

Review

# Molecular Catalysis for Utilizing CO<sub>2</sub> in Fuel Electro-Generation and in Chemical Feedstock

Chi-Fai Leung \* and Pui-Yu Ho

Department of Science and Environmental Studies, The Education University of Hong Kong, 10 Lo Ping Road, Tai Po, N. T., Hong Kong, China

\* Correspondence: cfleung@eduhk.hk; Tel.: +852-2948-7980

Received: 25 August 2019; Accepted: 3 September 2019; Published: 10 September 2019

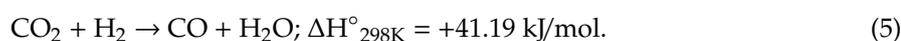
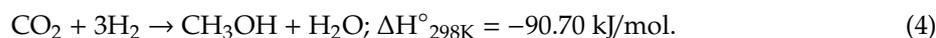
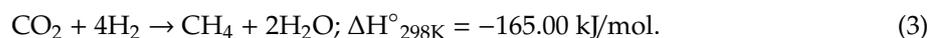
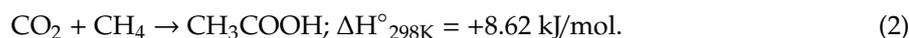
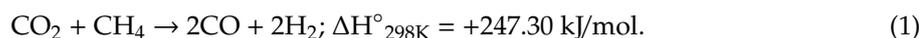


**Abstract:** Processes for the conversion of CO<sub>2</sub> to valuable chemicals are highly desired as a result of the increasing CO<sub>2</sub> levels in the atmosphere and the subsequent elevating global temperature. However, CO<sub>2</sub> is thermodynamically and kinetically inert to transformation and, therefore, many efforts were made in the last few decades. Reforming/hydrogenation of CO<sub>2</sub> is widely used as a means to access valuable products such as acetic acids, CH<sub>4</sub>, CH<sub>3</sub>OH, and CO. The electrochemical reduction of CO<sub>2</sub> using hetero- and homogeneous catalysts recently attracted much attention. In particular, molecular CO<sub>2</sub> reduction catalysts were widely studied using transition-metal complexes modified with various ligands to understand the relationship between various catalytic properties and the coordination spheres above the metal centers. Concurrently, the coupling of CO<sub>2</sub> with various electrophiles under homogeneous conditions is also considered an important approach for recycling CO<sub>2</sub> as a renewable C-1 substrate in the chemical industry. This review summarizes some recent advances in the conversion of CO<sub>2</sub> into valuable chemicals with particular focus on the metal-catalyzed reductive conversion and functionalization of CO<sub>2</sub>.

**Keywords:** transition metals; catalysis; carbon dioxide

## 1. Introduction

Many efforts were devoted in the recent decades to utilizing CO<sub>2</sub> as a source for renewable energy and materials. Direct gas-phase reactions of CO<sub>2</sub> with other readily accessible small molecules, e.g., via the reformation with CH<sub>4</sub> to produce syngas (CO/H<sub>2</sub>) and acetic acid (Equations (1) and (2)), as well as hydrogenation to produce CH<sub>4</sub>, CH<sub>3</sub>OH, and CO (Equations (3)–(5)), were widely studied using mainly heterogeneous or supported metal catalysts [1–7]. Although these gaseous reactions convert CO<sub>2</sub> into useful products, the binary processes, which involve the reactions of CO<sub>2</sub> with explosive gases such as H<sub>2</sub> and CH<sub>4</sub>, are usually pressure-sensitive and, thus, require careful control over the reaction conditions. More handy chemical approaches via which diversified products can be derived directly from CO<sub>2</sub> are, therefore, highly desirable.



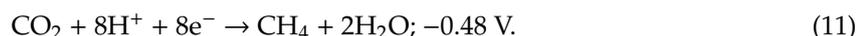
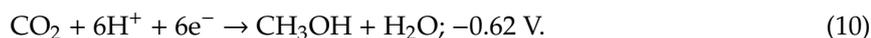
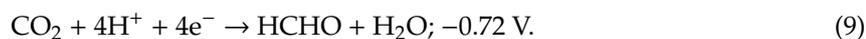
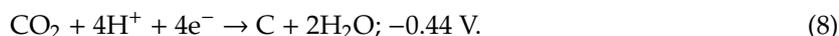
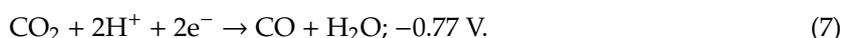
The catalytic reduction of CO<sub>2</sub> to CO, CH<sub>3</sub>OH, CH<sub>4</sub>, or higher hydrocarbons is considered an attractive approach for recycling CO<sub>2</sub>, whereby the energy from intermittent renewable sources is stored

at high density in the form of chemical bonds, mainly C–H. As one of the widely studied approaches, direct photochemical reduction of CO<sub>2</sub> using nano-sized hybrid heterogeneous photocatalysts, on which light is absorbed and charge separation takes place, occurs at the solid–liquid or solid–gas interface. The photogenerated charges are then transported to the surface, where the active sites mediate the catalytic reactions [8–14].

The electrochemical reduction of CO<sub>2</sub> on solid-state electrodes modified with nanocatalysts were recently shown to have good potential in yielding valuable products, e.g., acetate and ethylene, attracting much attention [15–17]; moreover, a large number of molecular metal catalysts were recently studied with the aim to reductively convert CO<sub>2</sub> into fuels using solar energy and electricity as the driving force [17–19]. The multiple accessible oxidation states of transition-metal complexes renders them suitable candidates for mediating multielectron redox processes such as CO<sub>2</sub> reduction, and the reactions are readily studied under homogeneous conditions using various conventional electrochemical and spectroscopic techniques. With the exception of the Lehn-type rhenium(I) tricarbonyl catalysts, i.e., Re(bpy)(CO)<sub>3</sub>Cl (bpy = 2,2'-bipyridine, see Section 2.1), which are capable of acting as both electro- and photocatalysts of CO<sub>2</sub> reduction, the majority of the catalysts discussed herein work as stand-alone CO<sub>2</sub> reduction electrocatalysts, although the photochemical CO<sub>2</sub> reduction mediated by some of these catalysts was also reported in the presence of suitable photosensitizers and sacrificial donors [17–20]. On the other hand, chemical technologies or processes that utilize CO<sub>2</sub> as a renewable, non-toxic, and cost-efficient C-1 feedstock via coupling with various nucleophiles to produce more valuable chemicals, particularly more reduced and energetic products, also gained much attention [21–23]. However, given the wide variety of related processes, the discussion below focuses on transition-metal catalysts for the electroreduction and functionalization of CO.

## 2. Electrochemical Reduction of CO<sub>2</sub> on Molecular Transition-Metal Catalysts

The substantial energy barrier in activating CO<sub>2</sub> is reflected by the highly negative formal reduction potential of –2.14 V vs. saturated calomel electrode (SCE) for the one-electron reduction of CO<sub>2</sub> to CO<sub>2</sub><sup>•–</sup> [18,19,24], where a large overpotential is required for the rapid reduction of CO<sub>2</sub> to occur, largely as a result of the structural difference between the linear CO<sub>2</sub> and bent CO<sub>2</sub><sup>•–</sup> [19,20,24–26]. Alternatively, CO<sub>2</sub> can be reduced more easily via proton-assisted multiple electron transfer, which is more favorable thermodynamically [19,20,24–26]. Equations (6)–(11) show the typical processes for the reduction of CO<sub>2</sub> to different products and the corresponding reduction potentials vs. SCE [24]. These alternative pathways in turn affect the nature of products.



### 2.1. 4d and 5d Metal CO<sub>2</sub> Reduction Electrocatalysts

A number of heavier transition-metal complexes were studied for their activity on CO<sub>2</sub> electroreduction. In particular, 4d and 5d transition-metal complexes bearing mainly bipyridyl and bidentate phosphine ligands were widely examined for their activity toward the two-electron reduction of CO<sub>2</sub>. As these complexes are usually substitution labile and the derivatization of the related ligands are well reported, these heavier transition-metal CO<sub>2</sub> reduction catalysts are generally well characterized, and their catalytic properties are more readily tunable. Therefore, the corresponding

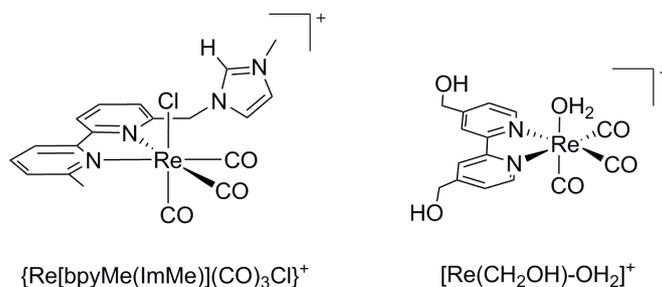
reaction mechanisms and intermediates are more widely reported. Examples of 4d and 5d metal catalysts are summarized in Tables 1 and 2.

**Table 1.** 4d and 5d metal 2,2'-bipyridine (bpy) catalysts for two-electron CO<sub>2</sub> electroreduction. SCE—saturated calomel electrode; TON—turnover number; DMF—dimethylformamide.

Catalyst	$E_{1/2}$ vs. SCE	TON			Solvent	Faradaic Efficiency	Reference
		CO	HCOO <sup>-</sup>	H <sub>2</sub>			
Re(bpy)(CO) <sub>3</sub> Cl	-1.49 V	300	- <sup>b</sup>	- <sup>a</sup>	DMF/H <sub>2</sub> O	98%	[27]
<i>fac</i> -Re(4,4'-OCH <sub>3</sub> -bpy)(CO) <sub>3</sub> X	-2.32 V <sup>c</sup>	3.9	- <sup>b</sup>	- <sup>b</sup>	MeCN	59%	[28]
<i>cis</i> -[Rh(bpy) <sub>2</sub> OTf <sub>2</sub> ] <sup>+</sup>	-1.55 V	- <sup>a</sup>	6.8–12.3	8.5–28.5	MeCN	64%	[29]
[Ru(bpy) <sub>2</sub> (CO)Cl] <sup>+</sup>	-1.50 V	10.7–25.5	7.8–10.1	2.1–21.7	DMF/H <sub>2</sub> O	- <sup>b</sup>	[29]
[Ru(bpy) <sub>2</sub> (CO) <sub>2</sub> ] <sup>2+</sup>	-1.50 V	8.8–26.2	18.2–19.9	0.2–19.2	DMF/H <sub>2</sub> O	- <sup>b</sup>	[29]
<i>cis</i> -[Os(bpy) <sub>2</sub> (CO)H] <sup>+</sup>	-1.50 V	5.5 <sup>a</sup>	- <sup>a</sup>	- <sup>b</sup>	MeCN	90%	[30]
<i>cis</i> -[Os(bpy) <sub>2</sub> (CO)H] <sup>+</sup>	-1.50 V	- <sup>b</sup>	1.8	- <sup>b</sup>	MeCN/H <sub>2</sub> O	25%	[30]
<i>trans</i> -Cl-Ru(mesbpy)(CO) <sub>2</sub> Cl <sub>2</sub>	-2.2 V <sup>c</sup>	5.2	- <sup>b</sup>	- <sup>b</sup>	MeCN	95%	[31]

<sup>a</sup> Not detected; <sup>b</sup> not mentioned; <sup>c</sup> vs. Fc/Fc<sup>+</sup>.

A number of 4d and 5d 2,2'-bipyridine complexes (Re, Rh, Ru, and Os) catalyze the two-electron electroreduction of CO<sub>2</sub> to CO or formic acid/formate. For example, Re(bpy)(CO)<sub>3</sub>Cl (-1.49 V vs. SCE, 98% Faradaic efficiency (FE) in dimethylformamide (DMF)/H<sub>2</sub>O) catalyzes CO<sub>2</sub> reduction to produce CO [27]. A series of related Re complexes with different substituted bpy and labile ligands, *fac*-Re(4,4'-R-bpy)(CO)<sub>3</sub>X (bpy = 2,2'-bipyridine, R = OCH<sub>3</sub>, CH<sub>3</sub>, *t*Bu, H, CN, CF<sub>3</sub>; X = Cl, Br, py(OTf), or CH<sub>3</sub>CN(OTf)) were studied for their electrocatalytic efficiency with and without addition of a proton source (PhOH, CH<sub>3</sub>COOH, CF<sub>3</sub>CH<sub>2</sub>OH) [28]. The results showed that the catalytic activity and overpotential increase with the electron-donating ability of the bpy substituents and the addition of acid positively shifted the catalytic current response of Re(*t*Bu-bpy)(CO)<sub>3</sub>Cl (~170 mV) [28]. Additionally, *cis*-[Rh(bpy)<sub>2</sub>X<sub>2</sub>]<sup>+</sup> (X = Cl or OTf) reduces CO<sub>2</sub> to formate (-1.55 V vs. SCE, 64% FE, turnover number (TON) = 6.8–12.3) [29]. A series of functionalized Re(I) tricarbonyl catalysts, {Re[bpyMe(ImMe)](CO)<sub>3</sub>Cl}PF<sub>6</sub> (Scheme 1), bearing redox-active imidazolium groups in the secondary coordination sphere, were reported to demonstrate improved catalytic activities as compared to the reference Re(bpy)(CO)<sub>3</sub>Cl catalyst such that the potentials of the reductive catalytic current was approximately 170 mV less negative, and the Faradaic efficiency for CO generation was increased by 19% [30]. Recently, a water-soluble rhenium(I) tricarbonyl electrocatalyst with two hydroxymethyl moieties, [Re(CH<sub>2</sub>OH)-OH<sub>2</sub>]<sup>+</sup> (Scheme 1), was studied for CO<sub>2</sub> reduction in aqueous solutions. Controlled-potential electrolysis using the catalyst at -1.1 V vs. normal hydrogen electrode (NHE) in a pH 6.9 CO<sub>2</sub>-saturated aqueous solution yielded CO and HCOOH at selectivities of 95% and 4%, respectively [31].



**Scheme 1.** Structures of {Re[bpyMe(ImMe)](CO)<sub>3</sub>Cl}<sup>+</sup> and [Re(CH<sub>2</sub>OH)-OH<sub>2</sub>]<sup>+</sup> [30,31]; bpy—2,2'-bipyridine.

$\text{Ru}(\text{bpy})_2(\text{CO})\text{X}$  ( $\text{X} = \text{CO}$  or  $\text{Cl}$ ) and  $[\text{M}(\text{bpy})_2(\text{CO})\text{H}]^+$  ( $\text{M} = \text{Os}$  and  $\text{Ru}$ ) reduce  $\text{CO}_2$  to  $\text{CO}/\text{H}_2/\text{HCOO}^-$  and  $\text{CO}$ , respectively [32,33]. Recently, *trans*- $\text{Cl-Ru}(\text{mesbpy})(\text{CO})_2\text{Cl}_2$  (*mesbpy* = 6,6'-dimesityl-2,2'-bipyridine) was reported to reduce  $\text{CO}_2$  to  $\text{CO}$  and formate with turnover frequencies (TOF) =  $1300 \text{ s}^{-1}$  [34]. Phosphine complexes of 4*d* and 5*d* transition metals such as  $\text{Rh}(\text{dppe})_2\text{Cl}$  (*dppe* = 1,2-bis(diphenylphosphino)ethane) ( $-1.55 \text{ V vs. SCE}$ , 42% FE) and  $\{m\text{-(triphos)}_2\text{-[Pd}(\text{CH}_3\text{CN})]_2\}(\text{BF}_4)_4$  (*triphos* = bis(diphenylphosphinoethyl)phenylphosphine) reduce  $\text{CO}_2$  to formate and  $\text{CO}$  (Table 2) [35–37].

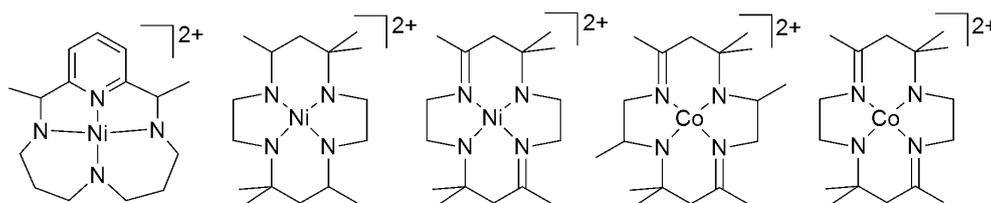
**Table 2.** Polyphosphine metal catalysts for two-electron  $\text{CO}_2$  electroreduction. *dppe*—1,2-bis(diphenylphosphino)ethane; *triphos*—bis(diphenylphosphinoethyl)phenylphosphine.

Catalyst	TON			Solvent	Faradaic Efficiency	Reference
	CO	$\text{HCOO}^-$	$\text{H}_2$			
$\text{Rh}(\text{dppe})_2\text{Cl}$	-	1.58	-	MeCN	42%	[35]
$[\text{Pd}(\text{etpC})(\text{DMF})](\text{BF}_4)_2$	130	-	154	DMF	85%	[36]
$\{m\text{-(triphos)}_2\text{-[Pd}(\text{CH}_3\text{CN})]_2\}(\text{BF}_4)_4$	190	-	-	DMF	80%	[37]

- Not mentioned.

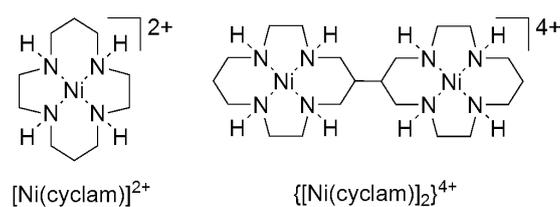
## 2.2. 3d Metal $\text{CO}_2$ Reduction Electrocatalysts

Although the 4*d* and 5*d*  $\text{CO}_2$  reduction catalysts of bidentate ligands, especially bipyridyl ligands, attracted much attention, the relatively low abundance of these metals prompted the development of cost-efficient catalysts and, subsequently, the study of 3*d* transition-metal catalysts for  $\text{CO}_2$  reduction. Probably as a result of their better stability in the reduced state, a number of 3*d* metal complexes bearing macrocyclic and tetradentate chelating ligands were investigated for activity toward  $\text{CO}_2$  electroreduction. Cobalt, iron, and nickel tetraaza macrocyclic complexes were reported to catalyze the electrochemical reduction of  $\text{CO}_2$ . Eisenberg first reported the use of cobalt and nickel tetraaza macrocyclic complexes as electrocatalysts for  $\text{CO}_2$  reduction (at  $-1.3$  to  $-1.6 \text{ V vs. SCE}$ ) to  $\text{CO}$  or  $\text{CO}/\text{H}_2$  mixture in aqueous acetonitrile at nearly quantitative FE (Scheme 2) [38]. Mechanistic studies for catalytic  $\text{CO}_2$  reduction were also reported using Co complexes of similar ligands [39–42].



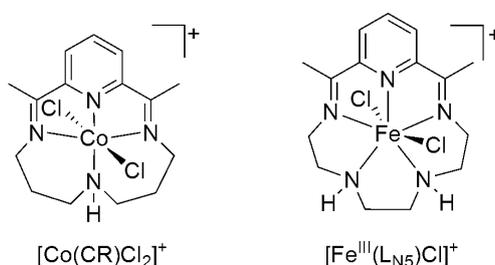
**Scheme 2.** Structures of Co and Ni tetraaza macrocyclic complexes [38–42].

$[\text{Ni}(\text{cyclam})]^{2+}$  and other structurally related Ni complexes (Scheme 3) exhibit remarkable efficiency and selectivity for reduction of  $\text{CO}_2$  to  $\text{CO}$  on a mercury electrode (at  $-0.86 \text{ V vs. SCE}$ ) in purely aqueous solution (pH 4–5) [43–45]. Product selectivity depends on the pH and potential at which the controlled potential electrolysis was performed [46,47]. Electrolysis of a  $\text{CO}_2$  saturated solution (pH 4.1) containing  $[\text{Ni}(\text{cyclam})]^{2+}$  at  $-1.00 \text{ V vs. SHE}$  (overpotential = 640 mV) on an Hg electrode yields  $\text{CO}$  almost quantitatively at 96% FE and a TON of 116 [43,44]. N-substituted Ni cyclams exhibit similar activity and produce  $\text{CO}$  at high FE of 84–92% at pH 5 and 550 mV overpotential. Formic acid is obtained similarly, with  $\text{CO}$  as the byproduct, using the dimeric  $\{[\text{Ni}(\text{cyclam})]_2\}^{4+}$  and related derivative (Scheme 3) at 75% and 68% FE, respectively, in DMF on an Hg electrode at  $-1.4 \text{ V vs. SCE}$  (460 mV overpotential) [48].



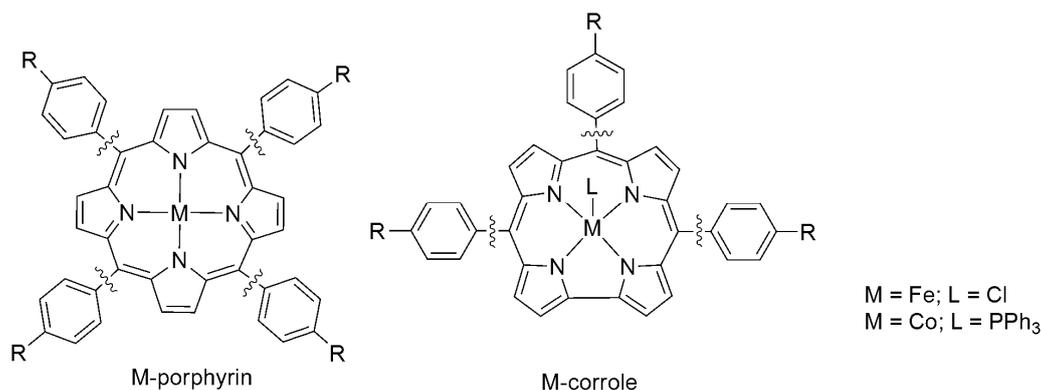
**Scheme 3.** Structures of [Ni(cyclam)]<sup>2+</sup> and {[Ni(cyclam)]<sub>2</sub>}<sup>4+</sup> [43–48].

The CO<sub>2</sub> reduction activity of Co<sup>II</sup> tetraazamacrocycle [Co(CR)]<sup>2+</sup> (CR = 2,12-dimethyl-3,7,11,17-tetra-azabicyclo [11.3.1]-heptadeca-1(17),2,11,13,15-pentaene) was studied by Tinnemans et al. and Che et al. (Scheme 4) [49,50]. Electrocatalysis using the complex on a carbon electrode yields CO selectively at 20–30% FE in acetonitrile (overpotential = 940 mV). Peters et al. later reported an enhanced FE of 45% in the presence of 10 M H<sub>2</sub>O. A related Fe pentaazamacrocycle [Fe<sup>III</sup>(L<sub>N5</sub>)Cl]<sup>+</sup> (Scheme 4) was recently reported by Lau and co-workers to catalyze the electroreduction of CO<sub>2</sub> to HCOOH in DMF at −1.25 V vs. SCE (310 mV overpotential) on a glassy carbon electrode, producing formic acid at 75% FE with a TOF of 0.12 s<sup>−1</sup> [51].



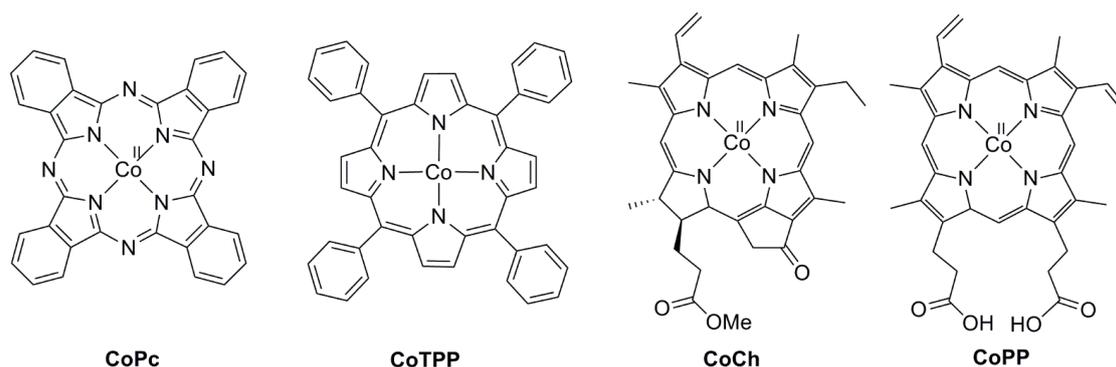
**Scheme 4.** Structures of [Co(CR)]<sup>2+</sup> and Fe(L<sub>N5</sub>)Cl]<sup>+</sup> [49–51].

Iron(0) porphyrin complexes were widely studied for electrocatalytic reduction of CO<sub>2</sub> to CO by Savéant et al. and are among the most efficient homogeneous molecular catalysts in aprotic solvent (DMF and acetonitrile (can)) [52–55]. Fe(TPP) was found to selectively catalyze the reduction of CO<sub>2</sub> to CO at −1.8 V vs. SCE in DMF (Scheme 5, R = H) [56–59]. The catalysis is significantly enhanced by the presence of weak Brønsted acids (water, trifluoroethanol, and phenol), as well as Lewis acids. For example, electrolysis using Fe(TPP) at −1.46 V vs. SHE on a mercury pool electrode in DMF, with phenol as the added acid, yields CO between 100% and 94% at varied phenol concentrations (0.1 to 1 M). When 1-propanol (6.7 M) is added instead, formic acid (35% yield) and CO (60% yield) were obtained on a mercury pool at −1.7 V vs. SCE, along with minor byproducts such as H<sub>2</sub> and oxalate [59]. Fujita et al. later reported that iron(IV) and cobalt(III) corrole complexes similarly catalyze the reduction of CO<sub>2</sub> to CO at −1.7 V vs. SCE under homogeneous conditions (Scheme 5) [60,61].



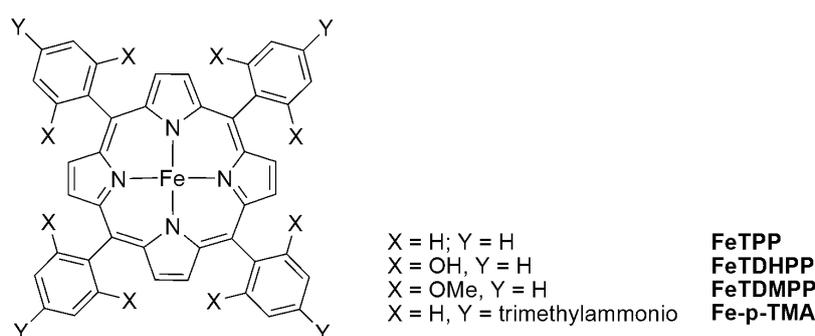
**Scheme 5.** Structures of Fe and Co porphyrin and corrole complexes [52–61].

Cobalt porphyrin (CoTPP) and phthalocyanine (CoPc) complexes were also found to be catalytically active in water on carbon electrodes film-coated with the complexes [24,62–65]. By using the Co(TPP) (Scheme 6) deposited on a carbon black gas-diffusion electrode, CO is produced at  $-0.76$  V vs. SHE (overpotential = 230 mV) at 97% FE in a 0.5 M  $\text{KHCO}_3$  solution under a high  $\text{CO}_2$  pressure of 20 atm. Similarly, CO is produced in 80% FE at pH 4.6 with  $\text{TOF} = 140 \text{ h}^{-1}$  and  $\text{TON} = 1100$  using cobalt chlorin (CoCh) deposited on carbon nanotubes (700 mV overpotential) [66]. Cobalt protoporphyrin (CoPP) deposited on pyrolytic graphite also catalyzes the  $\text{CO}_2$ -to-CO conversion at a low pH of 3 at 60% FE and 500 mV overpotential under 10 atm of  $\text{CO}_2$ , while 2.5%  $\text{CH}_4$  was obtained when the pH was lowered to 1 [24].



**Scheme 6.** Structures for Co porphyrin and related catalysts [24,62–66].

The introduction of intramolecular phenolic protons at the *ortho* and *ortho'* positions of Fe(TPP) was found to be effective in enhancing the efficiency of  $\text{CO}_2$  electroreduction to CO and the catalyst durability (Scheme 7) [53,54]. The catalyst (FeTDMPP) operates at a lower overpotential (450 mV) compared with FeTPP (600 mV), while the substitution of a trimethylammonio group (Fe-*p*-TMA) not only increases the CO conversion efficiency and selectivity, but also catalyzes the reduction of  $\text{CO}_2$  to methane [55,67,68].

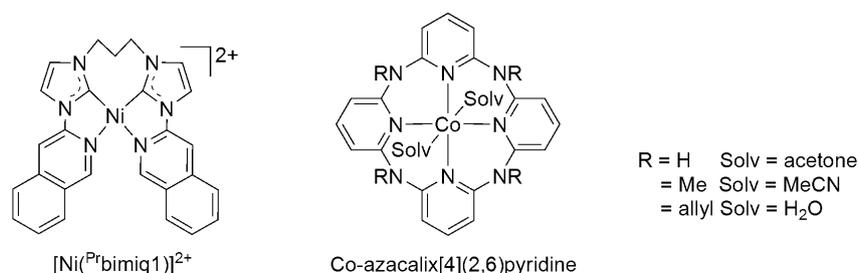


**Scheme 7.** Structure of porphyrin Fe catalysts bearing various pendant substituents. [53,54,67,68].

Heterogeneous catalytic materials based on solid-support or supramolecular porphyrin catalysts of Co, Cu, and Fe for the reduction of  $\text{CO}_2$  in aqueous solutions were explored. A catalytic electrode constructed from two-dimensional (2D) covalent organic frameworks (COFs) of cobalt tetrakis(4-aminophenyl)porphyrin (Co(TAP)) on porous conductive carbon fabric was found to demonstrate significantly improved (26-fold) catalytic activity for  $\text{CO}_2$ -to-CO conversion at an overpotential of  $-0.55$  V (FE of 90%, TON up to 290,000, and initial TOF of  $9400 \text{ h}^{-1}$ ) at pH 7 with respect to the molecular cobalt complex under the same condition [69]. A similar catalytic electrode was prepared by depositing a porous organic cage (Fe-PB), which bears six Fe(TPP) centers, onto a glassy carbon electrode coated with carbon nanotubes ( $\text{CNT}_5/\text{GCE}$ ) [70]. Both electrochemically active surface area ( $3.7 \text{ nmol EA-Fe}\cdot\text{cm}^{-2}$  vs.  $2.5 \text{ nmol EA-Fe}\cdot\text{cm}^{-2}$ ) and mass transport were increased

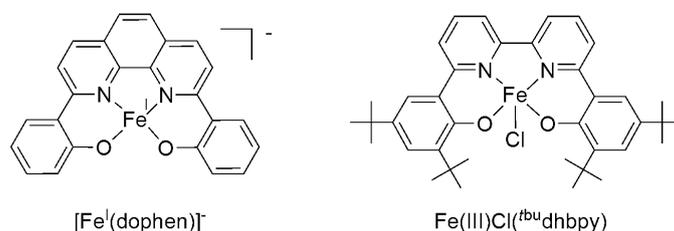
for Fe-PB/CNTs/GCE with respect to the Fe(TPP)/CNTs/GCE containing an equivalent amount of Fe(TPP), resulting in an enhanced catalytic current response, CO/H<sub>2</sub> selectivity, and product turnover (TON = 55,250 after 24 h and TOF = 0.64 s<sup>-1</sup> vs. TON = 32,770 after 24 h and TOF = 0.38 s<sup>-1</sup>) for controlled potential electrolysis at -0.63 V vs. RHE. Cu(II)-5,10,15,20-tetrakis-(2,6-dihydroxyphenyl)porphyrin Cu(TDMPP) deposited on a commercial porous polytetrafluoroethylene-treated carbon fiber paper reduces CO<sub>2</sub> to hydrocarbons (methane and ethane) at -0.976 V vs. RHE at 44% FE [71].

A number of 3d metal complexes (Co, Fe, and Ni) bearing tetradentate chelating ligands of N, C, and O donor atoms were reported to be active electrocatalysts for the selective reduction of CO<sub>2</sub> to CO. The *N*-heterocyclic carbene-isoquinoline complexes [Ni(<sup>Pr</sup>bimiq1)]<sup>2+</sup> (<sup>Pr</sup>bimiq1 = bis(3-(imidazolyl)isoquinolinyl)propane) (Scheme 8) were also reported to catalyze CO<sub>2</sub>-to-CO electroreduction, yielding CO at an optimal FE of 90% (overpotential = 840 mV) on a glassy carbon electrode; however, the catalytic efficiency was found to decrease significantly upon prolonged electrolysis [72]. Co-azacalix[4](2,6)pyridine catalysts (Scheme 8) containing methyl- and allyl-substituted macrocyclic aminopyridine ligands were reported to selectively produce (optimal FE = 98%) CO in a CO<sub>2</sub>-saturated DMF solution with 1.2 M trifluoroethanol on a glassy carbon electrode (680 mV overpotential) at a TON of 6.2, and the pendant NH moiety was suggested to stabilize the Co<sup>I</sup>-CO<sub>2</sub> adduct [73].



**Scheme 8.** Structures of Ni *N*-heterocyclic carbene-isoquinoline [Ni(<sup>Pr</sup>bimiq1)]<sup>2+</sup> and Co-azacalix[4](2,6)pyridine complexes [71,72]; <sup>Pr</sup>bimiq1—bis(3-(imidazolyl)isoquinolinyl)propane.

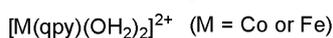
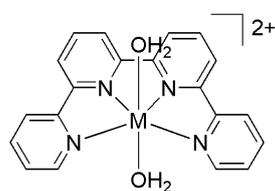
The Fe<sup>I</sup> catalyst containing 2,9-bis(2-hydroxyphenyl)-1,10-phenanthroline [Fe<sup>I</sup>(dophen)]<sup>-</sup> yields HCOOH at 74% FE, as well as oxalate (7%) and CO (13%) as minor byproducts, upon electrolysis in dimethyl sulfoxide (DMSO) at -1.76 V vs. SCE on a carbon electrode (Scheme 9) [74]. An iron(III) complex of 6,6'-di(3,5-di-*tert*-butyl-2-hydroxybenzene)-2,2'-bipyridine (Fe(III)Cl(<sup>tbu</sup>dhbpy)) was also reported to catalyze the reduction of CO<sub>2</sub> to formate in the presence of an added proton source (PhOH; FE = 68%, TON = 2.7, t = 10 h), whereas, in the absence of acid, only CO is formed (FE = 1.1%, TON = 3, t = 15 h) [75].



**Scheme 9.** Structures of [Fe<sup>I</sup>(dophen)]<sup>-</sup> and (Fe(III)Cl(<sup>tbu</sup>dhbpy)) [74,75]; dophen—2,9-bis(2-hydroxyphenyl)-1,10-phenanthroline; <sup>tbu</sup>dhbpy—6,6'-di(3,5-di-*tert*-butyl-2-hydroxybenzene)-2,2'-bipyridine.

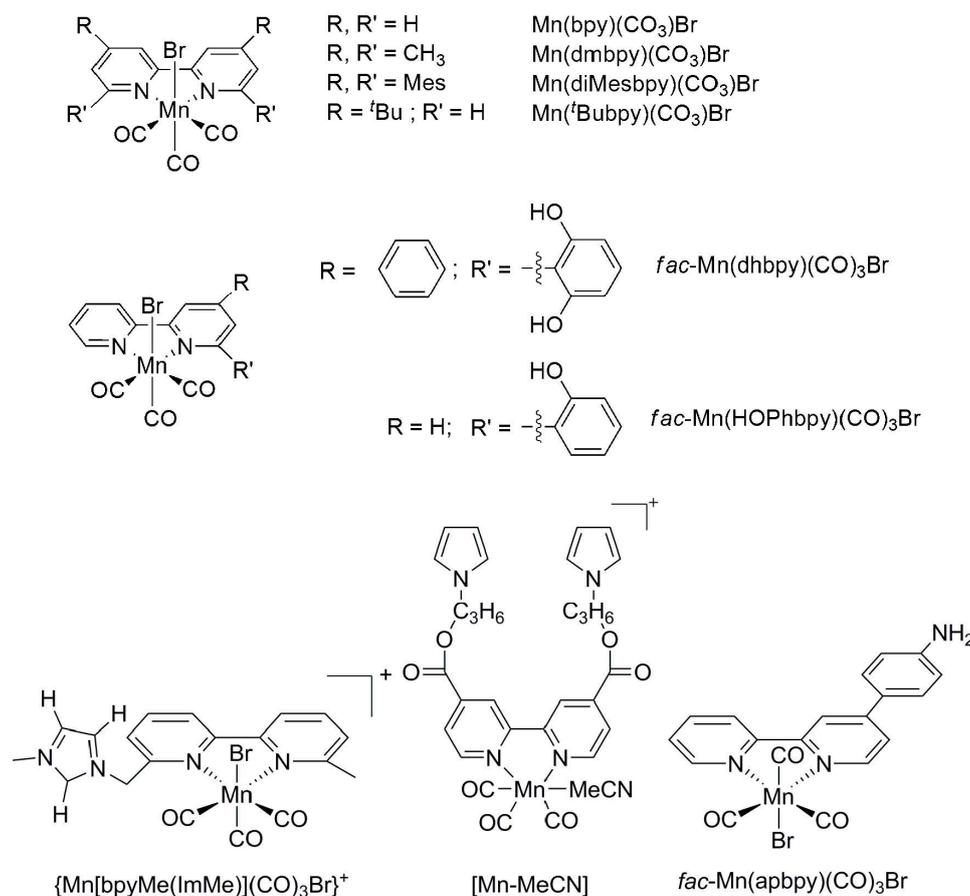
Recently, Lau and Robert reported Co and Fe quaterpyridine complexes (Scheme 10), [M(qpy)(OH<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> (qpy = 2,2':6',2'':6'',2''':6''',2''''-quaterpyridine), as catalysts for CO<sub>2</sub>-to-CO electroreduction in acetonitrile with a selectivity of >95% in the presence of phenol at low overpotentials of 140 and

240 mV, respectively, and an impressive turnover frequency (TOF) of  $3.3 \times 10^4 \text{ s}^{-1}$  was reported for the Fe catalyst [76].



**Scheme 10.** Structures of  $[\text{Co}^{\text{II}}(\text{qpy})(\text{OH}_2)_2]^{2+}$  and  $[\text{Fe}^{\text{II}}(\text{qpy})(\text{OH}_2)_2]^{2+}$  [76]; qpy—2,2':6',2'':6'',2''':-quaterpyridine.

Chardon-Noblat and Deronzier et al. reported *fac*-Mn(L)(CO)<sub>3</sub>Br complexes (L = 2,2'-bipyridine or 4,4'-dimethyl-2,2'-bipyridine) as an active electrocatalyst for CO<sub>2</sub> reduction (Scheme 11) [77,78]. Controlled-potential electrolysis with Mn(L)(CO)<sub>3</sub>Br (L = 2,2'-bipyridine) at −1.40 vs. SCE (420 mV overpotential) in ACN with 5% H<sub>2</sub>O converts CO<sub>2</sub> into CO quantitatively, while CO is also selectively obtained (TON = 34) with R = Me. Kubiak et al. later reported the activity of Mn(L)(CO)<sub>3</sub>Br bearing other substituents (R) on L in the presence of weak acids [79]. With R = *t*-butyl, CO is produced at quantitative FE (estimated TOF of 340 s<sup>−1</sup>) in controlled-potential electrolysis at −2.2 V vs. SCE with 1.4 M trifluoroethanol. When L = 6,6'-dimesityl-2,2'-bipyridine, CO is selectively produced at high FE in electrolysis and a TOF of  $5 \times 10^3 \text{ s}^{-1}$  in acetonitrile also containing 1.4 M trifluoroethanol.



**Scheme 11.** Structures of Mn(L)(CO)<sub>3</sub>Br and its derivatives with various pendant substituents [77–87]; L—2,2'-bipyridine or 4,4'-dimethyl-2,2'-bipyridine.

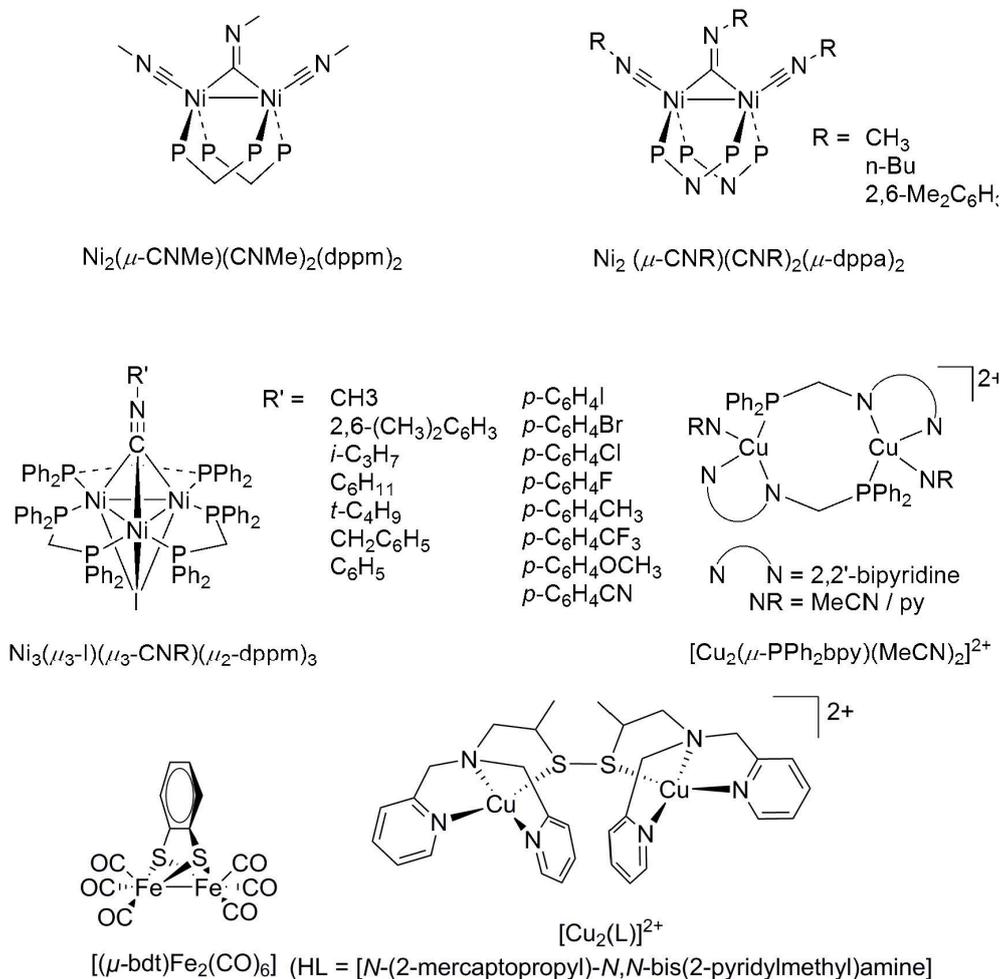
When pendent proton sources are introduced in proximity to the metal center on  $\text{Mn(L)(CO)}_3\text{Br}$ , i.e.,  $\text{L} = 4\text{-phenyl-6-(1,3-dihydroxybenzen-2-yl)-2,2'-bipyridine}$  (Scheme 11), the catalyst is active for  $\text{CO}_2$  reduction in acetonitrile at  $-1.8\text{ V vs. SCE}$  without added acids, producing both  $\text{CO}$  (70% FE) and  $\text{HCOOH}$  (22% FE) [80,81]. A reaction pathway involving the formation of  $\text{Mn}$  hydride via intramolecular proton transfer from the phenolic moiety was suggested. Interestingly, a similar  $\text{Mn(L)(CO)}_3\text{Br}$  with a single pendent hydroxyphenyl substituent on the *bpy* ligand selectively produces  $\text{CO}$  at 76% FE (at 540 mV overpotential) in electrolysis in acetonitrile containing 5%  $\text{H}_2\text{O}$  [82]. The reactivity of the similarly structured  $\text{Mn(I)}$ -tricarbonyl catalysts bearing two and three acidic hydroxyphenyl functions was also compared in the presence of added acids ( $\text{H}_2\text{O}$ , 2,2,2-trifluoroethanol (TFE), and phenol), and the product ( $\text{CO}$ ,  $\text{HCOOH}$ , and  $\text{H}_2$ ) distribution was dependent on the strength of the added acid. [81,83]. Recently, a series of *fac*- $\text{Mn(CO)}_3$  catalysts bearing imidazolium-functionalized bipyridine,  $[\text{Mn}[\text{bpyMe}(\text{ImMe})](\text{CO})_3\text{Br}]^+$  (Scheme 11), were found to demonstrate a superior reactivity (FE = approximately 70%) toward  $\text{CO}_2$  reduction in comparison to the dimesityl analogue (FE = 49.6%) at a mild potential ( $-1.44\text{ V vs. SCE}$ ) in acetonitrile with 9.25 M  $\text{H}_2\text{O}$  [84]. The imidazolium moiety is suggested to favor the formation of a local hydration shell which promotes more efficient protonation of the reaction intermediates [84].

An  $\text{Mn-MeCN/MWCNT}$  catalytic cathode ( $[\text{Mn-MeCN}] = [\text{Mn}\{4,4'\text{-di}(1H\text{-pyrrolyl-3-propylcarbonate})\text{-}2,2'\text{-bipyridine}\}(\text{CO})_3(\text{MeCN})]^+$  and  $\text{MWCNT} = \text{multi-walled carbon nanotube}$ ), prepared by loading the functionalized *fac*- $\text{Mn(CO)}_3$  catalysts (Scheme 11) onto conductive  $\text{MWCNTs}$ , promotes  $\text{CO}_2$  reduction at a low overpotential of 100 mV in the presence of  $\text{K}^+$  to produce  $\text{CO}$  at a steady rate for 48 h at  $-0.39\text{ V vs. RHE}$  [85]. The activities toward electrochemical  $\text{CO}_2$  reduction of a similar catalyst bearing an amine-functionalized *bpy* ligand, *fac*- $\text{Mn}(\text{apbpy})(\text{CO})_3\text{Br}$  (*apbpy* = 4-(4-aminophenyl)-2,2'-bipyridine), were studied under both heterogeneous and homogeneous conditions [86,87]. A glassy carbon electrode (GCE) functionalized with the complex was found to produce  $\text{CO}$  electrocatalytically in aqueous acetonitrile at a TON 30 times higher than that in homogeneous condition [86]. When grafted electrochemically onto carbon cloth, the catalyst also reduces  $\text{CO}_2$  to syngas in aqueous solution (FE for  $\text{CO}$  and  $\text{H}_2 = 60\%$  and  $40\%$ , respectively) at  $-1.35\text{ V}$  and a TON of up to 33,200 in 10 h [87].

Multinuclear catalysts of first-row transition metals draw much attention, as a their multiple reaction centers are considered potentially more effective for mediating the simultaneous reduction of more than one  $\text{CO}_2$ , thus leading to the formation of C-2 (or higher) products. Kubiak reported a number of multinuclear nickel and copper phosphine complexes as electrocatalysts for  $\text{CO}_2$  reduction (Scheme 12). The catalyst  $[\text{Ni}_2(\mu\text{-CNMe})(\text{CNMe})_2(\text{dppm})_2]$  (*dppm* = 1,1-bis(diphenylphosphino)methane) operates at  $-0.87\text{ V vs. SCE}$  [88]. The similar dinuclear nickel complex  $[\text{Ni}_2(\mu\text{-CNR})(\text{CNR})_2(\mu\text{-dppa})_2]$  (*dppa* = bis(diphenylphosphino)amine; *CNR* = isocyanide ligand) also catalyzes  $\text{CO}_2$  reduction [89]. However, these catalysts suffer from carbonylation upon extended cycles of catalysis [88]. Trinuclear nickel clusters  $[\text{Ni}_3(\mu_3\text{-I})(\mu_3\text{-CNR})(\mu_2\text{-dppm})_3]$  were also found to catalyze  $\text{CO}_2$  selective reduction to  $\text{CO}$  and  $\text{CO}_3^-$  at  $-1.08$  to  $-1.18\text{ V vs. SCE}$  [90,91]. The binuclear copper complexes  $[\text{Cu}_2(\mu\text{-PPh}_2\text{bpy})(\text{MeCN})_2][\text{PF}_6]_2$  (at  $-1.53\text{ V vs. SCE}$ ) and  $[\text{Cu}_2(\mu\text{-PPh}_2\text{bpy})(\text{py})_2][\text{PF}_6]_2$  (*PPh}\_2\text{bpy}* = 3-diphenylphosphino-2,2'-dipyridyl) were also reported to be active electrocatalysts for  $\text{CO}_2$  reduction [92]. More recently, the  $[\text{FeFe}]$ -hydrogenase model,  $[(\mu\text{-bdt})\text{Fe}_2(\text{CO})_6]$  (*bdt* = benzene-1,2-dithiolato), was found to demonstrate distinctive activity for electroreduction of  $\text{CO}_2$  in acetonitrile in the presence of  $\text{CH}_3\text{OH}$  or  $\text{H}_2\text{O}$  as the proton source at an estimated maximum TOF of  $195\text{ s}^{-1}$  [93]. Controlled-potential electrolysis using the catalyst under optimized conditions produces  $\text{HCOOH}$  at a good Faradaic yield of 88% as the major product (selectivity  $\approx 81\%$ ), together with a small amount of  $\text{CO}$  (selectivity  $\approx 11\%$ ) and  $\text{H}_2$  (selectivity  $\approx 8\%$ ) [93].

Despite the formation of C-2 or longer hydrocarbons being reported using electrode modified with nanocatalysts, C2 products are less common for the electroreduction of  $\text{CO}_2$  on molecular catalysts. Apart from the abovementioned  $\text{Cu(TDMPP)}$  supported on porous polytetrafluoroethylene-treated carbon fiber paper, which reduces  $\text{CO}_2$  to hydrocarbons (methane and ethane) [71], so far, only a dinuclear copper(I) complex,  $[\text{Cu}_2(\text{L})]^{2+}$  ( $\text{HL} = [N\text{-}(2\text{-mercaptopropyl})\text{-}N,N\text{-bis}(2\text{-pyridylmethyl})\text{amine}]$ ), was reported to produce a tetranuclear copper(II) complex bearing two  $\text{CO}_2$ -derived oxalate groups upon

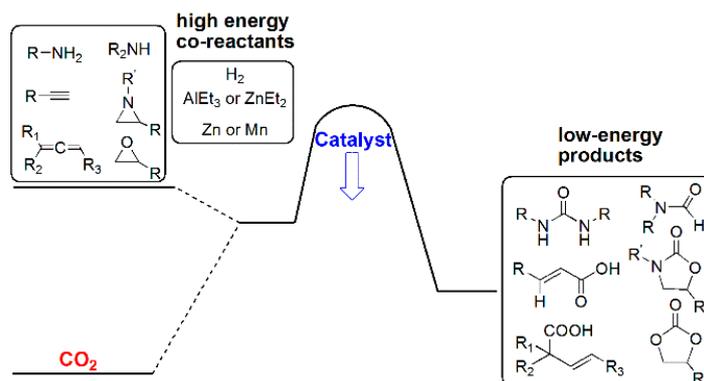
reaction with atmospheric CO<sub>2</sub> [94]. Treatment of the oxalate-bridged copper(II) complex with a soluble lithium salt in acetonitrile quantitatively produces lithium oxalate, and a subsequent electrochemical reduction of the copper(II) complex regenerates the initial dinuclear copper(I) compound, which reacts again with CO<sub>2</sub> and demonstrates six turnovers (producing 12 equivalents of oxalate) at an applied potential of −0.03 V vs. NHE in 7 h [94].



**Scheme 12.** Structures of multinuclear Ni, Cu, and Fe catalysts [88–94].

### 3. Functionalization of Carbon Dioxide

In parallel, chemical processes for using CO<sub>2</sub> as a renewable, non-toxic, and cost-efficient feedstock for producing fine chemicals are emerging [95–100]. Confined by the kinetic inertness of CO<sub>2</sub>, widely applied CO<sub>2</sub> functionalization processes include the industrial preparation of urea, salicylic acid, inorganic carbonates, cyclic/acyclic organic carbonates, and pigments, as well as application as an additive in methanol synthesis [95–102]. Therefore, novel and efficient catalytic processes for CO<sub>2</sub> functionalization are highly valuable. Two major approaches for the functionalization of CO<sub>2</sub>, i.e., “horizontal” and “diagonal” (reductive) approaches, evolved, and they both require the use of high-energy co-reactants, catalysts, and often stringent reaction conditions to overcome the kinetic barrier (Scheme 13) [96–105].



**Scheme 13.** Schematic illustration of thermodynamic barrier for CO<sub>2</sub> functionalization [96–105].

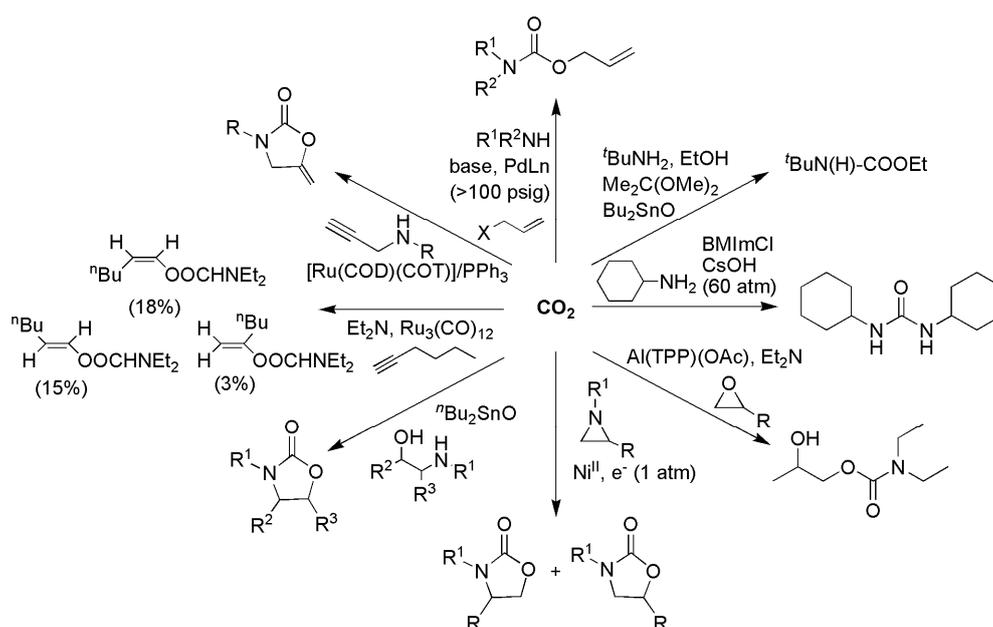
### 3.1. Horizontal Functionalization of CO<sub>2</sub>

A number of metal-catalyzed reactions, which utilize CO<sub>2</sub> as a single-carbon (C-1) feedstock, were reported, and they require usually high pressure and temperature to proceed. In these reactions, functionalization occurs “horizontally” via simple bond formation without changing the formal oxidation state of the CO<sub>2</sub> carbon, typically giving products such as R–X–C(O)–R’ (X = O, N, or C) with limited variety (Schemes 13 and 18). For example, porphine [106–112] and salen-type [113–119] complexes catalyze the coupling of CO<sub>2</sub> with epoxide to cyclic [113,114] and polycarbonates [115–119].

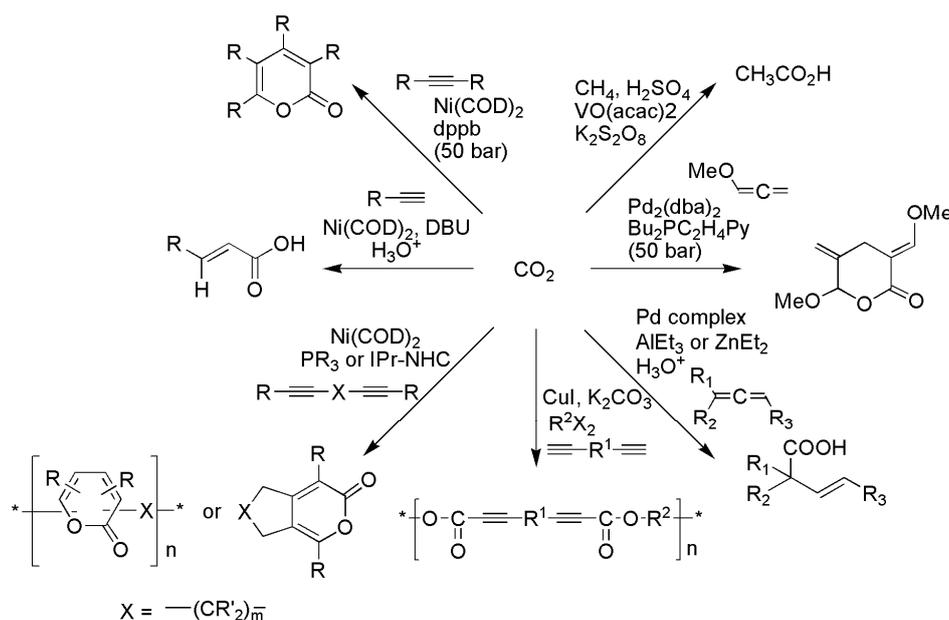
The reactions of CO<sub>2</sub> with amine-containing nucleophiles were studied (Scheme 14), mainly using precious-metal (Ag [120,121], Pd [122–124], and Ru [125,126] or organotin [127,128] (Sn)) catalysts, e.g., (a) oxazolidinones from aziridine [129], 1,2-aminoalcohols [127], and  $\alpha$ -allenyl amines [124]; (b) benzoxazin-2-ones from *o*-alkynylanilines [120,121]; (c) carbamates from amine/allylic chloride [122,123], amine/alkyne [130], and *N*-substituted propargylamine [126]; and (d) urea or urethane from primary amine [128,131]. The carboxylation of carbon nucleophiles with CO<sub>2</sub> was studied (Scheme 15), mainly with Cu [132,133], Ni [133–139], and Pd [140–145] catalysts, e.g., (a) substituted carboxylic acid from arylhalide [139,140], benzyl chloride [134], alkynes [135,136], allenes [122], and alkenes [132,146]; (b) ester from alkyne/allylic chloride [133], phenylpyridine [147], and aryl methane [148]; and (c) lactone from diene [142,149], 2-hydroxystyrene [144], allenes [138], and alkynes [137,138]. Similar CO<sub>2</sub> functionalization was also performed using organocatalysts, e.g., (a) organic *N*-heterocyclic bases (DBU) for coupling with primary amino alcohol to oxazolidinones [150–152] and carboxylation of cyclopentadiene [153]; (b) *N*-heterocyclic carbenes (iPrNHC) for coupling with epoxide, aziridine, or propargyl alcohol to yield heterocycles and carbonates [154–156]; and (c) organosalt or ionic liquid with aziridine or epoxide [157,158].

### 3.2. Electro- and Photocatalytic CO<sub>2</sub> Functionalization

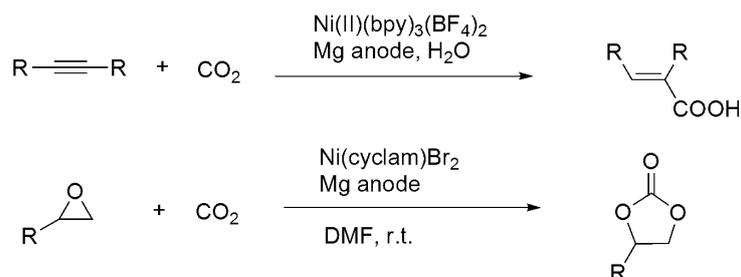
In contrast to chemical approaches, electro- and photocatalytic functionalizations of CO<sub>2</sub>, which usually proceed under mild conditions (room temperature and 1 atm), were much less investigated. In these reactions, CO<sub>2</sub> carbon was mostly incorporated with substrates without changing its oxidation state. Duñach et al. reported the Ni-catalyzed electrochemical carboxylation of alkynes and diynes, as well as electro-coupling with epoxides and aziridines under 1 atm CO<sub>2</sub>, using Ni-L (L = bpy, cyclam, PMDTA) catalysts and an Mg sacrificial anode (Schemes 14 and 16) [159–163]. Notably, electrocatalytic formylation of dimethyl amine (DMA) to DMF was reported using Ru(bpy)<sub>2</sub>(CO)<sub>2</sub> [164]. Visible-light-driven carboxylation of aryl halides [165] and alkenes [166] was carried out using Pd(OAc)<sub>2</sub>/PR<sub>3</sub>/Ir(ppy)<sub>2</sub>(dtbpy)(PF<sub>6</sub>) [165] and Rh(PPh<sub>3</sub>)<sub>3</sub>X or [Rh(PR<sub>3</sub>)<sub>2</sub>Cl]<sub>2</sub>/[Ru(bpy)<sub>3</sub>]<sup>2+</sup> (R = Cy or Ar; X = OAc, Cl, or H) [166] with *i*Pr<sub>2</sub>EtN as the sacrificial donor (Scheme 17). Ultraviolet (UV)-driven  $\alpha$ -carboxylation of tertiary *N*-benzylpiperidines C<sub>5</sub>H<sub>10</sub>N(CH<sub>2</sub>Ph) and carboxylation of alkenes were achieved using *p*-terphenyl/trifluoroacetate [167] and diphenylxanthone/Cu(*i*PrNHC)Cl [168], respectively.



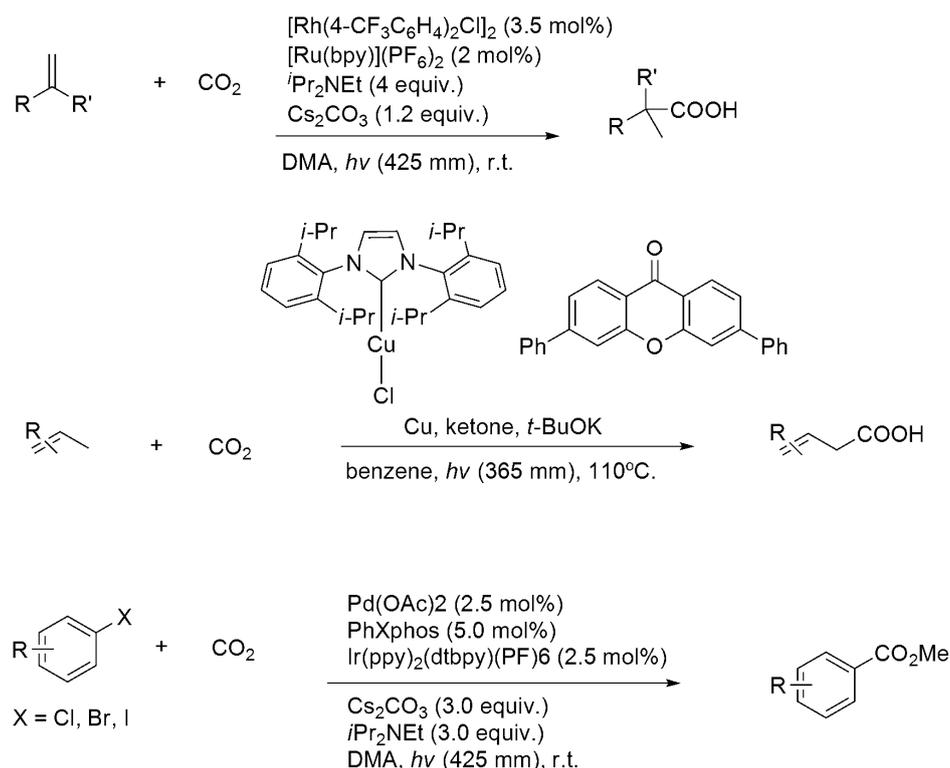
**Scheme 14.** Examples of metal-catalyzed CO<sub>2</sub> functionalization with amine-containing nucleophiles [120–131].



**Scheme 15.** Examples of metal-catalyzed carboxylation of carbon nucleophiles with CO<sub>2</sub> [132–158].



**Scheme 16.** Examples of electrocatalytic coupling of CO<sub>2</sub> with various carbon nucleophiles [161–163].



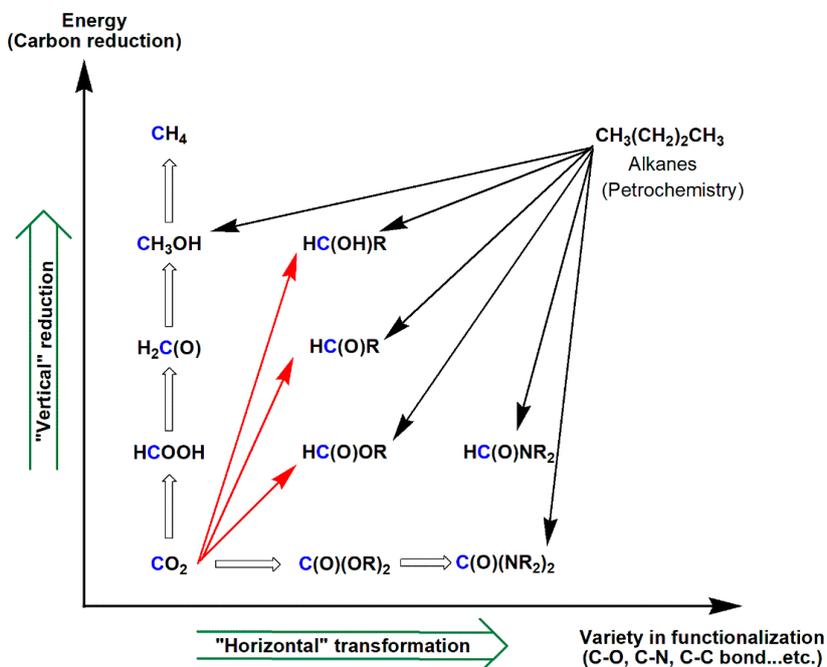
**Scheme 17.** Examples of photocatalytic carboxylation of carbon nucleophiles with  $\text{CO}_2$  [164–168].

### 3.3. Diagonal (Reductive) $\text{CO}_2$ Functionalization

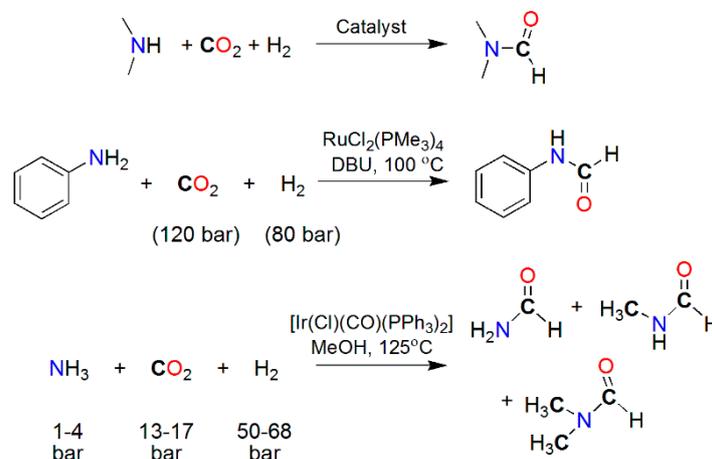
While, in the above “horizontal” transformations, the  $\text{CO}_2$  carbon is functionalized with its formal oxidation state unchanged, the “vertical” reduction of  $\text{CO}_2$  very often results in a lower oxidation state and, thus, higher-energy products, such as CO, formic acid/formate, methanol, and methane, in which no new bonds, other than C–H, are formed to the  $\text{CO}_2$  carbon (Scheme 18) [19,23–26]. For  $\text{CO}_2$  functionalization processes to be more versatile and widely applied, the spectrum of products directly obtained from  $\text{CO}_2$  has to be broadened in terms of functionalities and energy. Thus, a “diagonal” reductive approach, where  $\text{CO}_2$  is reacted in a concerted manner with a nucleophilic functionalization reagent and a reducing agent, was proposed and explored [98,169,170].

Recently, reductive coupling of  $\text{CO}_2$  with amine-type co-reactants emerged as a novel approach for accessing products bearing deoxygenated carbons, e.g., N–C(O)H, originated from  $\text{CO}_2$  (Scheme 19). Examples of metal-catalyzed N–H formylation with  $\text{CO}_2$  are shown in Table 3, and the structures of selected catalysts are shown in Scheme 20. The formylation of an N–H bond of primary or secondary amines to yield formamide derivatives was reported using precious-metal (Ir, Pd, Pt, and Ru) [164,171–176] catalysts, e.g.,  $(\text{PPh}_3)_3\text{Ir}(\text{CO})\text{Cl}$  [167],  $\text{PdCl}_2$  [172],  $[\text{Pt}_2(\mu\text{-dppm})_3]$  (dppm = bis(diphenylphosphino)methane) [173,177],  $\text{RuCl}_2(\text{PMe}_3)_4$  [178]  $\text{RuCl}_2(\text{dppe})$  (dppe = bis(diphenylphosphino)ethane) [164,179], and  $\text{Ru}(\text{PNP})(\text{CO})(\text{H})\text{Cl}$  (PNP = *N,N*-bis(2-(diphenylphosphinoethyl)methylamine) (Scheme 20), and  $\text{H}_2$  as the reductant at a usually moderate to high turnover number (TON). Similar N–H formylation was also explored using non-precious-metal catalysts, particularly with phosphine ligands, e.g.,  $\text{MX}_2/\text{dmpe}$  (M = Co, Cu, Fe, Ni, and Mn; X =  $\text{Cl}^-$ ,  $\text{CH}_3\text{CO}_2^-$  and  $\text{acac}^-$ ; dmpe = bis(dimethylphosphino)ethane) [180],  $\text{Cu}(\text{PPh}_3)_3\text{Cl}$  [141,150],  $\text{M}(\text{BF}_4)_2/\text{PP}_3$  (M = Fe and Co;  $\text{PP}_3$  = tris[2-(diphenylphosphino)ethyl]phosphine), and  $\text{Fe}(\text{BF}_4)_2/\text{PAr}_3$  ( $\text{PAr}_3$  = tris(2-(diphenylphosphino)phenyl)phosphine) [19,181–183]. A molybdenum silylphosphine hydride complex,  $[\text{MoH}_3\{\text{Si}(\text{Ph})[\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4\text{-}o\}_2\}]$ , also catalyzes DMF production from DMA and  $\text{CO}_2$  [184]. The formylations of aniline ( $\text{NH}_2\text{Ar}$ ) and ammonia ( $\text{NH}_3$ ) were demonstrated using  $\text{RuCl}_2(\text{PMe}_3)_4$  [185,186],  $[\text{Ru}(\text{triphos})(\text{tmm})]$  [187], and  $\text{IrCl}(\text{CO})(\text{PPh}_3)_3$  [188] with  $\text{H}_2$  as the

reductant. Amine–CO<sub>2</sub> reductive coupling was also performed using hydrosilane (R<sub>3</sub>Si–H) or hydroborane (R<sub>2</sub>B–H) as the reductant on metal (Cu, Fe, Ni, and Rh) [189–193] catalysts such as [Ni(μ-H)(dippe)]<sub>2</sub> (dippe = 1,2-bis(diisopropylphosphino)ethane) [192] and Cu(iPr-NHC)(O<sup>t</sup>Bu) (iPrNHC) [193].



**Scheme 18.** Horizontal and diagonal (reductive) approaches for CO<sub>2</sub> functionalization [19,23–26].



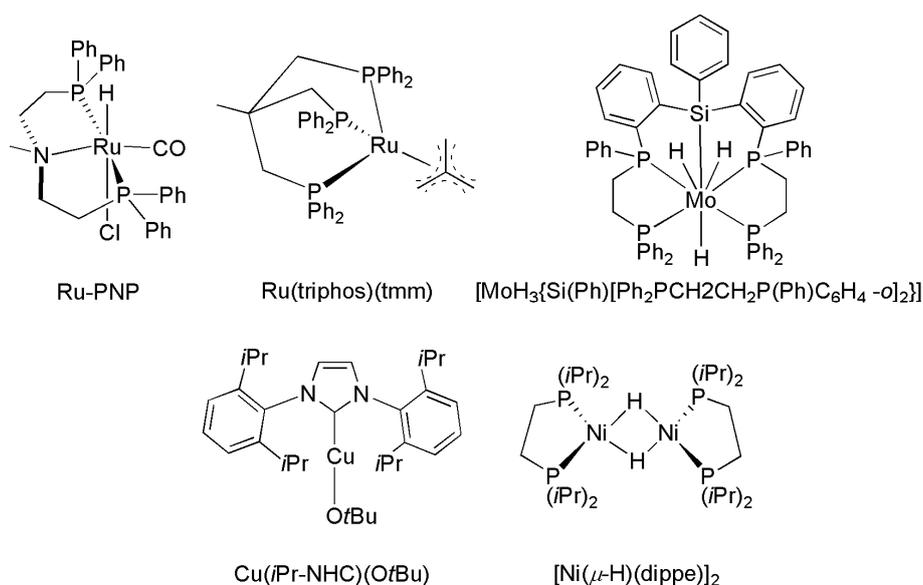
**Scheme 19.** Example of metal-catalyzed N–H bond formylation with CO<sub>2</sub> [185–188].

More recently, non-carbonyl or fully deoxygenated products, e.g., formamidines (RN = C(H)NR') and methylamines (R<sub>2</sub>NCH<sub>3</sub>) were obtained at elevated temperature and pressure (Scheme 21) from *o*-phenylenediamines with RuCl<sub>2</sub>(dppe)<sub>2</sub> [194], as well as from primary and secondary amines with Ru(acac)<sub>3</sub>/triphos [195] or Ru(triphos)(tmm) [187], [Ru<sup>II</sup>(dmsO)<sub>4</sub>Cl<sub>2</sub>]/P<sup>(*n*Bu)(Ad)<sub>2</sub> [196], and Zn(iPrNHC)Cl [196] using H<sub>2</sub> and PhSiH<sub>3</sub> as reductants. Recently, reductive coupling of CO<sub>2</sub> with amines and *o*-phenylenediamines was achieved using organo-base (TBD) [197,198], iPrNHC [199,200], and proazaphosphatrane (VB<sup>Me</sup>) [201] to produce formamides [196,199], formamidines [200], tertiary methylamines, and methylene diamines [198,201] using hydrosilane (PhSiH<sub>3</sub>) or hydroborane (9-BBN) as reductants (Scheme 22).</sup>

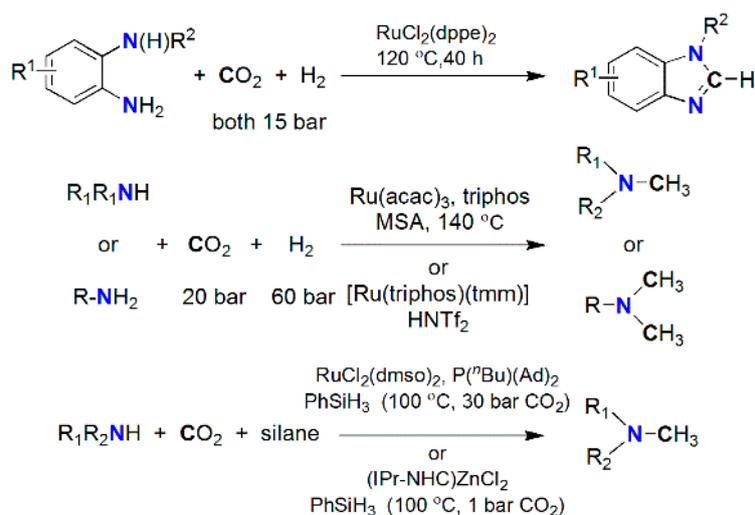
**Table 3.** A comparison of metal-catalyzed N–H formylation of selected primary and secondary amines with CO<sub>2</sub>. dppm—bis(diphenylphosphino)methane; dppe—bis(diphenylphosphino)ethane; PNP—*N,N*-bis(2-(diphenylphosphinoethyl)methylamine); dmpe—bis(dimethylphosphino)ethane; PP<sub>3</sub>—tris[2-(diphenylphosphino)ethyl]phosphine; PAr<sub>3</sub>—tris(2-(diphenylphosphino)phenyl)phosphine; dippe—1,2-bis(diisopropylphosphino)ethane.

Catalyst	Amine	P CO <sub>2</sub> /H <sub>2</sub> (T) Bar (°C)	Reductant	TON/Yield (%)	Reference
IrCl(CO)(PPh <sub>3</sub> ) <sub>2</sub>	Me <sub>2</sub> NH	27/27 (125)	H <sub>2</sub>	1200	[188]
PdCl <sub>2</sub>	Me <sub>2</sub> NH	40/80 (170)	H <sub>2</sub>	34	[172]
[Pt <sub>2</sub> (μ-dppm) <sub>3</sub> ]	Me <sub>2</sub> NH	12/94 (75)	H <sub>2</sub>	1460	[173,177]
RuCl <sub>2</sub> (dppe) <sub>2</sub>	Me <sub>2</sub> NH	130/85 (100)	H <sub>2</sub>	74,000	[164]
RuCl <sub>2</sub> (PMe <sub>3</sub> ) <sub>4</sub>	Me <sub>2</sub> NH	130/80 (100)	H <sub>2</sub>	370,000	[178]
Ru(PNP)(CO)(H)Cl	Morpholine	35/35 <sup>a</sup> (120)	H <sub>2</sub>	1,940,000	[176]
NiX <sub>2</sub> /dmpe (X = CH <sub>2</sub> COO <sup>-</sup> or acac)	Morpholine	100 <sup>b</sup> (100–135)	H <sub>2</sub>	18,000	[180]
(PPh <sub>3</sub> ) <sub>3</sub> CuCl	Me <sub>2</sub> NH	27/27 (125)	H <sub>2</sub>	900	[171]
[MoH <sub>3</sub> {Si(Ph)[Ph <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> P(Ph)C <sub>6</sub> H <sub>4</sub> -o] <sub>2</sub> }]	Me <sub>2</sub> NH	30/20 <sup>a</sup> (110)	H <sub>2</sub>	115	[184]
Fe(BF <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O/PP <sub>3</sub>	Me <sub>2</sub> NH	30/60	H <sub>2</sub>	727	[181]
Co(BF <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O/PP <sub>3</sub>	Me <sub>2</sub> NH	30/60	H <sub>2</sub>	1308	[182]
Fe(BF <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O/PAr <sub>3</sub>	Me <sub>2</sub> NH	30/60	H <sub>2</sub>	5104	[183]
Rh <sub>2</sub> (OAc) <sub>4</sub> /K <sub>2</sub> CO <sub>3</sub>	PhCH <sub>2</sub> NH <sub>2</sub> piperidine PhNH <sub>2</sub>	1 <sup>a</sup> (50)	PhMe <sub>2</sub> SiH	41% 43% 34%	[191]
[Ni(μ-H)(dippe)] <sub>2</sub> /BEt <sub>3</sub>	PhCH <sub>2</sub> NH <sub>2</sub> (PhCH <sub>2</sub> ) <sub>2</sub> NH piperidine	1 <sup>a</sup> (80)	Et <sub>3</sub> SiH	85% 47% 52%	[192]
Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O/Bz(PR <sub>2</sub> ) <sub>2</sub>	Piperidine	1 <sup>a</sup> (80)	PMHS	11,700/94%	[189]
Fe(acac) <sub>2</sub> /P(C <sub>2</sub> H <sub>4</sub> PPH <sub>2</sub> ) <sub>3</sub>	(Ph)(Me)NH	1 (RT)	PhSiH <sub>3</sub>	95%	[190]
Cu( <i>i</i> PrNHC)( <i>O</i> <i>t</i> Bu)	(Ph)(Me)NH Ph(CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub> Ph(CH <sub>2</sub> ) <sub>2</sub> NH	1 <sup>a</sup> (35/65)	H-Bpin	81% 98% 90%	[193]

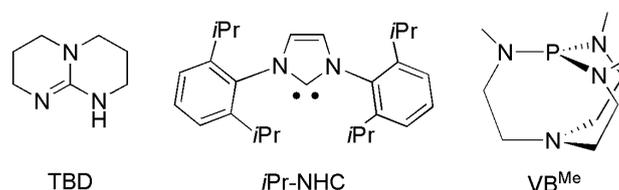
<sup>a</sup> Unit = atm; <sup>b</sup> total pressure.



**Scheme 20.** Transition-metal catalysts for reductive coupling of CO<sub>2</sub> and amines [189–193].



**Scheme 21.** Examples of non-carbonyl products formed via reductive coupling of amines with CO<sub>2</sub> [194–196].



**Scheme 22.** Organocatalysts for reductive coupling of CO<sub>2</sub> and amines [197–201].

#### 4. Summary and Outlook

While CO<sub>2</sub> utilization remains a major scientific challenge, it is also a promising means for providing petroleum substitutes, thus achieving sustainable and carbon-neutral resource utilization, in face of the current rising atmospheric CO<sub>2</sub> level. The direct reduction and the concerted reductive functionalization of CO<sub>2</sub> enable us to assess a broad spectrum of products which are higher in energy and varied in functionality, in comparison with the “horizontal” pathways. However, the search of novel, economic, and environmentally friendly catalysts, which circumvent the current reaction bottlenecks, will be highly important in terms of the access to desirable products, as well as the enhancement of catalyst stability and energy efficiency. Much is to be done for molecular catalysts with respect to understanding how the coordination spheres will facilitate yielding the desired products of varied oxidation states on the CO<sub>2</sub>-derived carbon, particularly in obtaining C-2 or higher hydrocarbons [30,53–55,67,68,71,80–87,94,98,169–193]. For the reductive transformations of CO<sub>2</sub> to be sustainably driven by renewable energy sources, the exploration of direct photo-driven redox catalysis using systems of photosensitizer–catalyst combinations without precious metals [17–20] and the development of catalytic electrodes bearing the immobilized macromolecular or molecular catalysts [24,62–65,69–71,85–87] will be essential, such that the technology will be further advanced and materialized in the form of photoelectrochemical cells [31].

**Author Contributions:** Conceptualization, C-F.L.; Bibliographic research, C-F.L. and P-Y.H.; Writing-Original Draft Preparation, C-F.L. and P-Y.H.; Writing-Review & Editing, C-F.L.; Visualization, C-F.L. and P-Y.H.

**Funding:** This research received no external funding. And APC was funded by the Education University of Hong Kong.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Ghaib, K.; Nitz, K.; Ben-Fares, F.-Z. Chemical Methanation of CO<sub>2</sub>: A Review. *ChemBioEng Rev.* **2016**, *3*, 266–275. [[CrossRef](#)]
2. Yu, K.M.K.; Curcic, I.; Gabriel, J.; Tsang, S.C.E. Recent Advances in CO<sub>2</sub> Capture and Utilization. *ChemSusChem Chem. Sustain. Energy Mater.* **2008**, *1*, 893–899. [[CrossRef](#)]
3. Spinner, N.S.; Vega, J.A.; Mustain, W.E. Recent Progress in the Electrochemical Conversion and Utilization of CO<sub>2</sub>. *Catal. Sci. Technol.* **2012**, *2*, 19–28. [[CrossRef](#)]
4. Wilcox, E.M.; Roberts, G.W.; Spivey, J.J. Direct Catalytic Formation of Acetic Acid from CO<sub>2</sub> and Methane. *Catal. Today* **2003**, *88*, 83–90. [[CrossRef](#)]
5. Ma, J.; Sun, N.; Zhang, X.; Zhao, N.; Xiao, F.; Wei, W.; Sun, Y. A Short Review of Catalysis for CO<sub>2</sub> Conversion. *Catal. Today* **2009**, *148*, 221–231. [[CrossRef](#)]
6. Bian, Z.; Das, S.; Wai, M.H.; Hongmanorom, P.; Kawi, S. A Review on Bimetallic Nickel-Based Catalysts for CO<sub>2</sub> Reforming of Methane. *ChemPhysChem* **2017**, *18*, 3117–3134. [[CrossRef](#)]
7. Buelens, L.C.; Galvita, V.V.; Poelman, H.; Detavernier, C.; Marin, G.B. Super-Dry Reforming of Methane Intensifies CO<sub>2</sub> Utilization via Le Chatelier's Principle. *Science* **2016**, *354*, 449–452. [[CrossRef](#)]
8. Habisreutinger, S.N.; Schmidt-Mende, L.; Stolarczyk, J.K. Photocatalytic Reduction of CO<sub>2</sub> on TiO<sub>2</sub> and Other Semiconductors. *Angew. Chem. Int. Ed.* **2013**, *52*, 7372–7408. [[CrossRef](#)]
9. Schreier, M.; Héroguel, F.; Steier, L.; Ahmad, S.; Luterbacher, J.S.; Mayer, M.T.; Luo, J.; Grätzel, M. Solar Conversion of CO<sub>2</sub> to CO Using Earth-Abundant Electrocatalysts Prepared by Atomic Layer Modification of CuO. *Nat. Energy* **2017**, *2*, 17087. [[CrossRef](#)]
10. Sorcar, S.; Hwang, Y.; Grimes, C.A.; In, S.-I. Highly Enhanced and Stable Activity of Defect-Induced Titania Nanoparticles for Solar Light-Driven CO<sub>2</sub> Reduction into CH<sub>4</sub>. *Mater. Today* **2017**, *20*, 507–515. [[CrossRef](#)]
11. Park, H.; Ou, H.-H.; Colussi, A.J.; Hoffmann, M.R. Artificial Photosynthesis of C1–C3 Hydrocarbons from Water and CO<sub>2</sub> on Titanate Nanotubes Decorated with Nanoparticle Elemental Copper and CdS Quantum Dots. *J. Phys. Chem. A* **2015**, *119*, 4658–4666. [[CrossRef](#)] [[PubMed](#)]
12. Sorcar, S.; Thompson, J.; Hwang, Y.; Park, Y.H.; Majima, T.; Grimes, C.A.; Durrant, J.R.; In, S.-I. High-Rate Solar-Light Photoconversion of CO<sub>2</sub> to Fuel: Controllable Transformation from C1 to C2 Products. *Energy Environ. Sci.* **2018**, *11*, 3183–3193. [[CrossRef](#)]
13. Li, N.; Wang, B.; Si, Y.; Xue, F.; Zhou, J.; Lu, Y.; Liu, M. Toward High-Value Hydrocarbon Generation by Photocatalytic Reduction of CO<sub>2</sub> in Water Vapor. *ACS Catal.* **2019**, *9*, 5590–5602. [[CrossRef](#)]
14. Thampi, K.R.; Lucarelli, L.; Kiwi, J. Characterization of a Ruthenium/Titania Catalyst for Selective Methanation at Room Temperature and Atmospheric Pressure. *Langmuir* **1991**, *7*, 2642–2648. [[CrossRef](#)]
15. Yang, X.; Fugate, E.A.; Mueangern, Y.; Baker, L.R. Photoelectrochemical CO<sub>2</sub> Reduction to Acetate on Iron–Copper Oxide Catalysts. *ACS Catal.* **2016**, *7*, 177–180. [[CrossRef](#)]
16. Jeon, H.S.; Kunze, S.; Scholten, F.; Roldan Cuenya, B. Prism-Shaped Cu Nanocatalysts for Electrochemical CO<sub>2</sub> Reduction to Ethylene. *ACS Catal.* **2017**, *8*, 531–535. [[CrossRef](#)]
17. Morris, A.J.; Meyer, G.J.; Fujita, E. Molecular approaches to the photocatalytic reduction of carbon dioxide for solar fuels. *Acc. Chem. Res.* **2009**, *42*, 1983–1994. [[CrossRef](#)]
18. Windle, C.D.; Perutz, R.N. Advances in molecular photocatalytic and electrocatalytic CO<sub>2</sub> reduction. *Coord. Chem. Rev.* **2012**, *256*, 2562–2570. [[CrossRef](#)]
19. Benson, E.E.; Kubiak, C.P.; Sathrum, A.J.; Smieja, J.M. Electrocatalytic and homogeneous approaches to conversion of CO<sub>2</sub> to liquid fuels. *Chem. Soc. Rev.* **2009**, *38*, 89–99. [[CrossRef](#)]
20. Takeda, H.; Cometto, C.; Ishitani, O.; Robert, M. Electrons, photons, protons and earth-abundant metal complexes for molecular catalysis of CO<sub>2</sub> reduction. *ACS Catal.* **2016**, *7*, 70–88. [[CrossRef](#)]
21. Hunt, A.J.; Sin, E.H.K.; Marriott, R.; Clark, J.H. Generation, capture, and utilization of industrial carbon dioxide. *ChemSusChem Chem. Sustain. Energy Mater.* **2010**, *3*, 306–322. [[CrossRef](#)] [[PubMed](#)]
22. Langanke, J.; Wolf, A.; Hofmann, J.; Böhm, K.; Subhani, M.A.; Müller, T.E.; Leitner, W.; Gürtler, C. Carbon dioxide (CO<sub>2</sub>) as sustainable feedstock for polyurethane production. *Green Chem.* **2014**, *16*, 1865–1870. [[CrossRef](#)]
23. Liu, Q.; Wu, L.; Jackstell, R.; Beller, M. Using carbon dioxide as a building block in organic synthesis. *Nat. Commun.* **2015**, *6*, 5933. [[CrossRef](#)] [[PubMed](#)]

24. Doherty, M.D.; Grills, D.C.; Muckerman, J.T.; Polyansky, D.E.; Fujita, E. Toward more efficient photochemical CO<sub>2</sub> reduction: Use of scCO<sub>2</sub> or photogenerated hydrides. *Coord. Chem. Rev.* **2010**, *254*, 2472–2482. [[CrossRef](#)]
25. Shen, J.; Kortlever, R.; Kas, R.; Birdja, Y.Y.; Diaz-Morales, O.; Kwon, Y.; Ledezma-Yanez, I.; Schouten, K.J.P.; Mul, G.; Koper, M.T.M. Electrocatalytic reduction of carbon dioxide to carbon monoxide and methane at an immobilized cobalt protoporphyrin. *Nat. Commun.* **2015**, *6*, 8177. [[CrossRef](#)]
26. Liu, X.; Inagaki, S.; Gong, J. Heterogeneous molecular systems for photocatalytic CO<sub>2</sub> reduction with water oxidation. *Angew. Chem. Int. Ed.* **2016**, *55*, 14924–14950. [[CrossRef](#)] [[PubMed](#)]
27. Hawecker, J.; Lehn, J.-M.; Ziessel, R. Electrocatalytic reduction of carbon dioxide mediated by Re(bipy)(CO)<sub>3</sub>Cl (bipy = 2,2'-bipyridine). *J. Chem. Soc. Chem. Commun.* **1984**, 328–330. [[CrossRef](#)]
28. Clark, M.L.; Cheung, P.L.; Lessio, M.; Carter, E.A.; Kubiak, C.P. Kinetic and Mechanistic Effects of Bipyridine (bpy) Substituent, Labile Ligand, and Brønsted Acid on Electrocatalytic CO<sub>2</sub> Reduction by Re(bpy) Complexes. *ACS Catal.* **2018**, *8*, 2021–2029. [[CrossRef](#)]
29. Bolinger, C.M.; Story, N.; Sullivan, B.P.; Meyer, T.J. Electrocatalytic reduction of carbon dioxide by 2, 2'-bipyridine complexes of rhodium and iridium. *Inorg. Chem.* **1988**, *27*, 4582–4587. [[CrossRef](#)]
30. Sung, S.; Kumar, D.; Gil-Sepulcre, M.; Nippe, M. Electrocatalytic CO<sub>2</sub> Reduction by Imidazolium-Functionalized Molecular Catalysts. *J. Am. Chem. Soc.* **2017**, *139*, 13993–13996. [[CrossRef](#)]
31. Nakada, A.; Ishitani, O. Selective Electrocatalysis of a Water-Soluble Rhenium (I) Complex for CO<sub>2</sub> Reduction Using Water as an Electron Donor. *ACS Catal.* **2017**, *8*, 354–363. [[CrossRef](#)]
32. Ishida, H.; Tanaka, K.; Tanaka, T. Electrochemical CO<sub>2</sub> reduction catalyzed by ruthenium complexes [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> and [Ru(bpy)<sub>2</sub>(CO)Cl]<sup>+</sup>. The effect of pH on the formation of CO and HCOO<sup>-</sup>. *Organometallics* **1987**, *6*, 181–186. [[CrossRef](#)]
33. Bruce, M.R.M.; Megehee, E.; Sullivan, B.P.; Thorp, H.; O'Toole, T.R.; Downard, A.; Meyer, T.J. Electrocatalytic reduction of carbon dioxide by associative activation. *Organometallics* **1988**, *7*, 238–240. [[CrossRef](#)]
34. Machan, C.W.; Sampson, M.D.; Kubiak, C.P. A molecular ruthenium electrocatalyst for the reduction of carbon dioxide to CO and formate. *J. Am. Chem. Soc.* **2015**, *137*, 8564–8571. [[CrossRef](#)] [[PubMed](#)]
35. Slater, S.; Wagenknecht, J.H. Electrochemical reduction of carbon dioxide catalyzed by Rh(diphos)<sub>2</sub>Cl. *J. Am. Chem. Soc.* **1984**, *106*, 5367–5368. [[CrossRef](#)]
36. DuBois, D.L.; Miedaner, A.; Haltiwanger, R.C. Electrochemical reduction of CO<sub>2</sub> catalyzed by [Pd(triphosphine)(solvent)](BF<sub>4</sub>)<sub>2</sub> complexes: Synthetic and mechanistic studies. *J. Am. Chem. Soc.* **1991**, *113*, 8753–8764. [[CrossRef](#)]
37. Raebiger, J.W.; Turner, J.W.; Noll, B.C.; Curtis, C.J.; Miedaner, A.; Cox, B.; DuBois, D.L. Electrochemical reduction of CO<sub>2</sub> to CO catalyzed by a bimetallic palladium complex. *Organometallics* **2006**, *25*, 3345–3351. [[CrossRef](#)]
38. Fisher, B.J.; Eisenberg, R. Electrocatalytic reduction of carbon dioxide by using macrocycles of nickel and cobalt. *J. Am. Chem. Soc.* **1980**, *102*, 7361–7363. [[CrossRef](#)]
39. Fujita, E. Photochemical carbon dioxide reduction with metal complexes. *Coord. Chem. Rev.* **1999**, *185*, 373–384. [[CrossRef](#)]
40. Fujita, E.; Szalda, D.J.; Creutz, C.; Sutin, N. Carbon dioxide activation: Thermodynamics of carbon dioxide binding and the involvement of two cobalt centers in the reduction of carbon dioxide by a cobalt (I) macrocycle. *J. Am. Chem. Soc.* **1988**, *110*, 4870–4871. [[CrossRef](#)]
41. Fujita, E.; Creutz, C.; Sutin, N.; Szalda, D.J. Carbon dioxide activation by cobalt (I) macrocycles: Factors affecting carbon dioxide and carbon monoxide binding. *J. Am. Chem. Soc.* **1991**, *113*, 343–353. [[CrossRef](#)]
42. Creutz, C.; Schwarz, H.A.; Wishart, J.F.; Fujita, E.; Sutin, N. Thermodynamics and kinetics of carbon dioxide binding to two stereoisomers of a cobalt (I) macrocycle in aqueous solution. *J. Am. Chem. Soc.* **1991**, *113*, 3361–3371. [[CrossRef](#)]
43. Beley, M.; Collin, J.P.; Ruppert, R.; Sauvage, J.P. Electrocatalytic reduction of carbon dioxide by nickel cyclam<sup>2+</sup> in water: Study of the factors affecting the efficiency and the selectivity of the process. *J. Am. Chem. Soc.* **1986**, *108*, 7461–7467. [[CrossRef](#)]
44. Beley, M.; Collin, J.-P.; Ruppert, R.; Sauvage, J.-P. Nickel(II)-cyclam: An extremely selective electrocatalyst for reduction of CO<sub>2</sub> in water. *J. Chem. Soc. Chem. Commun.* **1984**, 1315–1316. [[CrossRef](#)]

45. Fujita, E.; Haff, J.; Sanzenbacher, R.; Elias, H. High Electrocatalytic Activity of  $RRSS-[Ni^{II}HTIM](ClO_4)_2$  and  $[Ni^{II}DMC](ClO_4)_2$  for Carbon Dioxide Reduction (HTIM = 2,3,9,10-Tetramethyl-1,4,8,11-tetraazacyclotetradecane, DMC = C-meso-5,12-Dimethyl-1,4,8,11-tetraazacyclotetradecane). *Inorg. Chem.* **1994**, *33*, 4627–4628. [[CrossRef](#)]
46. Froehlich, J.D.; Kubiak, C.P. Homogeneous  $CO_2$  reduction by Ni(cyclam) at a glassy carbon electrode. *Inorg. Chem.* **2012**, *51*, 3932–3934. [[CrossRef](#)]
47. Schneider, J.; Jia, H.; Kobihiro, K.; Cabelli, D.E.; Muckerman, J.T.; Fujita, E. Nickel(II) macrocycles: Highly efficient electrocatalysts for the selective reduction of  $CO_2$  to CO. *Energy Environ. Sci.* **2012**, *5*, 9502–9510. [[CrossRef](#)]
48. Collin, J.P.; Jouaiti, A.; Sauvage, J.P. Electrocatalytic properties of  $Ni(cyclam)^{2+}$  and  $Ni_2(biscyclam)^{4+}$  with respect to  $CO_2$  and  $H_2O$  reduction. *Inorg. Chem.* **1988**, *27*, 1986–1990. [[CrossRef](#)]
49. Tinnemans, A.H.A.; Koster, T.P.M.; Thewissen, D.; Mackor, A. Tetraaza-macrocylic cobalt(II) and nickel(II) complexes as electron-transfer agents in the photo(electro)chemical and electrochemical reduction of carbon dioxide. *Recl. Trav. Chim. Pays Bas* **1984**, *103*, 288–295. [[CrossRef](#)]
50. Che, C.-M.; Mak, S.-T.; Lee, W.-O.; Fung, K.-W.; Mak, T.C.W. Electrochemical studies of nickel(II) and cobalt(II) complexes of tetra-azamacrocycles bearing a pyridine functional group and X-ray structures of  $[Ni^{II}(L^3)Cl]ClO_4$  and  $[Ni^{II}(L^3)][ClO_4]_2 \cdot H_2O$   $\{L^3 = \text{meso-2,3,7,11,12-pentamethyl-3,7,11,17-tetraazabicyclo}[11.3.1]\text{heptadeca-1,13,15-triene}\}$ . *J. Chem. Soc. Dalt. Trans.* **1988**, 2153–2159.
51. Chen, L.; Guo, Z.; Wei, X.-G.; Gallenkamp, C.; Bonin, J.; Anxolabéhère-Mallart, E.; Lau, K.-C.; Lau, T.-C.; Robert, M. Molecular catalysis of the electrochemical and photochemical reduction of  $CO_2$  with Earth-abundant metal complexes. Selective production of CO vs. HCOOH by switching of the metal center. *J. Am. Chem. Soc.* **2015**, *137*, 10918–10921. [[CrossRef](#)] [[PubMed](#)]
52. Savéant, J.-M. Molecular catalysis of electrochemical reactions. Mechanistic aspects. *Chem. Rev.* **2008**, *108*, 2348–2378. [[CrossRef](#)] [[PubMed](#)]
53. Costentin, C.; Drouet, S.; Robert, M.; Savéant, J.-M. A local proton source enhances  $CO_2$  electroreduction to CO by a molecular Fe catalyst. *Science* **2012**, *338*, 90–94. [[CrossRef](#)] [[PubMed](#)]
54. Costentin, C.; Robert, M.; Savéant, J.-M. Catalysis of the electrochemical reduction of carbon dioxide. *Chem. Soc. Rev.* **2013**, *42*, 2423–2436. [[CrossRef](#)] [[PubMed](#)]
55. Costentin, C.; Robert, M.; Savéant, J.-M. Current issues in molecular catalysis illustrated by iron porphyrins as catalysts of the  $CO_2$ -to-CO electrochemical conversion. *Acc. Chem. Res.* **2015**, *48*, 2996–3006. [[CrossRef](#)] [[PubMed](#)]
56. Hammouche, M.; Lexa, D.; Momenteau, M.; Saveant, J.M. Chemical catalysis of electrochemical reactions. Homogeneous catalysis of the electrochemical reduction of carbon dioxide by iron(“0”) porphyrins. Role of the addition of magnesium cations. *J. Am. Chem. Soc.* **1991**, *113*, 8455–8466. [[CrossRef](#)]
57. Bhugun, I.; Lexa, D.; Savéant, J.-M. Catalysis of the electrochemical reduction of carbon dioxide by iron(0) porphyrins: Synergistic effect of weak Brønsted acids. *J. Am. Chem. Soc.* **1996**, *118*, 1769–1776. [[CrossRef](#)]
58. Bhugun, I.; Lexa, D.; Savéant, J.-M. Catalysis of the electrochemical reduction of carbon dioxide by iron(0) porphyrins. Synergistic effect of Lewis acid cations. *J. Phys. Chem.* **1996**, *100*, 19981–19985. [[CrossRef](#)]
59. Costentin, C.; Drouet, S.; Robert, M.; Savéant, J.-M. Turnover numbers, turnover frequencies, and overpotential in molecular catalysis of electrochemical reactions. Cyclic voltammetry and preparative-scale electrolysis. *J. Am. Chem. Soc.* **2012**, *134*, 11235–11242. [[CrossRef](#)] [[PubMed](#)]
60. Ogata, T.; Yanagida, S.; Brunschwig, B.S.; Fujita, E. Mechanistic and kinetic studies of cobalt macrocycles in a photochemical  $CO_2$  reduction system: Evidence of Co- $CO_2$  adducts as intermediates. *J. Am. Chem. Soc.* **1995**, *117*, 6708–6716. [[CrossRef](#)]
61. Grodkowski, J.; Neta, P.; Fujita, E.; Mahammed, A.; Simkhovich, L.; Gross, Z. Reduction of cobalt and iron corroles and catalyzed reduction of  $CO_2$ . *J. Phys. Chem. A* **2002**, *106*, 4772–4778. [[CrossRef](#)]
62. Meshitsuka, S.; Ichikawa, M.; Tamaru, K. Electrocatalysis by metal phthalocyanines in the reduction of carbon dioxide. *J. Chem. Soc. Chem. Commun.* **1974**, 158–159. [[CrossRef](#)]
63. Furuya, N.; Matsui, K. Electroreduction of carbon dioxide on gas-diffusion electrodes modified by metal phthalocyanines. *J. Electroanal. Chem. Interfacial Electrochem.* **1989**, *271*, 181–191. [[CrossRef](#)]
64. Atoguchi, T.; Aramata, A.; Kazusaka, A.; Enyo, M. Cobalt(II)-tetraphenylporphyrin-pyridine complex fixed on a glassy carbon electrode and its prominent catalytic activity for reduction of carbon dioxide. *J. Chem. Soc. Chem. Commun.* **1991**, 156–157. [[CrossRef](#)]

65. Sonoyama, N.; Kirii, M.; Sakata, T. Electrochemical reduction of CO<sub>2</sub> at metal-porphyrin supported gas diffusion electrodes under high pressure CO<sub>2</sub>. *Electrochem. Commun.* **1999**, *1*, 213–216. [[CrossRef](#)]
66. Aoi, S.; Mase, K.; Ohkubo, K.; Fukuzumi, S. Selective electrochemical reduction of CO<sub>2</sub> to CO with a cobalt chlorin complex adsorbed on multi-walled carbon nanotubes in water. *Chem. Commun.* **2015**, *51*, 10226–10228. [[CrossRef](#)]
67. Bonin, J.; Chaussemier, M.; Robert, M.; Routier, M. Homogeneous photocatalytic reduction of CO<sub>2</sub> to CO using iron(0) porphyrin catalysts: Mechanism and intrinsic limitations. *ChemCatChem* **2014**, *6*, 3200–3207. [[CrossRef](#)]
68. Rao, H.; Schmidt, L.C.; Bonin, J.; Robert, M. Visible-light-driven methane formation from CO<sub>2</sub> with a molecular iron catalyst. *Nature* **2017**, *548*, 74. [[CrossRef](#)]
69. Lin, S.; Diercks, C.S.; Zhang, Y.-B.; Kornienko, N.; Nichols, E.M.; Zhao, Y.; Paris, A.R.; Kim, D.; Yang, P.; Yaghi, O.M.; et al. Covalent Organic Frameworks Comprising Cobalt Porphyrins for Catalytic CO<sub>2</sub> Reduction in Water. *Science* **2015**, *349*, 1208–1213. [[CrossRef](#)]
70. Smith, P.T.; Benke, B.P.; Cao, Z.; Kim, Y.; Nichols, E.M.; Kim, K.; Chang, C.J. Iron Porphyrins Embedded into a Supramolecular Porous Organic Cage for Electrochemical CO<sub>2</sub> Reduction in Water. *Angew. Chem. Int. Ed.* **2018**, *57*, 9684–9688. [[CrossRef](#)]
71. Weng, Z.; Jiang, J.; Wu, Y.; Wu, Z.; Guo, X.; Materna, K.L.; Liu, W.; Batista, V.S.; Brudvig, G.W.; Wang, H. Electrochemical CO<sub>2</sub> Reduction to Hydrocarbons on a Heterogeneous Molecular Cu Catalyst in Aqueous Solution. *J. Am. Chem. Soc.* **2016**, *138*, 8076–8079. [[CrossRef](#)] [[PubMed](#)]
72. Thoi, V.S.; Kornienko, N.; Margarit, C.G.; Yang, P.; Chang, C.J. Visible-light photoredox catalysis: Selective reduction of carbon dioxide to carbon monoxide by a nickel N-heterocyclic carbene-isoquinoline complex. *J. Am. Chem. Soc.* **2013**, *135*, 14413–14424. [[CrossRef](#)] [[PubMed](#)]
73. Chapovetsky, A.; Do, T.H.; Haiges, R.; Takase, M.K.; Marinescu, S.C. Proton-assisted reduction of CO<sub>2</sub> by cobalt aminopyridine macrocycles. *J. Am. Chem. Soc.* **2016**, *138*, 5765–5768. [[CrossRef](#)] [[PubMed](#)]
74. Pun, S.-N.; Chung, W.-H.; Lam, K.-M.; Guo, P.; Chan, P.-H.; Wong, K.-Y.; Che, C.-M.; Chen, T.-Y.; Peng, S.-M. Iron(I) complexes of 2,9-bis(2-hydroxyphenyl)-1,10-phenanthroline (H<sub>2</sub>dophen) as electrocatalysts for carbon dioxide reduction. X-ray crystal structures of [Fe(dophen)Cl]<sub>2</sub>·2HCON(CH<sub>3</sub>)<sub>2</sub> and [Fe(dophen)(N-MeIm)<sub>2</sub>]ClO<sub>4</sub> (N-MeIm = 1-methylimidazole). *J. Chem. Soc. Dalton Trans.* **2002**, 575–583. [[CrossRef](#)]
75. Nichols, A.W.; Chatterjee, S.; Sabat, M.; Machan, C.W. Electrocatalytic Reduction of CO<sub>2</sub> to Formate by an Iron Schiff Base Complex. *Inorg. Chem.* **2018**, *57*, 2111–2121. [[CrossRef](#)] [[PubMed](#)]
76. Cometto, C.; Chen, L.; Lo, P.-K.; Guo, Z.; Lau, K.-C.; Anxolabéhère-Mallart, E.; Fave, C.; Lau, T.-C.; Robert, M. Highly Selective Molecular Catalysts for the CO<sub>2</sub>-to-CO Electrochemical Conversion at Very Low Overpotential. Contrasting Fe vs. Co Quaterpyridine Complexes upon Mechanistic Studies. *ACS Catal.* **2018**, *8*, 3411–3417. [[CrossRef](#)]
77. Bourrez, M.; Molton, F.; Chardon-Noblat, S.; Deronzier, A. [Mn(bipyridyl)(CO)<sub>3</sub>Br]: An abundant metal carbonyl complex as efficient electrocatalyst for CO<sub>2</sub> reduction. *Angew. Chem. Int. Ed.* **2011**, *50*, 9903–9906. [[CrossRef](#)] [[PubMed](#)]
78. Bourrez, M.; Orio, M.; Molton, F.; Vezin, H.; Duboc, C.; Deronzier, A.; Chardon-Noblat, S. Pulsed-EPR Evidence of a Manganese(II) Hydroxycarbonyl Intermediate in the Electrocatalytic Reduction of Carbon Dioxide by a Manganese Bipyridyl Derivative. *Angew. Chem. Int. Ed.* **2014**, *53*, 240–243. [[CrossRef](#)] [[PubMed](#)]
79. Sampson, M.D.; Kubiak, C.P. Manganese electrocatalysts with bulky bipyridine ligands: Utilizing Lewis acids to promote carbon dioxide reduction at low overpotentials. *J. Am. Chem. Soc.* **2016**, *138*, 1386–1393. [[CrossRef](#)] [[PubMed](#)]
80. Smieja, J.M.; Sampson, M.D.; Grice, K.A.; Benson, E.E.; Froehlich, J.D.; Kubiak, C.P. Manganese as a substitute for rhenium in CO<sub>2</sub> reduction catalysts: The importance of acids. *Inorg. Chem.* **2013**, *52*, 2484–2491. [[CrossRef](#)]
81. Franco, F.; Cometto, C.; Vallana, F.F.; Sordello, F.; Priola, E.; Minero, C.; Nervi, C.; Gobetto, R. A Local Proton Source in a [Mn(bpy-R)(CO)<sub>3</sub>Br]-Type Redox Catalyst Enables CO<sub>2</sub> Reduction Even in the Absence of Brønsted Acids. *Chem. Commun.* **2014**, *50*, 14670–14673. [[CrossRef](#)] [[PubMed](#)]
82. Agarwal, J.; Shaw, T.W.; Schaefer III, H.F.; Bocarsly, A.B. Design of a catalytic active site for electrochemical CO<sub>2</sub> reduction with Mn(I)-tricarbonyl species. *Inorg. Chem.* **2015**, *54*, 5285–5294. [[CrossRef](#)] [[PubMed](#)]

83. Franco, F.; Cometto, C.; Nencini, L.; Barolo, C.; Sordello, F.; Minero, C.; Fiedler, J.; Robert, M.; Gobetto, R.; Nervi, C. Local Proton Source in Electrocatalytic CO<sub>2</sub> Reduction with [Mn(bpy-R)(CO)<sub>3</sub>Br] Complexes. *Chem. Eur. J.* **2017**, *23*, 4782–4793. [[CrossRef](#)] [[PubMed](#)]
84. Sung, S.; Li, X.; Wolf, L.M.; Meeder, J.R.; Bhuvanesh, N.S.; Grice, K.A.; Panetier, J.A.; Nippe, M. Synergistic Effects of Imidazolium-Functionalization on Fac-Mn(CO)<sub>3</sub> Bipyridine Catalyst Platforms for Electrocatalytic Carbon Dioxide Reduction. *J. Am. Chem. Soc.* **2019**, *141*, 6569–6582. [[CrossRef](#)] [[PubMed](#)]
85. Sato, S.; Saita, K.; Sekizawa, K.; Maeda, S.; Morikawa, T. Low-Energy Electrocatalytic CO<sub>2</sub> Reduction in Water over Mn-Complex Catalyst Electrode Aided by a Nanocarbon Support and K<sup>+</sup> Cations. *ACS Catal.* **2018**, *8*, 4452–4458. [[CrossRef](#)]
86. Sun, C.; Rotundo, L.; Garino, C.; Nencini, L.; Yoon, S.S.; Gobetto, R.; Nervi, C. Electrochemical CO<sub>2</sub> Reduction at Glassy Carbon Electrodes Functionalized by Mn<sup>I</sup> and Re<sup>I</sup> Organometallic Complexes. *ChemPhysChem* **2017**, *18*, 3219–3229. [[CrossRef](#)] [[PubMed](#)]
87. Rotundo, L.; Filippi, J.; Gobetto, R.; Miller, H.A.; Rocca, R.; Nervi, C.; Vizza, F. Electrochemical CO<sub>2</sub> Reduction in Water at Carbon Cloth Electrodes Functionalized with a Fac-Mn (apbpy)(CO)<sub>3</sub>Br Complex. *Chem. Commun.* **2019**, *55*, 775–777. [[CrossRef](#)] [[PubMed](#)]
88. Simón-Manso, E.; Kubiak, C.P. Dinuclear nickel complexes as catalysts for electrochemical reduction of carbon dioxide. *Organometallics* **2005**, *24*, 96–102. [[CrossRef](#)]
89. DeLaet, D.L.; DelRosario, R.; Fanwick, P.E.; Kubiak, C.P. Carbon dioxide chemistry and electrochemistry of a binuclear “Cradle” complex of Ni, Ni<sub>2</sub>(μ-CNMe)(CNMe)<sub>2</sub>(PPh<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>. *J. Am. Chem. Soc.* **1987**, *109*, 754–758. [[CrossRef](#)]
90. Ratliff, K.S.; Lentz, R.E.; Kubiak, C.P. Carbon dioxide chemistry of the trinuclear complex [Ni<sub>3</sub>(μ<sub>3</sub>-CNMe)(μ<sub>3</sub>-I)(dppm)<sub>3</sub>][PF<sub>6</sub>]. Electrocatalytic reduction of carbon dioxide. *Organometallics* **1992**, *11*, 1986–1988. [[CrossRef](#)]
91. Morgenstern, D.A.; Ferrence, G.M.; Washington, J.; Henderson, J.I.; Rosenhein, L.; Heise, J.D.; Fanwick, P.E.; Kubiak, C.P. A Class of Halide-Supported Trinuclear Nickel Clusters [Ni<sub>3</sub>(μ<sub>3</sub>-L)(μ<sub>3</sub>-X)(μ<sub>2</sub>-dppm)<sub>3</sub>]<sup>n+</sup> (L = I<sup>-</sup>, Br<sup>-</sup>, CO, CNR; X = I<sup>-</sup>, Br<sup>-</sup>; n = 0, 1; dppm = Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>): Novel Physical Properties and the Fermi Resonance of Symmetric μ<sub>3</sub>-η<sup>1</sup> Bound Isocyanide Ligands. *J. Am. Chem. Soc.* **1996**, *118*, 2198–2207. [[CrossRef](#)]
92. Haines, R.J.; Wittrig, R.E.; Kubiak, C.P. Electrocatalytic Reduction of Carbon Dioxide by the Binuclear Copper Complex [Cu<sub>2</sub>(6-(diphenylphosphino-2,2'-bipyridyl)<sub>2</sub>(MeCN)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub>. *Inorg. Chem.* **1994**, *33*, 4723–4728. [[CrossRef](#)]
93. Cheng, M.; Yu, Y.; Zhou, X.; Luo, Y.; Wang, M. Chemical Versatility of [FeFe]-Hydrogenase Models: Distinctive Activity of [μ-C<sub>6</sub>H<sub>4</sub>-1,2-(κ<sup>2</sup>-S)<sub>2</sub>][Fe<sub>2</sub>(CO)<sub>6</sub>] for Electrocatalytic CO<sub>2</sub> Reduction. *ACS Catal.* **2018**, *9*, 768–774. [[CrossRef](#)]
94. Angamuthu, R.; Byers, P.; Lutz, M.; Spek, A.L.; Bouwman, E. Electrocatalytic CO<sub>2</sub> Conversion to Oxalate by a Copper Complex. *Science* **2010**, *327*, 313–315. [[CrossRef](#)] [[PubMed](#)]
95. Mikkelsen, M.; Jørgensen, M.; Krebs, F.C. The teraton challenge. A review of fixation and transformation of carbon dioxide. *Energy Environ. Sci.* **2010**, *3*, 43–81. [[CrossRef](#)]
96. Maeda, C.; Miyazaki, Y.; Ema, T. Recent progress in catalytic conversions of carbon dioxide. *Catal. Sci. Technol.* **2014**, *4*, 1482–1497. [[CrossRef](#)]
97. Tlili, A.; Blondiaux, E.; Frogneux, X.; Cantat, T. Reductive functionalization of CO<sub>2</sub> with amines: An entry to formamide, formamidine and methylamine derivatives. *Green Chem.* **2015**, *17*, 157–168. [[CrossRef](#)]
98. Song, Q.-W.; Zhou, Z.-H.; He, L.-N. Efficient, selective and sustainable catalysis of carbon dioxide. *Green Chem.* **2017**, *19*, 3707–3728. [[CrossRef](#)]
99. Fiorani, G.; Guo, W.; Kleij, A.W. Sustainable conversion of carbon dioxide: The advent of organocatalysis. *Green Chem.* **2015**, *17*, 1375–1389. [[CrossRef](#)]
100. Borjesson, M.; Moragas, T.; Gallego, D.; Martin, R. Metal-catalyzed carboxylation of organic (pseudo)halides with CO<sub>2</sub>. *ACS Catal.* **2016**, *6*, 6739–6749. [[CrossRef](#)]
101. Huang, K.; Sun, C.-L.; Shi, Z.-J. Transition-metal-catalyzed C-C bond formation through the fixation of carbon dioxide. *Chem. Soc. Rev.* **2011**, *40*, 2435–2452. [[CrossRef](#)] [[PubMed](#)]
102. Sakakura, T.; Choi, J.-C.; Yasuda, H. Transformation of carbon dioxide. *Chem. Rev.* **2007**, *107*, 2365–2387. [[CrossRef](#)] [[PubMed](#)]

103. Martin, R.; Kleij, A.W. Myth or reality? Fixation of carbon dioxide into complex organic matter under mild conditions. *ChemSusChem* **2011**, *4*, 1259–1263. [[CrossRef](#)] [[PubMed](#)]
104. Peters, M.; Köhler, B.; Kuckshinrichs, W.; Leitner, W.; Markewitz, P.; Müller, T.E. Chemical technologies for exploiting and recycling carbon dioxide into the value chain. *ChemSusChem* **2011**, *4*, 1216–1240. [[CrossRef](#)] [[PubMed](#)]
105. Juliá-Hernández, F.; Gaydou, M.; Serrano, E.; van Gemmeren, M.; Martin, R. Ni- and Fe-catalyzed carboxylation of unsaturated hydrocarbons with CO<sub>2</sub>. In *Ni- and Fe-Based Cross-Coupling Reactions*; Springer: Dodrecht, The Netherlands, 2017; pp. 91–128. CO<sub>2</sub>. In *Ni- and Fe-Based Cross-Coupling Reactions*; Springer: Dodrecht, The Netherlands, 2017; pp. 91–128.
106. Aida, T.; Inoue, S. Activation of carbon dioxide with aluminum porphyrin and reaction with epoxide. Studies on (tetraphenylporphinato) aluminum alkoxide having a long oxyalkylene chain as the alkoxide group. *J. Am. Chem. Soc.* **1983**, *105*, 1304–1309. [[CrossRef](#)]
107. Kruper, W.J.; Dellar, D.D. Catalytic formation of cyclic carbonates from epoxides and CO<sub>2</sub> with chromium metalloporphyrinates. *J. Org. Chem.* **1995**, *60*, 725–727. [[CrossRef](#)]
108. Paddock, R.L.; Hiyama, Y.; McKay, J.M.; Nguyen, S.T. Co(III) porphyrin/DMAP: An efficient catalyst system for the synthesis of cyclic carbonates from CO<sub>2</sub> and epoxides. *Tetrahedron Lett.* **2004**, *45*, 2023–2026. [[CrossRef](#)]
109. Jin, L.; Jing, H.; Chang, T.; Bu, X.; Wang, L.; Liu, Z. Metal porphyrin/phenyltrimethylammonium tribromide: High efficient catalysts for coupling reaction of CO<sub>2</sub> and epoxides. *J. Mol. Catal. A Chem.* **2007**, *261*, 262–266. [[CrossRef](#)]
110. Bai, D.; Wang, Q.; Song, Y.; Li, B.; Jing, H. Synthesis of cyclic carbonate from epoxide and CO<sub>2</sub> catalyzed by magnetic nanoparticle-supported porphyrin. *Catal. Commun.* **2011**, *12*, 684–688. [[CrossRef](#)]
111. Ahmadi, F.; Tangestaninejad, S.; Moghadam, M.; Mirkhani, V.; Mohammadpoor-Baltork, I.; Khosropour, A.R. Highly efficient chemical fixation of carbon dioxide catalyzed by high-valent tetraphenylporphyrinatot(IV) triflate. *Inorg. Chem. Commun.* **2011**, *14*, 1489–1493. [[CrossRef](#)]
112. Ema, T.; Miyazaki, Y.; Koyama, S.; Yano, Y.; Sakai, T. A bifunctional catalyst for carbon dioxide fixation: Cooperative double activation of epoxides for the synthesis of cyclic carbonates. *Chem. Commun.* **2012**, *48*, 4489–4491. [[CrossRef](#)] [[PubMed](#)]
113. Melendez, J.; North, M.; Villuendas, P. One-component catalysts for cyclic carbonate synthesis. *Chem. Commun.* **2009**, 2577–2579. [[CrossRef](#)] [[PubMed](#)]
114. Escárcega-Bobadilla, M.V.; Martinez Belmonte, M.; Martin, E.; Escudero-Adán, E.C.; Kleij, A.W. A Recyclable Trinuclear Bifunctional Catalyst Derived from a Tetraoxo Bis-Zn(salphen) Metalloligand. *Chem. Eur. J.* **2013**, *19*, 2641–2648. [[CrossRef](#)] [[PubMed](#)]
115. Nakano, K.; Nakamura, M.; Nozaki, K. Alternating copolymerization of cyclohexene oxide with carbon dioxide catalyzed by (salalen)CrCl complexes. *Macromolecules* **2009**, *42*, 6972–6980. [[CrossRef](#)]
116. Wu, G.-P.; Wei, S.-H.; Ren, W.-M.; Lu, X.-B.; Xu, T.-Q.; Darensbourg, D.J. Perfectly alternating copolymerization of CO<sub>2</sub> and epichlorohydrin using cobalt(III)-based catalyst systems. *J. Am. Chem. Soc.* **2011**, *133*, 15191–15199. [[CrossRef](#)] [[PubMed](#)]
117. Li, H.; Niu, Y. Bifunctional cobalt Salen complex: A highly selective catalyst for the coupling of CO<sub>2</sub> and epoxides under mild conditions. *Appl. Organomet. Chem.* **2011**, *25*, 424–428. [[CrossRef](#)]
118. Vagin, S.I.; Reichardt, R.; Klaus, S.; Rieger, B. Conformationally flexible dimeric salphen complexes for bifunctional catalysis. *J. Am. Chem. Soc.* **2010**, *132*, 14367–14369. [[CrossRef](#)] [[PubMed](#)]
119. Nakano, K.; Hashimoto, S.; Nozaki, K. Bimetallic mechanism operating in the copolymerization of propylene oxide with carbon dioxide catalyzed by cobalt-salen complexes. *Chem. Sci.* **2010**, *1*, 369–373. [[CrossRef](#)]
120. Ishida, T.; Kikuchi, S.; Yamada, T. Efficient preparation of 4-hydroxyquinolin-2(1H)-one derivatives with silver-catalyzed carbon dioxide incorporation and intramolecular rearrangement. *Org. Lett.* **2013**, *15*, 3710–3713. [[CrossRef](#)]
121. Ishida, T.; Kikuchi, S.; Tsubo, T.; Yamada, T. Silver-catalyzed incorporation of carbon dioxide into *o*-alkynylaniline derivatives. *Org. Lett.* **2013**, *15*, 848–851. [[CrossRef](#)]
122. Jessop, P.G.; Ikariya, T.; Noyori, R. Homogeneous hydrogenation of carbon dioxide. *Chem. Rev.* **1995**, *95*, 259–272. [[CrossRef](#)]
123. McGhee, W.D.; Riley, D.P.; Christ, M.E.; Christ, K.M. Palladium-catalyzed generation of O-allylic urethanes and carbonates from amines/alcohols, carbon dioxide, and allylic chlorides. *Organometallics* **1993**, *12*, 1429–1433. [[CrossRef](#)]

124. Kayaki, Y.; Mori, N.; Ikariya, T. Palladium-catalyzed carboxylative cyclization of  $\alpha$ -allenyl amines in dense carbon dioxide. *Tetrahedron Lett.* **2009**, *50*, 6491–6493. [[CrossRef](#)]
125. Sasaki, Y.; Dixneuf, P.H. A novel catalytic synthesis of vinyl carbamates from carbon dioxide, diethylamine, and alkynes in the presence of  $\text{Ru}_3(\text{CO})_{12}$ . *J. Chem. Soc. Chem. Commun.* **1986**, 790–791. [[CrossRef](#)]
126. Mitsudo, T.; Hori, Y.; Yamakawa, Y.; Watanabe, Y. Ruthenium catalyzed selective synthesis of enol carbamates by fixation of carbon dioxide. *Tetrahedron Lett.* **1987**, *28*, 4417–4418. [[CrossRef](#)]
127. Tominaga, K.; Sasaki, Y. Synthesis of 2-oxazolidinones from  $\text{CO}_2$  and 1,2-aminoalcohols catalyzed by *n*- $\text{Bu}_2\text{SnO}$ . *Synlett* **2002**, *2002*, 307–309. [[CrossRef](#)]
128. Shi, F.; Deng, Y.; SiMa, T.; Peng, J.; Gu, Y.; Qiao, B. Alternatives to phosgene and carbon monoxide: Synthesis of symmetric urea derivatives with carbon dioxide in ionic liquids. *Angew. Chem.* **2003**, *115*, 3379–3382. [[CrossRef](#)]
129. Kawanami, H.; Matsumoto, H.; Ikushima, Y. Effective  $\text{scCO}_2$ -ionic liquid reaction system based on symmetric aliphatic ammonium salts for the rapid  $\text{CO}_2$  fixation with aziridine to 2-oxazolidinone. *Chem. Lett.* **2004**, *34*, 60–61. [[CrossRef](#)]
130. Mahe, R.; Sasaki, Y.; Bruneau, C.; Dixneuf, P.H. Catalytic synthesis of vinyl carbamates from carbon dioxide and alkynes with ruthenium complexes. *J. Org. Chem.* **1989**, *54*, 1518–1523. [[CrossRef](#)]
131. Abila, M.; Choi, J.-C.; Sakakura, T. Halogen-free process for the conversion of carbon dioxide to urethanes by homogeneous catalysis. *Chem. Commun.* **2001**, 2238–2239. [[CrossRef](#)]
132. Ohmiya, H.; Tanabe, M.; Sawamura, M. Copper-catalyzed carboxylation of alkylboranes with carbon dioxide: Formal reductive carboxylation of terminal alkenes. *Org. Lett.* **2011**, *13*, 1086–1088. [[CrossRef](#)] [[PubMed](#)]
133. Zhang, W.-Z.; Li, W.-J.; Zhang, X.; Zhou, H.; Lu, X.-B. Cu(I)-catalyzed carboxylative coupling of terminal alkynes, allylic chlorides, and  $\text{CO}_2$ . *Org. Lett.* **2010**, *12*, 4748–4751. [[CrossRef](#)] [[PubMed](#)]
134. Leon, T.; Correa, A.; Martin, R. Ni-catalyzed direct carboxylation of benzyl halides with  $\text{CO}_2$ . *J. Am. Chem. Soc.* **2013**, *135*, 1221–1224. [[CrossRef](#)] [[PubMed](#)]
135. Pérez, E.R.; Santos, R.H.A.; Gambardella, M.T.P.; DeMacedo, L.G.M.; Rodrigues-Filho, U.P.; Launay, J.-C.; Franco, D.W. Activation of carbon dioxide by bicyclic amidines. *J. Org. Chem.* **2004**, *69*, 8005–8011. [[CrossRef](#)] [[PubMed](#)]
136. Saito, S.; Nakagawa, S.; Koizumi, T.; Hirayama, K.; Yamamoto, Y. Nickel-mediated regio- and chemoselective carboxylation of alkynes in the presence of carbon dioxide. *J. Org. Chem.* **1999**, *64*, 3975–3978. [[CrossRef](#)]
137. Inoue, Y.; Itoh, Y.; Kazama, H.; Hashimoto, H. Reaction of dialkyl-substituted alkynes with carbon dioxide catalyzed by nickel(0) complexes. Incorporation of carbon dioxide in alkyne dimers and novel cyclotrimerization of the alkynes. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3329–3333. [[CrossRef](#)]
138. Tsuda, T.; Maruta, K.; Kitaike, Y. Nickel(0)-catalyzed alternating copolymerization of carbon dioxide with diynes to poly(2-pyrones). *J. Am. Chem. Soc.* **1992**, *114*, 1498–1499. [[CrossRef](#)]
139. Fujihara, T.; Nogi, K.; Xu, T.; Terao, J.; Tsuji, Y. Nickel-catalyzed carboxylation of aryl and vinyl chlorides employing carbon dioxide. *J. Am. Chem. Soc.* **2012**, *134*, 9106–9109. [[CrossRef](#)] [[PubMed](#)]
140. Correa, A.; Martin, R. Palladium-catalyzed direct carboxylation of aryl bromides with carbon dioxide. *J. Am. Chem. Soc.* **2009**, *131*, 15974–15975. [[CrossRef](#)] [[PubMed](#)]
141. Takaya, J.; Iwasawa, N. Hydrocarboxylation of allenes with  $\text{CO}_2$  catalyzed by silyl pincer-type palladium complex. *J. Am. Chem. Soc.* **2008**, *130*, 15254–15255. [[CrossRef](#)] [[PubMed](#)]
142. Behr, A.; Brehme, V.A. Homogeneous and heterogeneous catalyzed three-step synthesis of 2-ethylheptanoic acid from carbon dioxide, butadiene and hydrogen. *J. Mol. Catal. A Chem.* **2002**, *187*, 69–80. [[CrossRef](#)]
143. Feng, X.; Sun, A.; Zhang, S.; Yu, X.; Bao, M. Palladium-catalyzed carboxylative coupling of benzyl chlorides with allyltributylstannane: Remarkable effect of Palladium nanoparticles. *Org. Lett.* **2012**, *15*, 108–111. [[CrossRef](#)] [[PubMed](#)]
144. Sasano, K.; Takaya, J.; Iwasawa, N. Palladium(II)-catalyzed direct carboxylation of alkenyl C-H bonds with  $\text{CO}_2$ . *J. Am. Chem. Soc.* **2013**, *135*, 10954–10957. [[CrossRef](#)] [[PubMed](#)]
145. Tsuda, T.; Yamamoto, T.; Saegusa, T. Palladium-catalyzed cycloaddition of carbon dioxide with methoxyallene. *J. Organomet. Chem.* **1992**, *429*, C46–C48. [[CrossRef](#)]
146. Greenhalgh, M.D.; Thomas, S.P. Iron-catalyzed, highly regioselective synthesis of  $\alpha$ -aryl carboxylic acids from styrene derivatives and  $\text{CO}_2$ . *J. Am. Chem. Soc.* **2012**, *134*, 11900–11903. [[CrossRef](#)] [[PubMed](#)]
147. Mizuno, H.; Takaya, J.; Iwasawa, N. Rhodium(I)-catalyzed direct carboxylation of arenes with  $\text{CO}_2$  via chelation-assisted C-H bond activation. *J. Am. Chem. Soc.* **2010**, *133*, 1251–1253. [[CrossRef](#)]

148. Mita, T.; Michigami, K.; Sato, Y. Sequential Protocol for C(sp<sup>3</sup>)-H Carboxylation with CO<sub>2</sub>: Transition-Metal-Catalyzed Benzylic C-H Silylation and Fluoride-Mediated Carboxylation. *Org. Lett.* **2012**, *14*, 3462–3465. [[CrossRef](#)]
149. Dai, Y.; Feng, X.; Wang, B.; He, R.; Bao, M. Preparation and application of air-stable P,N-bidentate ligands for the selective synthesis of  $\delta$ -lactone via the palladium-catalyzed telomerization of 1,3-butadiene with carbon dioxide. *J. Organomet. Chem.* **2012**, *696*, 4309–4314. [[CrossRef](#)]
150. Saylik, D.; Horvath, M.J.; Elmes, P.S.; Jackson, W.R.; Lovel, C.G.; Moody, K. Preparation of Isocyanates from Primary Amines and Carbon Dioxide Using Mitsunobu Chemistry<sup>1</sup>. *J. Org. Chem.* **1999**, *64*, 3940–3946. [[CrossRef](#)]
151. Mitsunobu, O. The use of diethyl azodicarboxylate and triphenylphosphine in synthesis and transformation of natural products. *Synthesis* **1981**, *1981*, 1–28. [[CrossRef](#)]
152. Dinsmore, C.J.; Mercer, S.P. Carboxylation and Mitsunobu reaction of amines to give carbamates: Retention vs. inversion of configuration is substituent-dependent. *Org. Lett.* **2004**, *6*, 2885–2888. [[CrossRef](#)] [[PubMed](#)]
153. Haruki, E.; Hara, T.; Inoue, H. Syntheses of Tricyclo (5.2. 1.02, 6) deca-3, 8-diene-1, 8-dicarboxylic Acid and Its Derivatives from Cyclopentadiene and Carbon Dioxide. *Chem. Express.* **1990**, *5*, 493.
154. Ashley, A.E.; Thompson, A.L.; O'Hare, D. Non-metal-mediated homogeneous hydrogenation of CO<sub>2</sub> to CH<sub>3</sub>OH. *Angew. Chem. Int. Ed.* **2009**, *48*, 9839–9843. [[CrossRef](#)] [[PubMed](#)]
155. Kayaki, Y.; Yamamoto, M.; Ikariya, T. N-Heterocyclic Carbenes as Efficient Organocatalysts for CO<sub>2</sub> Fixation Reactions. *Angew. Chem.* **2009**, *121*, 4258–4261. [[CrossRef](#)]
156. Ueno, A.; Kayaki, Y.; Ikariya, T. Cycloaddition of tertiary aziridines and carbon dioxide using a recyclable organocatalyst, 1,3-di-*tert*-butylimidazolium-2-carboxylate: Straightforward access to 3-substituted 2-oxazolidones. *Green Chem.* **2013**, *15*, 425–430. [[CrossRef](#)]
157. He, Q.; O'Brien, J.W.; Kitselman, K.A.; Tompkins, L.E.; Curtis, G.C.T.; Kerton, F.M. Synthesis of cyclic carbonates from CO<sub>2</sub> and epoxides using ionic liquids and related catalysts including choline chloride-metal halide mixtures. *Catal. Sci. Technol.* **2014**, *4*, 1513–1528. [[CrossRef](#)]
158. Calo, V.; Nacci, A.; Monopoli, A.; Fanizzi, A. Cyclic carbonate formation from carbon dioxide and oxiranes in tetrabutylammonium halides as solvents and catalysts. *Org. Lett.* **2002**, *4*, 2561–2563. [[CrossRef](#)]
159. Derien, S.; Clinet, J.C.; Dunach, E.; Perichon, J. Activation of carbon dioxide: Nickel-catalyzed electrochemical carboxylation of diynes. *J. Org. Chem.* **1993**, *58*, 2578–2588. [[CrossRef](#)]
160. Tascadda, P.; Dunach, E. Electrosynthesis of cyclic carbamates from aziridines and carbon dioxide. *Chem. Commun.* **2000**, 449–450. [[CrossRef](#)]
161. Derien, S.; Dunach, E.; Perichon, J. From stoichiometry to catalysis: Electroreductive coupling of alkynes and carbon dioxide with nickel-bipyridine complexes. Magnesium ions as the key for catalysis. *J. Am. Chem. Soc.* **1991**, *113*, 8447–8454. [[CrossRef](#)]
162. Tascadda, P.; Dunach, E. Novel electrochemical reactivity of Ni(cyclam)Br<sub>2</sub>: Catalytic carbon dioxide incorporation into epoxides. *J. Chem. Soc. Chem. Commun.* **1995**, 43–44. [[CrossRef](#)]
163. Dérien, S.; Clinet, J.-C.; Duñach, E.; Périchon, J. First example of direct carbon dioxide incorporation into 1,3-diynes: A highly regio- and stereo-selective nickel-catalysed electrochemical reaction. *J. Chem. Soc. Chem. Commun.* **1991**, 549–550. [[CrossRef](#)]
164. Kröcher, O.; Köppel, R.A.; Baiker, A. Highly active ruthenium complexes with bidentate phosphine ligands for the solvent-free catalytic synthesis of *N,N*-dimethylformamide and methyl formate. *Chem. Commun.* **1997**, 453–454. [[CrossRef](#)]
165. Shimomaki, K.; Murata, K.; Martin, R.; Iwasawa, N. Visible-light-driven carboxylation of aryl halides by the combined use of palladium and photoredox catalysts. *J. Am. Chem. Soc.* **2017**, *139*, 9467–9470. [[CrossRef](#)] [[PubMed](#)]
166. Murata, K.; Numasawa, N.; Shimomaki, K.; Takaya, J.; Iwasawa, N. Construction of a visible light-driven hydrocarboxylation cycle of alkenes by the combined use of Rh(I) and photoredox catalysts. *Chem. Commun.* **2017**, *53*, 3098–3101. [[CrossRef](#)] [[PubMed](#)]
167. Seo, H.; Katcher, M.H.; Jamison, T.F. Photoredox activation of carbon dioxide for amino acid synthesis in continuous flow. *Nat. Chem.* **2017**, *9*, 453–456. [[CrossRef](#)] [[PubMed](#)]
168. Ishida, N.; Masuda, Y.; Uemoto, S.; Murakami, M. A Light/Ketone/Copper System for Carboxylation of Allylic C-H Bonds of Alkenes with CO<sub>2</sub>. *Chem. Eur. J.* **2016**, *22*, 6524–6527. [[CrossRef](#)]

169. DasNeves Gomes, C.; Jacquet, O.; Villiers, C.; Thuéry, P.; Ephritikhine, M.; Cantat, T. A diagonal approach to chemical recycling of carbon dioxide: Organocatalytic transformation for the reductive functionalization of CO<sub>2</sub>. *Angew. Chem. Int. Ed.* **2012**, *51*, 187–190. [[CrossRef](#)]
170. Li, Y.; Cui, X.; Dong, K.; Junge, K.; Beller, M. Utilization of CO<sub>2</sub> as a C1 Building Block for Catalytic Methylation Reactions. *ACS Catal.* **2017**, *7*, 1077–1086. [[CrossRef](#)]
171. Haynes, P.; Slaugh, L.H.; Kohnle, J.F. Formamides from carbon dioxide, amines and hydrogen in the presence of metal complexes. *Tetrahedron Lett.* **1970**, *11*, 365–368. [[CrossRef](#)]
172. Kudo, K.; Phala, H.; Sugita, N.; Takezaki, Y. Synthesis of dimethyl formamide from carbon dioxide, hydrogen and dimethyl amine catalyzed by palladium (II) chloride. *Chem. Lett.* **1977**, *6*, 1495–1496. [[CrossRef](#)]
173. Schreiner, S.; Yu, J.Y.; Vaska, L. Reversible homogeneous catalysis of carbon dioxide hydrogenation/reduction at room temperature and low pressures. *J. Chem. Soc. Chem. Commun.* **1988**, 602–603. [[CrossRef](#)]
174. Morimoto, Y.; Fujiwara, Y.; Taniguchi, H.; Hori, Y.; Nagano, Y. PdCl<sub>2</sub>(MeCN)<sub>2</sub>-catalyzed carbonylation of diethylamine with carbon dioxide: Selective synthesis of tetraethylurea and diethylformamide. *Tetrahedron Lett.* **1986**, *27*, 1809–1810. [[CrossRef](#)]
175. Süß-Fink, G.; Langenbahn, M.; Jenke, T. Rutheniumcluster als Katalysatoren für die Carbonylierung von cyclischen Aminen. *J. Organomet. Chem.* **1989**, *368*, 103–109. [[CrossRef](#)]
176. Zhang, L.; Han, Z.; Zhao, X.; Wang, Z.; Ding, K. Highly Efficient Ruthenium-Catalyzed N-Formylation of Amines with H<sub>2</sub> and CO<sub>2</sub>. *Angew. Chem.* **2015**, *127*, 6284–6287. [[CrossRef](#)]
177. Schreiner, S.; Yu, J.Y.; Vaska, L. Carbon dioxide reduction via homogeneous catalytic synthesis and hydrogenation of *N,N*-dimethylformamide. *Inorg. Chim. Acta* **1988**, *147*, 139–141. [[CrossRef](#)]
178. Jessop, P.G.; Hsiao, Y.; Ikariya, T.; Noyori, R. Catalytic production of dimethylformamide from supercritical carbon dioxide. *J. Am. Chem. Soc.* **1994**, *116*, 8851–8852. [[CrossRef](#)]
179. Liu, F.; Abrams, M.B.; Baker, R.T.; Tumas, W. Phase-separable catalysis using room temperature ionic liquids and supercritical carbon dioxide. *Chem. Commun.* **2001**, 433–434. [[CrossRef](#)]
180. Affan, M.A.; Jessop, P.G. Catalytic Formylation of Primary and Secondary Amines with CO<sub>2</sub> and H<sub>2</sub> Using Abundant-Metal Catalysts. *Inorg. Chem.* **2017**, *56*, 7301–7305. [[CrossRef](#)]
181. Federsel, C.; Boddien, A.; Jackstell, R.; Jennerjahn, R.; Dyson, P.J.; Scopelliti, R.; Laurency, G.; Beller, M. A Well-Defined Iron Catalyst for the Reduction of Bicarbonates and Carbon Dioxide to Formates, Alkyl Formates, and Formamides. *Angew. Chem. Int. Ed.* **2010**, *49*, 9777–9780. [[CrossRef](#)]
182. Federsel, C.; Ziebart, C.; Jackstell, R.; Baumann, W.; Beller, M. Catalytic Hydrogenation of Carbon Dioxide and Bicarbonates with a Well-Defined Cobalt Dihydrogen Complex. *Chem. Eur. J.* **2012**, *18*, 72–75. [[CrossRef](#)] [[PubMed](#)]
183. Ziebart, C.; Federsel, C.; Anbarasan, P.; Jackstell, R.; Baumann, W.; Spannenberg, A.; Beller, M. Well-Defined Iron Catalyst for Improved Hydrogenation of Carbon Dioxide and Bicarbonate. *J. Am. Chem. Soc.* **2012**, *134*, 20701–20704. [[CrossRef](#)] [[PubMed](#)]
184. Minato, M.; Zhou, D.-Y.; Sumiura, K.; Hirabayashi, R.; Yamaguchi, Y.; Ito, T. Reactions of quadruply chelated silyl- and germyl-molybdenum hydrido complexes with carboxylic acids and carbon dioxide: A first example of carbon dioxide fixation utilizing the trans effect of a silyl ligand. *Chem. Commun.* **2001**, 2654–2655. [[CrossRef](#)]
185. Jessop, P.G.; Hsiao, Y.; Ikariya, T.; Noyori, R. Homogeneous Catalysis in Supercritical Fluids: Hydrogenation of Supercritical Carbon Dioxide to Formic Acid, Alkyl Formates, and Formamides. *J. Am. Chem. Soc.* **1996**, *118*, 344–355. [[CrossRef](#)]
186. Munshi, P.; Heldebrant, D.J.; McKoon, E.P.; Kelly, P.A.; Tai, C.-C.; Jessop, P.G. Formanilide and carbanilide from aniline and carbon dioxide. *Tetrahedron Lett.* **2003**, *44*, 2725–2727. [[CrossRef](#)]
187. Beydoun, K.; vomStein, T.; Klankermayer, J.; Leitner, W. Ruthenium-Catalyzed Direct Methylation of Primary and Secondary Aromatic Amines Using Carbon Dioxide and Molecular Hydrogen. *Angew. Chem.* **2013**, *125*, 9733–9736. [[CrossRef](#)]
188. Vaska, L.; Schreiner, S.; Felty, R.A.; Yu, J.Y. Catalytic Reduction of Carbon Dioxide to Methane and Other Species via Formamide Intermediation: Synthesis and Hydrogenation of HC(O)NH<sub>2</sub> in the Presence of (Ir(Cl)CO)(Ph<sub>3</sub>P)<sub>2</sub>. *J. Mol. Catal.* **1988**, *52*, L11–L16. [[CrossRef](#)]
189. Motokura, K.; Takahashi, N.; Kashiwame, D.; Yamaguchi, S.; Miyaji, A.; Baba, T. Copper-diphosphine complex catalysts for *N*-formylation of amines under 1 atm of carbon dioxide with polymethylhydrosiloxane. *Catal. Sci. Technol.* **2013**, *3*, 2392–2396. [[CrossRef](#)]

190. Frogneux, X.; Jacquet, O.; Cantat, T. Iron-catalyzed hydrosilylation of CO<sub>2</sub>: CO<sub>2</sub> conversion to formamides and methylamines. *Catal. Sci. Technol.* **2014**, *4*, 1529–1533. [[CrossRef](#)]
191. Itagaki, S.; Yamaguchi, K.; Mizuno, N. Catalytic synthesis of silyl formates with 1 atm of CO<sub>2</sub> and their utilization for synthesis of formyl compounds and formic acid. *J. Mol. Catal. A Chem.* **2013**, *366*, 347–352. [[CrossRef](#)]
192. González-Sebastián, L.; Flores-Alamo, M.; García, J.J. Nickel-catalyzed hydrosilylation of CO<sub>2</sub> in the presence of Et<sub>3</sub>B for the synthesis of formic acid and related formates. *Organometallics* **2013**, *32*, 7186–7194. [[CrossRef](#)]
193. Shintani, R.; Nozaki, K. Copper-catalyzed hydroboration of carbon dioxide. *Organometallics* **2013**, *32*, 2459–2462. [[CrossRef](#)]
194. Yu, B.; Zhang, H.; Zhao, Y.; Chen, S.; Xu, J.; Huang, C.; Liu, Z. Cyclization of *o*-phenylenediamines by CO<sub>2</sub> in the presence of H<sub>2</sub> for the synthesis of benzimidazoles. *Green Chem.* **2013**, *15*, 95–99. [[CrossRef](#)]
195. Li, Y.; Sorribes, I.; Yan, T.; Junge, K.; Beller, M. Selective methylation of amines with carbon dioxide and H<sub>2</sub>. *Angew. Chem.* **2013**, *125*, 12378–12382. [[CrossRef](#)]
196. Jacquet, O.; Frogneux, X.; Gomes, C.D.N.; Cantat, T. CO<sub>2</sub> as a C1-building block for the catalytic methylation of amines. *Chem. Sci.* **2013**, *4*, 2127–2131. [[CrossRef](#)]
197. Li, Y.; Fang, X.; Junge, K.; Beller, M. A general catalytic methylation of amines using carbon dioxide. *Angew. Chem.* **2013**, *125*, 9747–9750. [[CrossRef](#)]
198. Frogneux, X.; Blondiaux, E.; Thuéry, P.; Cantat, T. Bridging amines with CO<sub>2</sub>: Organocatalyzed reduction of CO<sub>2</sub> to amins. *ACS Catal.* **2015**, *5*, 3983–3987. [[CrossRef](#)]
199. Jacquet, O.; DasNeves Gomes, C.; Ephritikhine, M.; Cantat, T. Recycling of carbon and silicon wastes: Room temperature formylation of N-H bonds using carbon dioxide and polymethylhydrosiloxane. *J. Am. Chem. Soc.* **2012**, *134*, 2934–2937. [[CrossRef](#)]
200. Jacquet, O.; DasNeves Gomes, C.; Ephritikhine, M.; Cantat, T. Complete catalytic deoxygenation of CO<sub>2</sub> into formamidine derivatives. *ChemCatChem* **2013**, *5*, 117–120. [[CrossRef](#)]
201. Blondiaux, E.; Pouessel, J.; Cantat, T. Carbon Dioxide Reduction to Methylamines under Metal-Free Conditions. *Angew. Chem. Int. Ed.* **2014**, *53*, 12186–12190. [[CrossRef](#)]



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).