc)_4$.

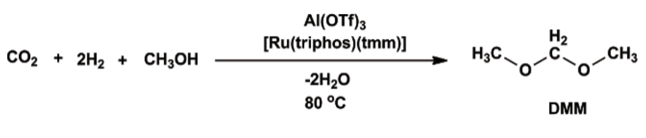
the catalyst and inhibiting CO_2 conversion into CO, and thus contributing to the high selectivity of acetic acid.

A novel protocol for the synthesis of dimethoxymethane (DMM) through the reaction of methanol with CO_2 and H_2 using Ru(triphos)(tmm) as catalyst (Scheme 29) was implemented [84]. Compared with other methods, this process employs CO_2 as C_1 resource to build the $–CH_2–$ unit, resulting in reducing manufacturing cost of DMM. Furthermore, the catalytic system is suitable for the formation of dialkoxymethanes via CO_2, H_2 and corresponding alcohols.

In addition, other reductive products, including ketones [85], HOCCOOH, $HOCH_2COOH$ [86], malic acid, isocitric acid [87] and acetoacetic acid [88] can also be obtained through CO_2 reduction by Ru catalysis.

8 Conclusions and outlook

This review highlights the reductive transformation of CO_2 catalyzed by Ru complexes. In almost all kinds of reductive transformations of CO_2, Ru complexes are demonstrated to be efficient catalysts by tuning the ligands and additives (bases or hydrogen bonding donors). Several systems e.g. RuCl(H)(CO)(PNP) are really active with high TONs and TOFs. The reduction of CO_2 to MeOH, ethanol or larger alcohols could provide an alternative energy source. Formic acid from CO_2 is regarded as a hydrogen carrier [11]. The reduction of CO_2 is beneficial for the environment and sustainable development [1–3]. However, there are still challenges. High CO_2 pressure and/or temperature are commonly needed. And the catalytic efficiency and product selectivity remain to be improved. Furthermore, the mechanism is not clear yet except for CO_2 reduction to formic acid.



Scheme 29 The reaction of methanol with CO_2 and H_2 using Ru(triphos)(tmm) as catalyst for the synthesis of dimethoxymethane.

The tendency in the reductive transformation of CO_2 catalyzed by Ru complexes can be roughly summarized as below: (1) using the CO_2 directly from the air (around 400 ppm) is quite challenging [89]. The CO_2 capture and utilization (CCU) strategy [27,28] is a potential strategy and will be promising in this field. (2) The choice of ligand is crucial to improving both catalytic efficiency and the product selectivity. As a result, pincer ligands that are able to activate CO_2 and H_2 are the most effective to obtain high TONs and TOFs, and triphos ligands are universally applicable in the hydrogenation of CO_2 [90]. (3) There are still potential tools for the mechanism investigation, for example, by using *in situ* IR, NMR and DFT calculation [24b,91], to help us know more about the essence i.e. catalytic cycle on a molecular level, leading to designing the efficient catalysts.

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Conflict of interest The authors declare that they have no conflict of interest.

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